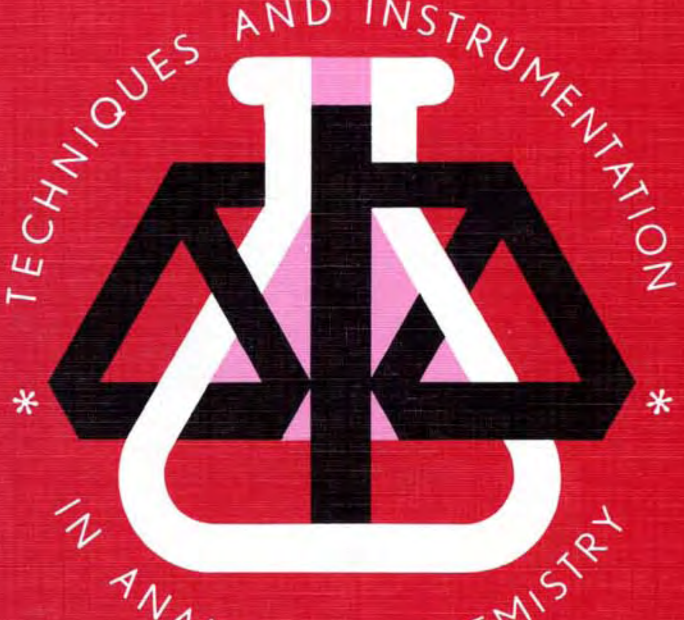
2



HANDBOOK OF LABORATORY DISTILLATION

completely revised second edition

by **Erich Krell**

ELSEVIER SCIENTIFIC PUBLISHING COMPANY

TECHNIQUES AND INSTRUMENTATION IN ANALYTICAL CHEMISTRY – VOLUME 2

Handbook of Laboratory Distillation

With an Introduction to Pilot Plant Distillation

TECHNIQUES AND INSTRUMENTATION IN ANALYTICAL CHEMISTRY

Volume 1 **Evaluation and Optimization of Laboratory Methods and Analytical Procedures. A Survey of Statistical and Mathematical Techniques**
by D. L. Massart, A. Dijkstra and L. Kaufman

Volume 2 **Handbook of Laboratory Distillation**
by E. Krell

TECHNIQUES AND INSTRUMENTATION IN ANALYTICAL CHEMISTRY - VOLUME 2

Handbook of Laboratory Distillation

With an Introduction to Pilot Plant Distillation

Completely revised second edition

Erich Krell
Akademie der Wissenschaften der DDR
Zentralinstitut für Isotopen- und Strahlenforschung, Leipzig

Translation, exclusive of the parts retained from the 1st English edition as prepared by C. G. Verver, Amsterdam, by Dr. phil. Manfred Hecker, Leipzig.

ELSEVIER SCIENTIFIC PUBLISHING COMPANY
Amsterdam — Oxford — New York **1982**

Published in co-edition with
VEB Deutscher Verlag der Wissenschaften, Berlin
Distribution of this book is being handled by the following publishers

for the U.S.A. and Canada

Elsevier North-Holland, Inc.
52 Vanderbilt Avenue
New York, NY 10017

for all remaining areas

Elsevier Scientific Publishing Company
1 Molenwerf
P.O. Box 211, 1000 AE Amsterdam, The Netherlands

Library of Congress Cataloging in Publication Data

Krell, Erich.
Handbook of laboratory distillation.

(Techniques and instrumentation in analytical
chemistry ; v. 2)
Translation of: 3., bearb. und erw. Aufl. Handbuch
der Laboratoriumsdestillation.
Bibliography: p.
Includes index.
1. Distillation—Laboratory manuals. I. Title.
II. Series.
QD63.D6K713 1982 542′.4 82-9855
ISBN 0-444-99723-7 AACR2

Printed in the German Democratic Republic

Foreword to the third edition

The first edition of 1958 was sold out in a relatively short time. The second edition followed in 1960. The book has become a standard work and has been translated into Russian, English and Hungarian.

This edition has again been written with the object of giving an account of the subject of laboratory distillation including recent views and developments. The literature has been reviewed up to the year 1979. The author has adopted the course of dealing only with generally accepted facts; there are still numerous problems in simple and countercurrent distillation which have not yet been completely clarified and in which there exist differences of opinion among various investigators. Distinct trends in development have nevertheless been mentioned, in order to give an incentive for further work. Owing to the large mass of material, a critical selection has been necessary. An attempt has been made to introduce the mathematical deductions and formulae required in laboratory work in a readily understandable form. Readers with a mathematical turn of mind and those interested in particular problems will find extensive references to the literature for further study.

The fundamental scheme of arrangement as applied in the first edition has been retained. Section 5.1.3 has been extended to cover pilot plant distillation. Section 4.2 now deals with fluid and interface dynamics. Chapter 8 could be drastically shortened as there are a variety of components of distillation apparatus and the pertaining measuring and control devices commercially available. The nomograms, which were presented separately, have been inserted in the text. The references for the various chapters have been rearranged and important new items added to them. A great number of review articles serve to provide comprehensive lists of references for a longer period.

The book is intended primarily for physicists, chemists and engineers engaged in chemical industry and in research or development centres, whose work includes distillation on a laboratory or semi-technical scale. It will, however, also be useful to undergraduates, chemical technologists and laboratory assistants as a source of answers to many questions in the field of practical distillation and separating processes. It is hoped that it will prove a guide to better and more economical methods of operation for all these who have to carry out distillation in the laboratory.

The author wishes to express his special gratitude to Prof. Dr. habil. Kl. Wetzel for his interest in the book, his valuable suggestions and constant support. He also wishes to thank Dr. H. Stage and E. Giebeler for the numerous helpful comments they have made. Further his thanks are due to the various manufacturers of laboratory apparatus and glassware who have provided him with prospectuses and technical data. Last but not least, he is grateful to the publishers for the generous lay-out of the book, in particular to the staff of the chemistry department for their thorough work on the manuscript.

It is to be hoped that this third edition will also contribute to the further development of laboratory distillation and that, in laboratories, in industry, in technical schools and universities, it will serve as a textbook and as a guide in the solution of problems of separation by distillation.

Dr.-Ing. Erich Krell
Akademie der Wissenschaften der DDR
Zentralinstitut für Isotopen- und Strahlenforschung, Leigzig

Contents

List of symbols

A	bottom product rate in continuous distillation
a_{eff}	effective surface area
B	quantity of charge to a batch distillation
B_{g}	degree of wetting
BP	boiling point
c	specific heat
c_{p}	specific heat at constant pressure
c_{v}	specific heat at constant volume
D	quantity of vapour
D	diffusion coefficient
Di	degree of air-tightness
d	diameter
E	product rate
F	volatility
$F.$	melting point
FP	solidification point
Fr	fractionating factor
f	cross-sectional area
$\boldsymbol{g}$	acceleration due to gravity
g_0	standard value of $\boldsymbol{g}$
H	quantity of operating hold-up
H_{K}	column height (separating length)
h	height equivalent to a theoretical plate
I	intensity
I	heat content
I_{D}	heat content of vaporized distillate
I_{R}	heat content of vaporized reflux
K	Kelvin
K_{g}	equilibrium constant
Kp	boiling point
k	heat transfer coefficient
k_{G}	velocity constant
L	molar heat of vaporization
$\bar{L}$	mean liquid flow density over column cross-section
$\bar{L}_1$	liquid flow density at a given point
l	length (also, maldistribution = uneven distribution)
$\bar{l}$	mean free path
$l.W.$	inner diameter
M	molecular weight
M_b	mole fraction
M_z	number of moles
m	mass
m_g	mixing number
N	column efficiency
n_{D}	refractive index for the sodium D line

n_a	number of transfer units
n_s	specific stage number
n_{th}	number of theoretical plates or stages
O	surface area
P	total pressure
p	pressure (partial pressure, distillation pressure)
p_*	vapour pressure of a pure substance
Q	quantity of heat
Q_B	heat supplied to still pot
Q_{Ko}	heat removed by condenser
Q_V	heat loss
Q_Z	heat supplied to preheater in continuous distillation
$\mathbf{R}$	universal gas constant
R	reflux rate
r	heat of vaporization
S	gas flow rate
s	stage efficiency
s_m	mean stage efficiency
T	thermodynamic temperature
T_b	equilibration time
t	time
U	voltage
V	volume
V_b	fraction by volume
V_{mol}	molecular volume
v	reflux ratio
v_{gew}	selected reflux ratio
v_{min}	minimum reflux ratio
W	work
WS	constructional material
w	velocity of flow
w_G	limiting velocity
w_k	velocity constant for packing unit
X	quantity of liquid
x	liquid composition referred to low-boiling component
x_A	liquid concentration of bottoms
x_Z	liquid concentration of feed
x_B	mole fraction of low-boiling component in still pot
x_E	mole fraction of low-boiling component in distillate
x_0	initial concentration
x_e	final concentration
y	vapour composition referred to low-boiling component
y^*	vapour composition in equilibrium
Z	feed rate in continuous distillation
α	separation factor (vapour pressure ratio, relative volatility)
β	evaporation coefficient (molecular distillation)
γ	activity coefficient
Δ	difference
δ	separation parameter ($\log_e \alpha$)
ε	relative free volume of packing
η	dynamic viscosity
θ	characteristic temperature (reduced temperature)
ϑ	temperature, °C
$\varkappa$	ratio of specific heats
λ	thermal conductivity

μ	reduced mass
ν	kinematic viscosity
ξ	composition, in fractions by weight or weight %
π	reduced pressure
ϱ	density
σ	surface tension
τ	time interval, time constant
Φ	reduced volume
φ	contact angle

Subscripts and abbrevations

0	initial state	ges	total
1, 2, 3	pure components of a mixture	i	ideal
A	bottoms	K	column
aequ	equivalent	korr	corrected
az	azeotropic	krit	critical state
D	vapour	R	reflux
E	product	S	side stream
e	final state	sa	saturated
eff	effective	TGL	Technische Normen, Gütevorschriften und Lieferbedingungen (GDR)
eq	equilibrium state		
F	liquid		
Fk	packing unit	W	water vapour
g	gaseous	Z	feed

1. Introduction

Although simple and countercurrent (rectified) distillation are among the most important physical separating methods employed in chemical industry, and hence also in research and works laboratories, it is often found that the apparatus used for this purpose in the laboratory has a low efficiency by present-day standards. Furthermore, calculations on the process are seldom made; instead, the work is as a rule based entirely on experience and empirical data.

In this field, nevertheless, a large amount of research work has been carried out during the last thirty years. Today we have available modern components, high-vacuum and completely automatic equipment; methods of calculation have been developed, whilst laboratory separations now range from micro-distillations with less than 1 gram of charge to continuous operations with a throughput of up to 5 litres per hour, from the distillation of liquefied gases at low temperatures to that of tars at high temperatures and from separations at normal pressures to so-called molecular distillations at pressures below 10^{-4} mm of mercury. Selective procedures have been perfected, and it is now possible to separate mixtures formerly considered inseparable by appropriately influencing the vapour pressure relationship.

The classical textbooks of v. Rechenberg [1] and Young [2] provide an excellent review of theory and practice, including that of industrial installations, but are now out of date in many respects, particularly as regards methods of calculation and apparatus. The works written by Thormann [3] and Badger and McCabe [4] around 1930 already contain the graphical method of computation of McCabe and Thiele [5] and excel in clarity of presentation. They are, however, mainly concerned with large-scale operations and fall short in their treatment of the special problems of laboratory distillation. A great impetus to research in the latter field was given by the work of Jentzen and his students. In a Dechema monograph [6] published in 1932 he gave a detailed description of the fundamental requirements for columns (previously presented in 1923); these are still largely valid today. The books of Kirschbaum [7], Gyula [8] and Jacobs [9] have a mainly industrial orientation; this also applies to that of Robinson and Gilliland [10] which, apart from the theory, deals with difficult separations of multi-component mixtures and with azeotropic and extractive distillation. Perry's Chemical Engineer's Handbook [10a] contains a chapter on distillation with numerous examples, tables and nomograms for calculating industrial installations; laboratory distillation is, however, but briefly discussed. All these books presuppose a knowledge of the basic theory and a measure of practical experience as do the 1944 work of Schultze and Stage [11] on problems of column distillation and the Dechema booklets published by Thormann [12] on "Arbeitsmethoden und Geräte — Destillieren und Rektifizieren" and "Destillieren —

Betriebstechnik" [13] covering laboratory methods and engineering aspects, respectively. The development of distillation techniques between 1920 and 1944 is reflected by a bibliography of Stage-Schultze [14] containing about 2300 publications which are basic to the theory, apparatus and methods of distillation and rectification.

The entire distillation literature of the world for the years 1941 to 1945 and 1946 to 1952 was summarized in short references by A. and E. Rose [15]; the first group contains 1000 investigations, the second 5000. In the publication „Fortschritte der Verfahrenstechnik" [16] biannual reviews are given in the sections on „Destillieren und Rektifizieren", „Rektifikation bei tiefen Temperaturen", „Stoffübertragung", „Gleichgewichtsverhalten von Ein- und Mehrstoffsystemen" and „Vakuumtechnik und Verfahren im Vakuum".

Walsh [17] annually gives a critical summary of literature in "Unit Operations Reviews". As regards material constants and methods of calculation valuable suggestions are found in the manual for petroleum engineers by Orlicek-Pöll [18] which includes an extensive chapter on boiling points and phase equilibria. The latest state of distillation techniques both in the laboratory and in industry is discussed by Sigwart [19] in a very good survey of the field for Ullmann's Encyclopaedia of Engineering Chemistry. The theory of distillation and extraction is dealt with on a strictly thermodynamical basis in the books of Kortüm and Buchholz-Meisenheimer [20] and Bosnjaković [21]. The books of Gattermann-Wieland [22] and Wittenbecher [23] which are well-known to every student of chemistry are intended to introduce the organic chemist into practical work. Distillation, however, is only represented by brief synopses. Although Weygand [24] and Bernhauer [25] devoted shorter sections to modern apparatus and methods in their books on laboratory techniques an extensive discussion of laboratory distillation problems including methods of calculation was lacking until the works of Carney [26], Rosengart [27] and Rose et al. [28] gave a systematic treatment of the special requirements of laboratory distillation. The contribution of von Weber [29] concentrates on the preparation of essential oils by distillation, especially by means of steam distillation. Sigwart wrote the chapter on distillation and rectification for the 4th edition of the Houben-Weyl manual [30]. It offers an excellent survey together with numerous examples of laboratory problems. The 13 problems set in the chapter are all based on situations where some difficulty, expected or unexpected, has to be overcome. Short books based on fundamental principles have been published by Zuiderweg [31] and by Coulson and Herington [32]. Problems of fractional distillation in the laboratory are treated thoroughly in a monograph written by Bukala, Majewski and Rodziński [33].

Since 1960 the number of publications dealing especially with the theoretical foundation of distillation has increased considerably. Hence documentation has been done largely by computer since the number of abstracts is steadily increasing. Periodical reviews of the literature on distillation still appear in various journals [34]. Information is readily obtained through bibliography cards and abstracts [35, 16]. It became necessary to publish extensive laboratory handbooks for undergraduates which include chapters on distillation methods [36], since most of the textbooks for practical courses do not give enough attention to separating techniques [37]. A number of monographs deal with important special fields of distillation. Thus, the book of Röck [38] gives an excellent introduction to extractive and azeotropic distillation and in their books Stage et al. [39] make clear the loading conditions in packed columns and the experimental determination of vapour-liquid phase equilibria as exemplified by the boiling behaviour of fatty acids. The 1960 standard work of Hála et al. on the theory and the experimental determination of liquid-vapour equilibria [40] has been complemented by an extensive collection of equilibrium data [41]. A new edition of Kogan-Fridman's compilation of tables contains equilibrium data for over 2000 systems. Besides, these authors have published a large collection of azeotropic data (21069 systems of 2 to 5 components) [42]. The data on vapour-liquid phase equilibria edited by Hirata et al. [59] were prepared using computers. The book contains 1000 systems for 800 of which experimental data and computed curves are given. It should be noted that 200 high-pressure equilibria covering 133 systems are included. Systems with solubility gaps are not represented. By order of DECHEMA, Gmehling and Onken [66] compiled a collection of equilibrium data. Valuable suggestions for obtaining material data required for distillation calculations are made by Bittrich et al. [60]. Billet has written 3 very instructive monographs on the fundamentals of the thermal decomposition of liquids [43] and on optimization in rectification (with special consideration of vacuum rectification) [44]. These books refer particularly to technical distillation but they provide a number of calculating methods for laboratory and even more for semitechnical distillation. The two more comprehensive books of Oliver [45] on "Diffusional Separation Processes" and of Pratt [46] on "Countercurrent Separation Processes" as well as the books of Sattler [62] on thermal separation processes and of Kafarov [62a] on the fundamentals of material transfer illustrate the general trend of jointly presenting separation techniques from a particular aspect. From a theoretical point of view this offers great advantages. The introduction to separation processes written by Krell et al. [47] also attempts to give a general survey of the various separation processes and possible combinations for students of chemistry and process chemistry. The state of dimensioning and precalculating processes of the thermal separation of material is reported by Wünsch et al. [63].

Apart from this the last few years have brought more books on special problems of distillation, such as those of Hoppe and Mittelstrass [48] and of Stichelmair [61] on the fundamentals of plate and plate column dimensioning, resp., and of Jungnickel and Otto [49] on the use of low temperatures in process engineering. While the book of Frank and Kutsche [50] deals with the distillation of sensitive substances in the laboratory that of Olewskij and Rutschinskij [51] refers to the same problem on a semitechnical scale. The applications of molecular distillation in the laboratory as well as in pilot and industrial plants are described in a monograph written by Holló et al. [52] which includes an extensive list of references and a large number of tables and illustrations. For their book on "Recent Developments in Boiling and Condensation" Winter, Merte and Herz [65] collected over 500 references, 250 of which were evaluated. The book is an excellent description of the state of the art which also includes interface phenomena.

Part I of Schuberth's [53] „Thermodynamische Grundlagen der Destillation und

Extraktion" treats the fundamental principles of the thermodynamics of mixed phases, the classification of binary systems and the distillative separation of two components. Part II will contain ternary systems, the extractive separation of two components by means of one or more solvents, special methods of selective distillation, and problems of multicomponent distillation and extraction. It is reasonable to consider this exact theoretical presentation as a complement to the theoretical hints concerning distillation problems given in the present book. The theoretical basis of material exchange and of single- and multi-phase separation has been summarized by Brauer [54]. He considers material transport in fluids both at rest and in motion. Of particular interest for distillation are section 10 on material transfer in packing layers at rest and with turbulence as well as part V on material transport through the interfaces of simple two-phase systems and part VI on material transport in technical apparatus with a stream of two phases. Kaibel et al. [64] give an account of reaction columns in which the column dynamics are complicated by the superposition of reaction and distillation. Holland [55] presents a thorough discussion of questions of multicomponent distillation while those of technical distillation are dealt with in a more recent book of Billet [43a]. Scharov and Serafimov [58] have devoted their book especially to questions of the countercurrent distillation of azeotropic multicomponent mixtures.

The international symposium on distillation at Brighton, England, in 1969 [56] clearly showed the necessity to enlarge the theoretical basis of separation by distillation using computers, especially for the precalculation of separation processes. The symposium covered the whole field of research and development and reviewed the latest developments. It became evident, however, that even now there are a host of problems waiting to be solved in the complex area of distillation. In comparing the present state, the developments and prospects of simple and countercurrent distillation with other thermal separation methods Billet [57] comes to the same assessment. He points out that our knowledge of material exchange processes and of column loading limits is far from sufficient for optimizations so that further extensive and detailed experimental and theoretical work will have to be done. This situation was again brought out at the second international symposium on distillation in London, 1979. The 55 papers held in 4 sections were published in the proceedings of the symposium [56a]. As was seen from the literature of the years before, the symposium demonstrated considerable progress for laboratory distillation in the area of the precalculation of vapour-liquid equilibria of non-ideal systems and of multicomponent mixtures. The calculation of the azeotropic composition of binary mixtures by means of the UNIFAC method is also gaining ground. Moreover it was pointed out that increasing attention is paid to experimental results from laboratory and pilot plants, *e.g.*, in the examination of problems involved in the combined process of distillation and chemical reaction.

The present state and trends in the field of material transfer in distillation columns have been discussed by Weiss [67]. In the future, emphasis will be placed on the optimization and intensification of techniques, particularly from the point of view of saving energy.

In view of the enormous development in laboratory distillation during the last thirty years and the extensive specialization in this field it seemed desirable that an introduction to laboratory and pilot-plant distillation technique should appear, not assuming any previous knowledge in this field, but nevertheless containing the methods for determining vapour pressures and equilibrium curves and giving a detailed description of continuous and selective separating processes, together with a chapter on measuring and control devices. This review has the object of removing many erroneous notions about the factors affecting the process of separation and of giving a comprehensive account of the performance of simple and difficult distillations.

The chapter entitled "A review of the history of laboratory distillation" at once introduces the general ideas, whilst chapter 3 clarifies concepts and defines the units of measurement and the symbols. Special attention is given to standardization since it brings about conventions concerning instrument and process parameters and thus makes data comparable, which is a prerequisite for successful research. After the physical theory of separation and the properties of the mixtures to be separated have been discussed, the general and selective separating processes used in various cases are dealt with from several points of view (chaps. 4 to 6). The apparatus required, together with auxiliary equipment such as measuring and control apparatus, is described in chapters 7 and 8. Finally chapter 9 details points to be considered in fitting out a distillation laboratory and preparing the apparatus.

It was considered particularly important to deal with the procedures followed in laboratory and pilot-plant distillation from the aspect of large-scale distillations, since the former are often the forerunners of the latter. Formerly it happened all too often that distillation methods were developed in the laboratory without any consideration of development; the result was that serious difficulties frequently occurred in scaling up the laboratory experiments to the full dimensions. If, however, the experiments are properly designed at the outset for technical interpretation, much expense and time can often be saved and the data obtained can be employed in technical calculations without appreciable correction. This does not, of course, exclude the need for using conditions in certain cases, say in analytical distillation, that would be entirely uneconomic in industrial operation. Only with a knowledge of the fundamentals of the separating process it is possible to decide on the optimum conditions for every problem. It is the purpose of the present book to provide this knowledge.

The symbols for physico-chemical quantities and units have for the most part been adopted unchanged since distillation technique requires some special notation. It has been attempted, however, to use internationally adopted symbols wherever possible. The references have been grouped according to the chapters. Figures, formulae and tables have been given running numbers throughout the book.

2. A review of the history of laboratory distillation

Not only it is interesting to study the development of a chemical operation through the centuries from a historical point of view, but it is often found that valuable pointers for research are obtained from parallels between old and present-day methods. As an introduction to a special field of chemical technology, such as distillation, a historical review gives the reader an appreciation of how the human mind has always sought for new ways of achieving better processes and more efficient apparatus with the facilities available at the time.

Schelenz [1], Gildemeister [2] and von Rechenberg [3] have considered much historical material concerning the development of distillation for their discussions of the preparation of essential oils. Underwood [4] presents a brief outline of the evolution of distillation technique up to the 19th century, and in his excellent book Forbes [5] tells the history of the art of distillation from its beginnings to the death of Cellier-Blumenthal. The latter, a French engineer who died in Brussels in 1840, was one of the most talented column designers of the early 19th century. Further historical details can be found scattered in the various accounts of the history of alchemy and chemistry. Of the more recent publications, the history of science and technology of Forbes and Dijksterhuis [6] may be mentioned. In two volumes, the evolution of technology, astronomy, mathematics, chemistry, and, in particular detail, of physics is presented in an easily comprehensible way. The development of distillation methods is described in some detail in Bittel's [16] paper on the history of multiplicative separating methods. W. Schneider [7] has published a lexicon of alchemistic and pharmaceutical symbols which helps to understand ancient writings.

In the book of Strube [15] the main strands of development are described. Distillation is dealt with according to its significance and its history from the 3rd century A. D. is illustrated by numerous pictures.

The present review has been written, not with the object of providing complete historical details or etymological derivations, but rather of giving a clear account of the steps by which laboratory methods and apparatus (not omitting those for semi-technical use) have developed to their present forms.

Distillation is an art that was practised long before the Christian era by the ancient Egyptians and was cultivated and protected as secret science by temple priests. It also appears to have been carried out in early times in India, Persia and China. Schelenz [1] is of the opinion that the discovery of distillation must be ascribed to the Persians, who employed the art for the preparation of rose water. Another view shared by v. Lippmann [8—10] is that the principle of distillation found its origin in the carbonization of wood, since descending distillation is referred to in the "Ebers papyrus" of about 1500 B.C., so that the process would be almost 3500 years old. It should be noted in this connection that the word distillation was at that time a collective term for all separating processes then known; the word may be translated as "separation drop by drop" and in alchemistic speech denoted the separation of more or less subtle (or "fine") elements from each other. The concept of distillation also covered operations such as filtration, crystallization, extraction and the expression of oil.

We shall here deal only with the history of distillation in the present meaning of the term: the separation of bodies by evaporation and condensation of the vapour. In this connection it should be observed that by the foregoing definition descending distillation is a true distillative operation.

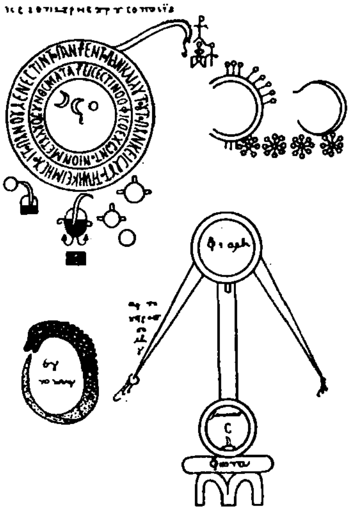


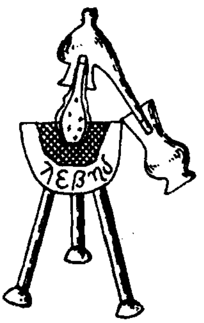
Fig. 1
Alembic on furnace, surrounded by magic signs. From a treatise on the making of gold by the Egyptian alchemist Cleopatra (2nd century A.D.)

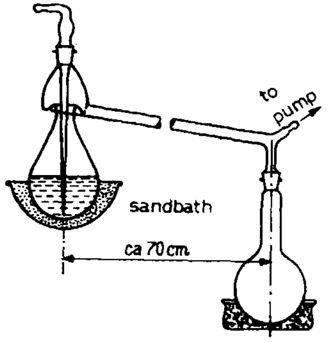
The earliest uses of distillation were the preparation of rose oil and other ethereal oils, distilled water for sailors (Aristoteles mentions how fresh water can be made from salt water) and a large number of alchemical mixtures and draughts. Fig. 1 shows a so-called alembic (helmet) on a furnace, surrounded by the magic inscriptions which in early ages played such a large part in the process of distillation. The illustration is taken from a treatise on the preparation of gold dating from the second century A.D., by the Egyptian woman alchemist Cleopatra. A typical apparatus of this period is shown in the next figure (2a). It is a glass still on a sand or water bath, an arrangement still in use today, as demonstrated by the adjoining illustration of a mercury still (2b). The four separate parts — the heating bath, the still (curcurbita), the head (alembic) and the receiver (receptacula) — have remained in use as components to this day. It is interesting to note that the collar for collecting the distillate is also still found in a number of modern forms of equipment. The material employed for the apparatus in antiquity was chiefly glass, a ceramic compound or copper.

From about 1300 A.D. onwards the methods of distillation may be divided into two basic types:

per ascensum = "rising distillation", *per descensum* = "descending distillation".

The descending procedure (Fig. 3a) sank into oblivion after about 1800, although it is the best method for certain types of separation. We find the principle again in a water still of the year 1952, where it is chosen to ensure an economical use of heat (see Fig. 3b).


a)



b)

Fig. 2a)
Glass distillation apparatus with sand or water bath (2nd century A.D.)

Fig. 2b)
Vacuum still for mercury with collecting collar for the distillate (20th century)


a)

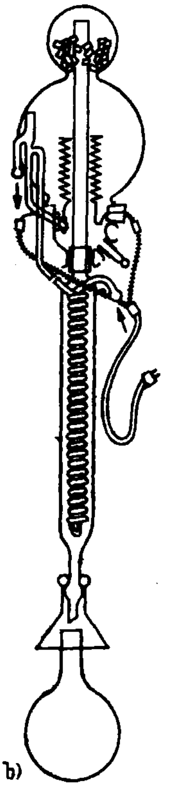

b)

Fig. 3a)
Dry distillation of bark and herbs "*per descensum*" (1300 A.D.)

Fig. 3b)
Water still of Blome according to the "*per descensum*" principle (20th century)

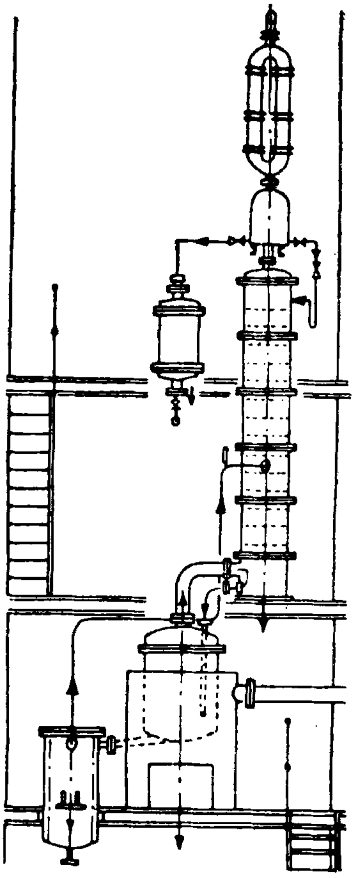
Soon after the invention of printing a series of very graphic descriptions of distillation were published, showing the state of development at the end of the middle ages. The most important of these were the following:

1483, Schrick: Verzeichnis der ausgeprannten Wässer (Account of the burnt-out waters);
1500, Brunswig: Das Buch der rechten Kunst zu destillieren die eintzige Ding (Book of the true art of distilling the sole things);
1507, Brunswig: Das Buch der wahren Kunst zu destillieren (Book of the true art of distilling);
1528, Ulstad: Coelum philosophorum (The philosopher's heaven);
1536, Ryff: Neu gross Destillierbuch wohl begründeter künstlicher Destillation (New large distilling book of well-founded artificial distillation).

After the 16th century a large variety of methods of heating the stills is observed. Heating is carried out by air bath, water bath, sand or ash bath and also with the aid of wax candles. The furnaces are provided with fuel hoppers, in order to permit of working without interruption. Very strange systems of heating are also encountered,

a)

Fig. 4a)
Separate heating furnace for wooden distilling apparatus, with condensing coil (17th century)



b)

Fig. 4b)
Separate boiler for continuous industrial plant (20th century)

such as those utilizing the heat of fermentation of bread dough or pressed-out fruit. In hot climates heat was occasionally obtained from burning mirrors and it is of interest to find that the same method of heating is covered by a patent in the year 1943. In industrial installations it is often necessary to separate the heating from the actual still (Fig. 4b). This arrangement had already been described by Glauber (1604—1668), as shown in Fig. 4a. For obtaining larger amounts of distillate it was customary, even in the 16th century, to operate several stills simultaneously on a furnace, which was often arranged in terraces (Fig. 5). The first attempts at heat

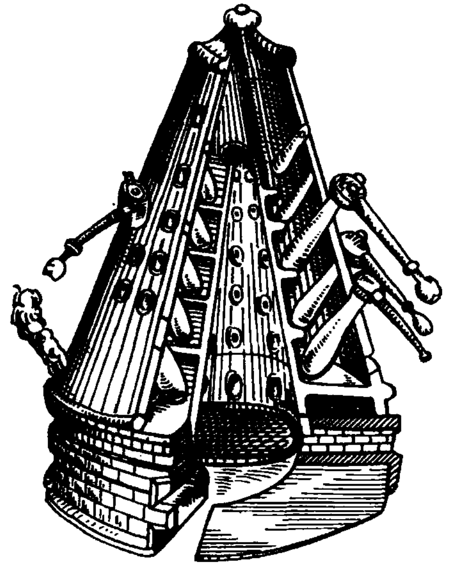
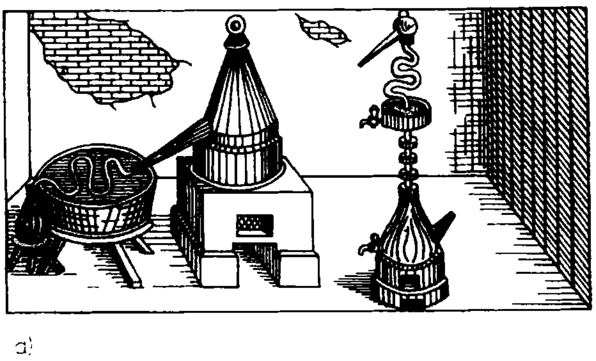


Fig. 5
Distilling furnace in terraces. The fire is in the centre of the cone; at the sides there are draught channels for temperature regulation. The earthenware fans support the alembics (air bath heating) (16th century)



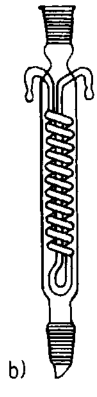
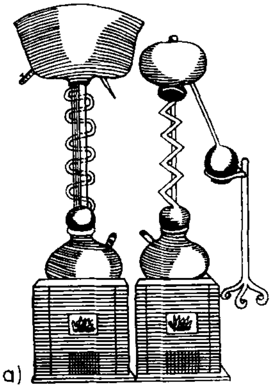


Fig. 6a)
Semi-technical or laboratory distilling apparatus with serpentine air or water condenser (16th century)

Fig. 6b)
Coil condenser (Dimroth) with standard joints (20th century)

insulation, using clay mixed with animal hair, are due to Lully (1415). In the 16th century the advantages of heating in stages were recognized and steam distillation was already practised. The use of steam as heat carrier first became general, however, around the year 1800.

For condensing the vapour, air-cooling was the only method available up to about 1300. Long vapour tubes were necessary to obtain the required effect. Later these were led through a barrel or trough filled with water. Finally it was found that the best form of condenser was a coil (Fig. 6a), a type still very common today (Fig. 6b).


a)

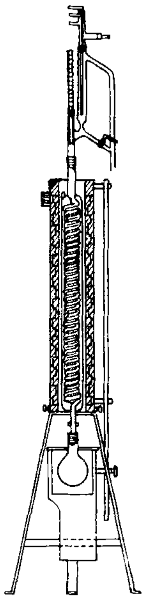
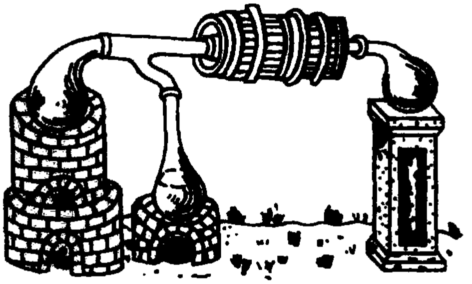

b)

Fig. 7a)
Distilling apparatus of the *Pharmacopoeia Medico-Chymica*. Large Turk's-head still and still with helm, using air cooling, on furnaces. Zig-zag ascending tube. Receiver with adjustable support (1709)

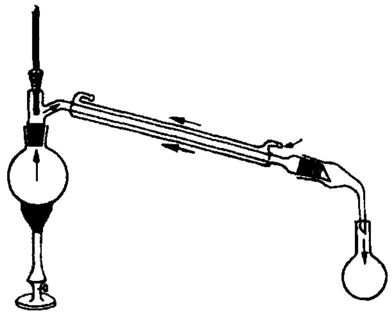
Fig. 7b)
Distilling apparatus with coil (Jantzen; 20th century)

In the 16th century continuous condensation by water followed. The concentrating effect of a long vapour riser and of partial condensation (Fig. 7a) were also recognized (1648). The modern counterpart is illustrated in Fig. 7b. The countercurrent principle in condensation was introduced by Pissonnier in 1770, the same principle found today in the well-known Liebig condensers (Fig. 8b), which date back to Dariot (1533–1594; see Fig. 8a).

The development of distillation technique from the 16th to the 19th century kept pace with the general improvement in equipment construction. By the middle of the 16th century it was known that metal stills are subject to corrosion, whereupon glass and ceramics came to be the preferred materials. Kunkel (1638–1703) was the first to use glass as a general laboratory material, as is done to this day. Fig. 9 shows the large variety of still heads employed at that time. Micro-forms were already in use. The appearance of an alchemical laboratory of about 1700 is illustrated by Fig. 10, representing the apothecary's laboratory of the Capuchin monastery in Paris. The large number of distilling devices proves that they were among the most frequently used laboratory apparatus. Up to the 18th century laboratory stills were almost



a)



b)

Fig. 8a)
Dariot's condenser with continuous countercurrent cooling (16th century)

Fig. 8b)
Liebig condenser using countercurrent principle (19th century)

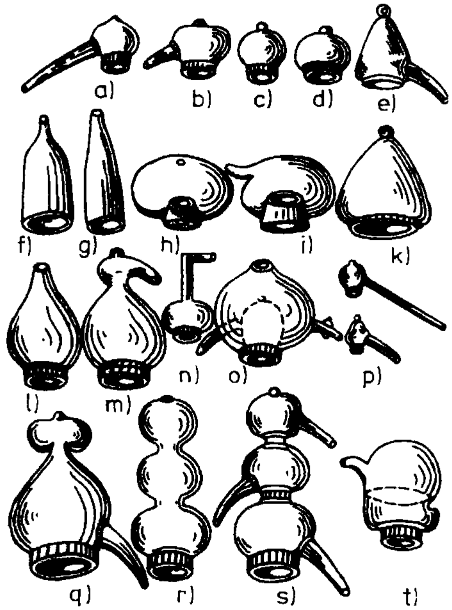


Fig. 9
Still heads after Andreas Libau, about 1600

a)	Alembic with long beak
b)	Alembic with short beak
c, d, h)	Blind alembics
e)	Alembic of tin
f, g)	Sublimation heads
i, t)	Blind alembics with tube
k)	Bell-shaped alembic
l)	Tiara
m)	Tin head with beak-shaped end
n)	Head with extension tube
o)	Alembic with cooler
p)	Dwarf types
q)	Blind beaked alembic
r)	Triple blind alembic
s)	Triple beaked alembic

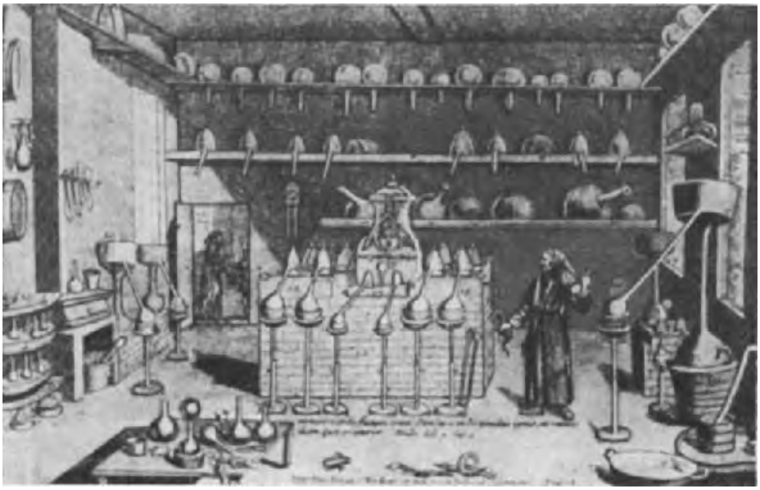


Fig. 10
Apothecary's laboratory of the Capuchin monastery in Paris (about 1700)

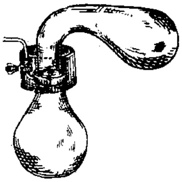


Fig. 11
Boyle's apparatus for vacuum distillation (1627–1691)

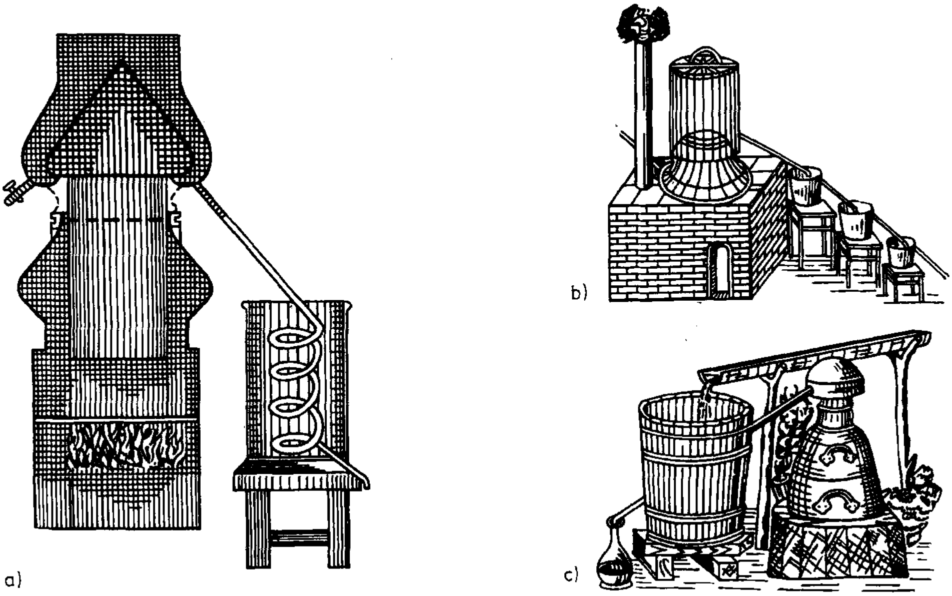


Fig. 12
Semi-technical distillation equipment in the 19th century
a) Germany, b) China, c) Bulgaria

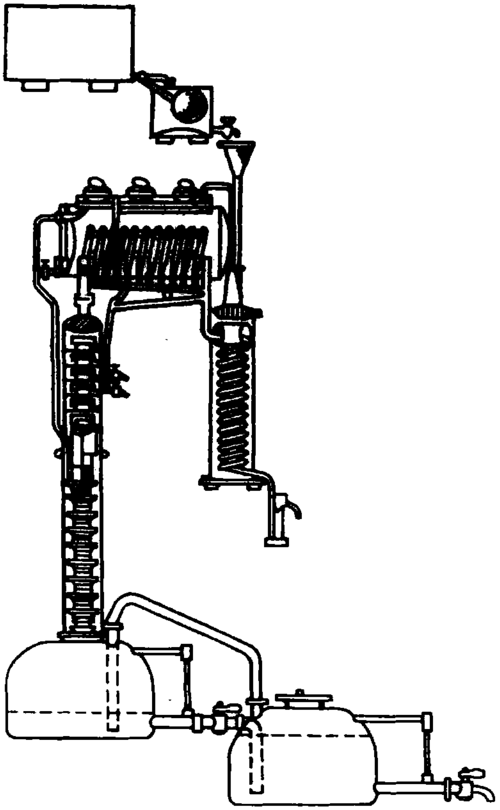
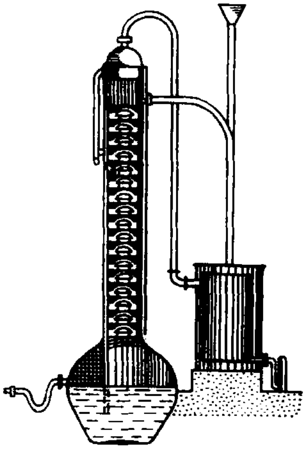


Fig. 13
Continuous distillation apparatus of Cellier-Blumenthal (1813)



a)

b)

Fig. 14a)
Bubble-cap column of Champonnois (1854)

Fig. 14b)
Glass plate column of Bruun with 20 actual trays and vacuum jacket (1931)

exact copies of those utilized in early antiquity, but towards the middle of the 18th century chemists like Baumé and Woulff began to create new forms. Systematic experiments on distillation were first performed by the physicist Boyle in England (1627—1691), who even carried out experiments in vacuum and under pressure (Fig. 11). By the middle of the 18th century a few standard types of equipment had evolved, which were used in all countries (Fig. 12). The diameter was about 45 to 75 cm and the height 90 to 120 cm. In the 19th century there were considerable developments, particularly as a result of the activity of French constructors concerned with the alcohol industry. After several stages of development (Adam, Berard, Perrier) a continuous still was patented in 1813 by Cellier-Blumenthal; in its basic features it corresponded to modern apparatus (Fig. 13). Stills for vacuum distillation were built in 1828 by Tritton, and the sieve-plate column of Coffey (1830) constituted

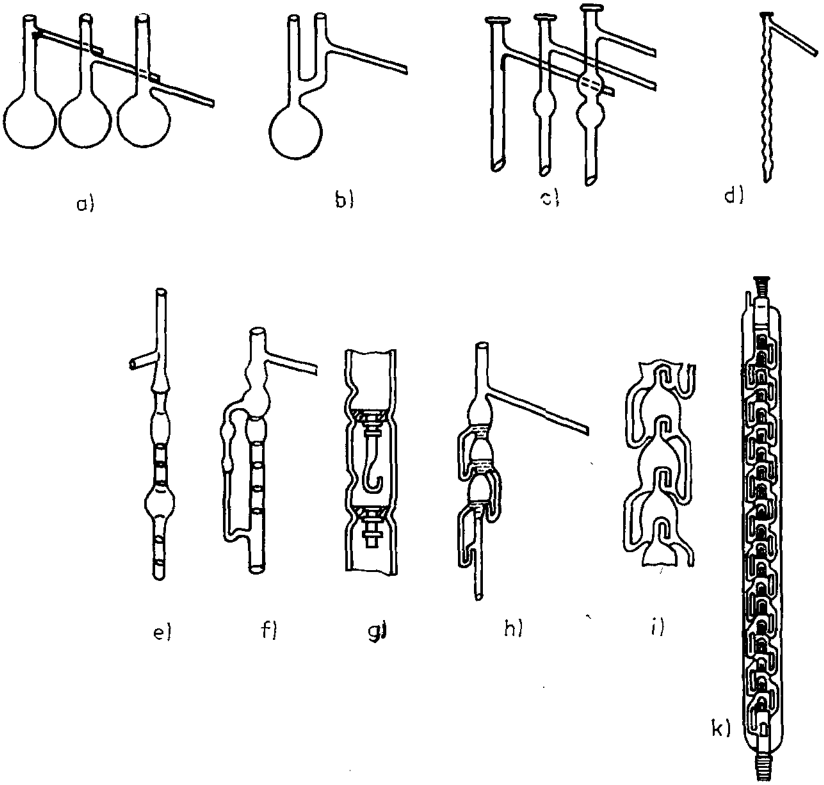
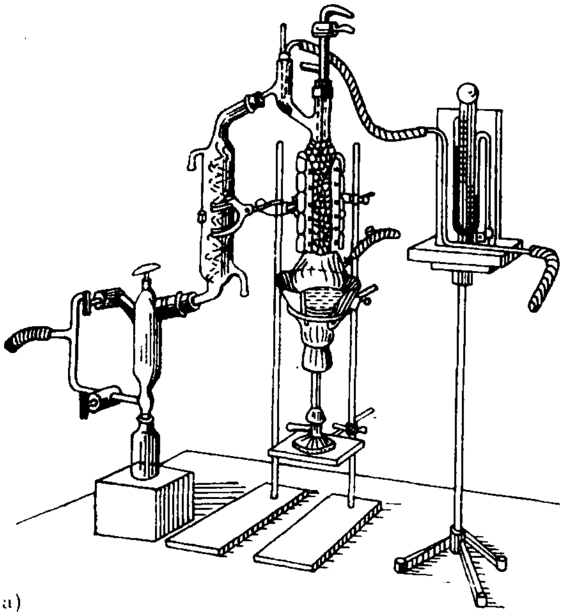


Fig. 15
Stages of evolution of the bubble-cap column

a) Distillation flask with vapour side-tube
b) Claisen flask
c) Still heads without and with bulbs
d) Ball head according to Wurtz (1854)
e) Sieve-plate head of Linnemann (1871)
f) Sieve-plate head of Glinsky (1875)
g) Spray-plate column of Le Bel-Henniger (1875)
h) Rectifier of Young and Thomas (1889)
i) Baum's plate column (1910)
k) Bubble-cap column of Bruun (1951)

another advance. The principle of bubble-cap plates was introduced in 1854 by Champonnois for industrial installations (Fig. 14a). This process is basically that used in large-scale units up to the present day, together with packed columns. The latter were introduced by Ilges, who first utilized spheres as packing material in 1873.

Reviewing what has been said above, we realize that the basic principles of distillation were already known in antiquity and in the middle ages, in spite of the simple equipment then available. Until the middle of the 19th century, laboratory and semi-technical apparatus differ in their dimensions only. It was not until the tempestuous development of organic chemistry around the middle of the 19th century that distillation equipment evolved entirely designed for experiments in the laboratory. Noted chemists, between this time and 1900, such as Claisen, Dimroth, Glinsky, Hempel, Le Bel, Liebig, Mitscherlich, Mohr and Wurtz, evolved apparatus for laboratory distillation practice. Retorts were used as stills and as receivers; the distillation flask with air-cooled side tube developed, by way of the Claisen flask and the Wurtz ball head, into the spray-plate column. The still heads of Linnemann, Glinsky and Le Bel-Henniger are precursors of the bubble-cap column [11] (Figs. 14b and 15). The column packed with glass beads was introduced into the laboratory in 1881 by Hempel.


a)

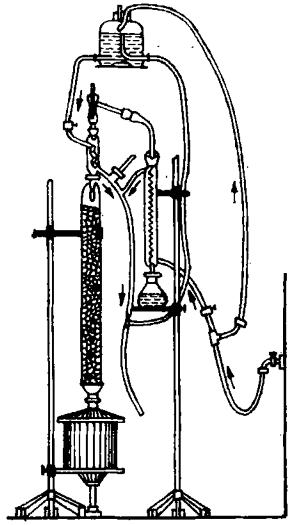

b)

Fig. 16a)
Von Rechenberg's vacuum distillation apparatus (1920) with Hempel column and Bertrand receiver

Fig. 16b)
Elsner's rectifier for normal pressure and vacuum (1920)

Towards the end of the 19th century came the need to compare the many still heads thus available as regards efficiency. Kreis, Young and Friedrichs [12] carried out measurements in this field, and also studied condensers. Besides the Liebig condenser, that of Dimroth (Fig. 6b) became of importance; a specially effective condenser for low-boiling substances, designed by Mitscherlich, led to the construction of similar types.

During the period between 1900 and 1920 numerous pieces of apparatus at present still in use were developed; for instance the Jantzen column (Fig. 7b), and the Raschig and Prym rings for column packing (1916 and 1919, respectively). Heating systems were improved, whilst pressure controllers for work in vacuum were evolved. Fig. 16a shows an apparatus used for vacuum distillation by the well-known specialist von Rechenberg [3] between 1900 and 1920, which, like Elsner's rectifier (Fig. 16b), illustrates the stage of development at the end of this period.

It was not, however, until Jantzen [13] and his pupils had systematically investigated the physical fundamentals of the distillation process that the numerous developments after 1920 could take place. This later phase is still too recent to allow us to consider it historically. Ever and again we find, however, that multiple threads lead us back from our present complicated apparatus and methods to long-vanished times when the fundamental principles of our modern knowledge were first recognized and elaborated [14].

3. Standardization and data on concentrations

3.1 Standardization of distillation apparatus

The significance of standardization from both a scientific and an economic point of view is generally accepted. No detailed arguments supporting it need, therefore, be given here. It may suffice to point out that it always pays to use standardized apparatus. In all countries there is a tendency to provide standard apparatus for the various separations to be carried out: it can then be mass-produced and hence is relatively cheap. Further, it is readily available and gives reproducible results. The first step in this direction were taken when the well-known Engler and ASTM devices were designed. Even for vacuum work, for example, similar apparatus can be assembled from standardized components (Fig. 17). Components and apparatus as well as special methods for distillation are listed in [1, 2].

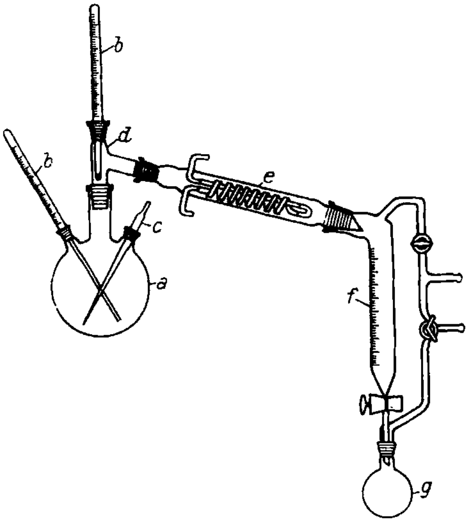


Fig. 17
Apparatus for simple distillation in vacuum assembled from standard components

a = three-neck round-bottomed flask NS 29 with 2 side tubes NS 14.5; *b* = thermometer with ground joint NS 14.5; *c* = boiling capillary; *d* = still head with ground joints NS 29 and 14.5; *e* = Dimroth condenser; *f* = vacuum adapter; *g* = short-necked round-bottomed flask

The main advantages of standard components are that the apparatus required can be assembled safely and quickly and that in many cases expensive special apparatus can be dispensed with, since the components can be combined in many ways. Moreover, it is possible to copy the set-up of technical plants to a considerable extent. In the case of a fracture only the demaged component needs to be replaced.

Today, apparatus having standard ground-glass joints is used almost exclusively in every organic laboratory and hence in every distillation laboratory (Tab. 1). An encyclopaedia of chemical laboratory apparatus including the G.D.R. standards has been edited by Telle [3].

Table 1

Sizes of standard ground-glass joints for interchangeable connections

a) Conical joints (NS), cone 1:10, according to TGL 14972 (Nov. 1972) and DIN 12242 with cone length K 6 (ISO recommendation)

Symbol		Largest diameter of cone (mm)	Length in mm
NS	5/13	5	13
	7/16	7.5	16
	10/19	10	19
	12/21	12.5	21
x	14/23	14.5	23
x	19/26	18.8	26
	24/29	24	29
x	29/32	29.2	32
	34/35	34.5	35
x	45/40	45	40
	60/46	60	46
x	71/51	71	51
	85/55	85	55
	100/60	100	60

x = preferred sizes

b) Spherical joints (S), according to TGL 20678 (Nov. 1971) and DIN 12244 (July 1963, Spherical joints)

Symbol			Diameter of sphere in mm
TGL		DIN[1])	
S	7		7.144
	13.2	13/2	12.700
	13	13/5	12
x	19	19/9	19.050
	29	29/15	28.575
	35	35/20	34.925
x	38	40/25	38.100
	41	41/25	41.275
	51	51/30	50.800
x	64	64/40	63.500
	76		76.200
	102		101.600

x = preferred sizes

---

[1]) The second number refers to the inner diameter of the glass pipe

Conical joints (Fig. 18) are usually employed: they have been in use as interchangeable joints since the beginning of this century. Spherical joints (Fig. 19) have so far been restricted to those devices that would be too rigid if conical joints were used. Spherical joints are made according to standards TGL 20678 and DIN 12244. The precision spherical joints of nominal widths NW 25 to 150 mm (manufacturer, W. Büchi, Flawil/Switzerland) ensure high vacuum tightness without the use of any packing.

The standard DIN 12242 specifies types of ground-glass joints and their applications in laboratory apparatus. The sizes of the interchangeable standard joints (conical, 1:10) are covered by TGL 14972, sheet No. 2, and DIN 12242. Laboratory apparatus is equipped with joints of series 1 and 2, of which specimens 14.5/23, 29/32 and 45/40 are preferably employed. In micro and semi-micro apparatus, NS 7.5/16, 10/19 and 19/26 are also used. It is desirable to construct general laboratory apparatus using exclusively size NS 14.5/23, which is now commonly employed for thermometers (TGL 40-339, DIN 12784), and NS 29/32 since this strongly enhances the interchangeability and combining-power of components. In the author's Destinorm series this principle has been followed and has proved to be very successful. According to standards TGL 14972/3 and DIN 12243, ground joints with a 1:5 cone are required for special purposes where the joint must loosen more easily, as in the distillation of high-boiling mixtures, and particularly in high-vacuum work. Moreover, lenticular and plane joints are in use, mostly for larger apparatus. Even some draft standards concerning glass components and piping for use on a technical scale have been prepared [7].

Fig. 18
Standard conical ground joint. 1:10

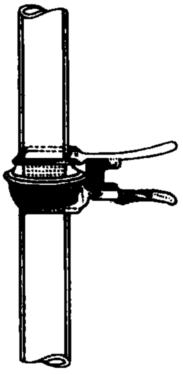


Fig. 19
Standard spherical ground joint with clip

The testing and handling of standard ground joints are dealt with by Friedrichs [4] and Fliedner [5].

As for distillation procedures, numerous conventional methods have become known which are concerned with particular mixtures, such as the determination of the boiling behaviour of phenol crude acids. A rapid analysis for petrols up to 180 °C has been elaborated by Kuehnhanss et al. [6] which covers the paraffins, 5- and 6-ring cycloparaffins and aromatics present. The Destinorm column head shown in Fig. 312 is used. So far the boiling analyses listed in Table 2 have been standardized, with the dimensions of the apparatus exactly determined.

Since ground-glass joints have to be greased attempts have been made to design new joints for glass apparatus. A conical joint where vacuum tightness is provided by labyrinth packing instead of by ground glass has been developed by Wissenschaftlich-Technische Glasgeräte GmbH of Wertheim. Two teflon gaskets render greasing unnecessary. No packing at all is required for Büchi spherical ground joints. Precision grinding ensures high vacuum tightness and pressure resistance. These spherical joints are available for nominal widths 25, 50, 80, 100 and 150 mm. The French laboratory glassware manufacturers Sovirel have developed a connection which employs novel connecting pieces. The principle makes use of a chemically inert gasket placed between two grease-free glass pieces (Fig. 20). The joints are also pressure resistant and vacuum tight. Their temperature resistance corresponds to that of the packing material.

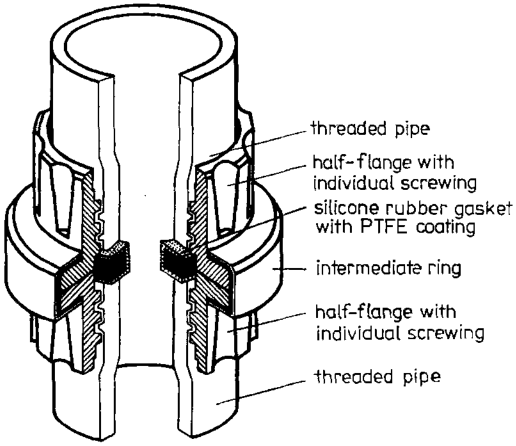


Fig. 20
Sovirel connection (manufacturer, Sovirel, Levallois)

According to Kramer [16] who described modern systems of joints for glass laboratory apparatus these can be classified as follows:

a) Ground-glass joints
   conical joints
   spherical joints
   cylindrical joints
   plane joints
   spherical flanges
   combination joints

b) Polished joints
   precision clear-glass joints
   precision calibrated pipes

Table 2

Standard distillation methods

Standard	Distillation method
TGL 21120	Analysis of mineral oils, liquid fuels and related products; determination of boiling behaviour
21125	Analysis of liquid fuels; vapour pressure determination after Reid
0-51761	Analysis of technical benzenes; determination of boiling behaviour after Kraemer-Spilker
0-51786	Analysis of liquid fuels; determination of the content of non-settling water in fuel oils by distillation with the xylene method
DIN 51751	Determination of the boiling behaviour of Otto fuels and petrols
51752	Analysis of the boiling behaviour of Diesel fuels and similar substances
51761	Determination of boiling behaviour after Kraemer-Spilker
51567	Analysis of mineral oils, higher boiling mineral oil fractions and mineral oil distillation residues — Fractional distillation — after Grosse-Oetringhaus
51611	Low-temperature distillation of gases

c) Joints with packing (except screw joints)
flexible ball joint
conical joint with gasket
plane flange with gasket
spherical flange with packing insert

d) Screw joints
stuffing boxes
screw caps
screw couplings

e) Screw flanges
screwed plastic flange coupling
flanged stuffing boxes
flanged screw caps

f) Accessories for joints
plugs
flexible tubes
sleeves
bellows
safety devices for ground joints
joint greases, and the like

With the screw cap systems, Kramer [16] distinguishes between the designs offered by the manufacturers Quickfit, Witeg and Sovirel.

3.2 Definition of concepts

When comparing various publications on distillation technique it is repeatedly found that fundamental concepts are defined in different ways, a fact often leading to misunderstanding. The word "distillation" itself is employed for the most diverse operations in this field, so that a distinction between "simple" and "countercurrent" distillation (the latter also known as rectification) seems useful. In this way the word distillation becomes a collective term for processes in which liquid mixtures are separated by evaporation and condensation of the outgoing vapour. Hampel [7a] has dealt with the difficult question of the "purity" of solvents and discussed the concept of "ultrapurity". By this he means the highest degree of purity at present achievable. In many cases the impurity concentration is required not to exceed a few ppb. Besides extraction, distillation is a method of achieving this aim. As early as 1943 German standards were elaborated on the "decomposition of liquid mixtures by distillation and rectification" (DIN 7052) which are no longer up to date and, in addition, do not apply to the specific conditions of laboratory distillation. Therefore, new definitions based on a proposal of the author's [8] have been worked out by the Working Committee on Apparatus for Distillation and Rectificatoin of the section of the German standardization committee on Laboratory Apparatus. They have been included in the respective passages of the text.

3.3 Symbols and units

The recent alterations are due to a resolution of the X. General Conference of Weights and Measures in 1954. In the GDR the change was enacted by the first regulation on physical and technological units issued on 14th August, 1958, which has been replaced by that of 31st May, 1967.

In the FRG the regulations pertaining to the law on units of measurement appeared on 28th June, 1970. Information on the practical use and the area of application of the new international system of units (SI) as compared to the previous systems is given in the books of Padelt and Laporte [9], Förster [10] and Haeder and Gärtner [11]. In the meantime further standards have been elaborated (Table 3).

Table 3

Standards on symbols, quantities and units

TGL 0-1304	General signs and symbols; signs and symbols for generally used physical quantities
TGL 18-762	Sheet 1: Quantities and units; names, symbols and abbreviations Sheet 2: Explanations
DIN 1301	Units; symbols and abbreviations
DIN 1313	Notation of physical equations in science and technology

The SI unit of force now is the newton = N = m × kg × s^{-2}. It replaces the kilogramme force and is defined as follows:

$$1\ \text{kgf} = 1\ \text{kg}\ 9.80665\ \text{m} \times \text{s}^{-2} = 9.80665\ \text{N}.$$

For liquid and gas pressures the SI unit pascal = Pa = N × m^{-2} has to be used now. In addition, the larger unit bar = 10^5 Pa is provided. Conversion is done according to

$$\text{atm.} = \text{kg f} \times \text{cm}^{-2} = 0.980665\ \text{bar} = 735.56\ \text{torr},$$
$$1\ \text{torr} = 1.333 \times 10^{-3}\ \text{bar}.$$

The thermal unit used so far, the calorie = cal, is replaced with the joule:

$$1\ \text{cal} = 4.1868\ \text{J}.$$

For thermodynamic temperatures the unit Kelvin (no longer degree Kelvin) is now in use. The degree Celsius for Celsius temperatures $T - T_0$ where T_0 is the thermodynamic temperature of the triple point of water is a special name for the Kelvin. Grad = grd is no longer used to denote temperature differences.

When using the list of symbols, as is done in the following pages, the use of the same symbol for more than one concept is to be avoided. The Latin alphabet proves to be insufficient for this purpose, so that Greek letters have had to be added, whilst further variations have been made possible by the addition of suffixes [12].

3.4 Definitions and conversion of concentrations

In the technique of distillation it is usual to calculate with mole fractions and mole percentages, as this greatly facilitates the computation of vapour volumes, vapour velocities, limiting velocities and so on. Since as a rule it is further the practice to consider the separability of components in sequence, the calculation may be based on that of binary mixtures, in which case of course, the second component may represent a mixture of several constituents. The *average molecular weight* is then determined by the formula:

$$M_m = \frac{W_1 + W_2 + W_3}{W_1/M_1 + W_2/M_2 + W_3/M_3} = \frac{W_1 + W_2 + W_3}{M_{n1} + M_{n2} + M_{n3}}. \qquad (1)$$

number of moles $M_n = W/M$

Example: Determination of the average molecular weight of a mixture:

$W_1 = 300$ g of benzene; $\qquad W_1/M_1 = M_{n1} = \dfrac{300}{78.11} = 3.84$

$W_2 = 400$ g of toluene; $\qquad W_2/M_2 = M_{n2} = \dfrac{400}{92.13} = 4.35$

$W_3 = 500$ g of xylene; $\qquad W_3/M_3 = M_{n3} = \dfrac{500}{106.16} = 4.71$

$W_1 + W_2 + W_3 = 1200$ g of mixture; $\qquad M_{n1} + M_{n2} + M_{n3} = 12.90$

$M_1 = 78.11$; $M_2 = 92.13$; $M_3 = 106.16$; $\qquad M_m = \dfrac{1200}{12.90} = 93.0.$

If it is not otherwise stated, concentrations refer to the low-boiling component. The concentration can be reported as a fraction or percentage by volume or weight or as a molecular fraction or percentage. The fractional concentration is the ratio of the component to the sum of all components.

Fraction by volume; component 1 $v_1 = V_1/(V_1 + V_2)$ (2)

component 2 $v_2 = V_2/(V_1 + V_2)$ (3)

Fraction by weight; component 1 $w_1 = W_1/(W_1 + W_2)$ (4)

component 2 $w_2 = W_2/(W_1 + W_2)$ (5)

Mole fraction; component 1 $x_1 = M_{n1}/(M_{n1} + M_{n2})$ (6)

component 2 $x_2 = M_{n2}/(M_{n1} + M_{n2})$ (7)

To convert these numbers into percentages multiply by 100.
Example: Determination of the molecular fractions and percentages in a mixture:

Component 1	300 g of benzene;	$W_1/M_1 = M_{n1} = 3.84$
Component 2	400 g of toluene;	$W_2/M_2 = M_{n2} = 4.35$
	700 g of mixture;	$M_{n1} + M_{n2} = 8.19$

$$\text{Mole fraction } x_1 = \frac{3.84}{8.19} = 0.47\text{; molecular percentage: 47.0}$$

$$\text{Mole fraction } x_2 = \frac{4.35}{8.19} = 0.53\text{; molecular percentage: 53.0.}$$

In the case of multi-component mixtures the denominator must be extended to contain the additional components:

$$\text{Mole fraction } x_1 = M_{n1}/(M_{n1} + M_{n2} + M_{n3}) \tag{8}$$

$$\text{Mole fraction } x_2 = M_{n2}/(M_{n1} + M_{n2} + M_{n3}) \tag{9}$$

$$\text{Mole fraction } x_3 = M_{n3}/(M_{n1} + M_{n2} + M_{n3}) \tag{10}$$

For the conversion of weight % to mole % in ternary mixtures Lessels [13] gives a useful nomogram.

In the case of binary mixtures the various conversions are performed with the following formulae, which all refer to the low-boiling component 1.

Weight% to Mol%:
$$\text{Mol\%} = \frac{W_1/M_1}{W_1/M_1 + W_2/M_2} \cdot 100 \tag{11}$$

Volume% to Weight%:
where ϱ = density
$$\text{Weight\%} = \frac{V_1\varrho_1}{V_1\varrho_1 + V_2\varrho_2} \cdot 100 \tag{12}$$

Mol% to Weight%:
$$\text{Weight\%} = \frac{M_1x_1}{M_1x_1 + M_2x_2} \cdot 100 \tag{13}$$

Weight% to Volume%: $$\text{Volume\%} = \frac{W_1/\varrho_1}{W_1/\varrho_1 + W_2/\varrho_2} \cdot 100 \qquad (14)$$

Mol% to Volume%: $$\text{Volume\%} = \frac{M_1x_1/\varrho_1}{M_1x_1/\varrho_1 + M_2x_2/\varrho_2} \cdot 100 \qquad (15)$$

As these calculations are often time-consuming, various nomograms have been developed for carrying out the conversions rapidly. In converting from molecular or weight percentages to percentages by volume it should be remembered that the formulae are valid only if no change in volume (contraction) occurs on mixing the components. A nomogram suitable for many purposes has been designed by Orlicek, Pöll and Walenda [14] (Fig. 21).

In using it the following directions should be followed:

For converting from	Value to be used for Q	For component 1 the following values are read off	
		on scale Z	on scale X
Mol. fraction to wt. fraction	M_1/M_2	wt. fraction	mol. fraction
Vol. fraction to mol. fraction	$V_{\text{mol}(1)}/V_{\text{mol}(2)}$	vol. fraction	mol. fraction
Vol. fraction to wt. fraction	ϱ_2/ϱ_1	vol. fraction	wt. fraction

M = molecular weight; V_{mol} = molecular volume; ϱ = density

The choice of the indices should always be so made that Q becomes greater than unity. The use of the nomograms is illustrated by the example. What weight percentage corresponds to 88 mol % if the two components have molecular weights of 150 and 60, respectively?

$$M_1 = 150 \qquad\qquad X = 0.88 \text{ mol. fraction}$$
$$M_1/M_2 = 2.5$$
$$M_2 = 60 \qquad\qquad Z = 0.948 \text{ wt. fraction} = 94.8 \text{ wt.\%}$$

The opposite conversions, weight per cent to mol. per cent, mol. per cent to volume per cent, weight per cent to volume per cent, are of course also possible.

Baehr's circular diagram [15] for converting molecular into weight percentages or vice versa is very convenient, though its accuracy is not so great as that obtained by calculation. Its use will be seen from the example indicated in the nomogram (Fig. 22). What molecular percentage corresponds to 30% by weight of benzene in a benzene-toluene mixture:

M_1 for benzene = 78.11
M_2 for toluene = 92.13

M_1/M_2 0.85

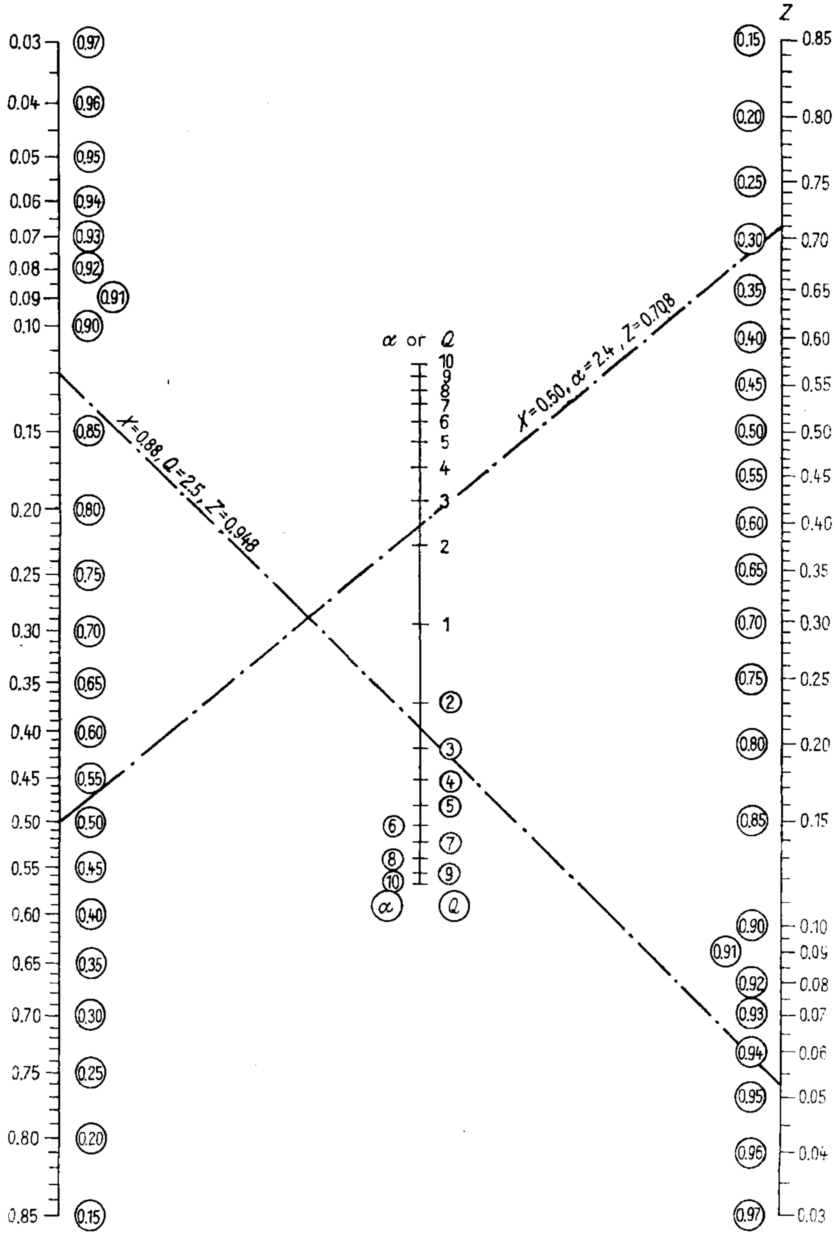


Fig. 21
Nomogram for concentration calculations (Orlicek-Pöll-Walenda)

A straight line is drawn through the point for 30 wt.% on the lower semicircle and 0.85 on the horizontal scale for M_1/M_2; it intersects the upper semicircle at 33.6 mol%.

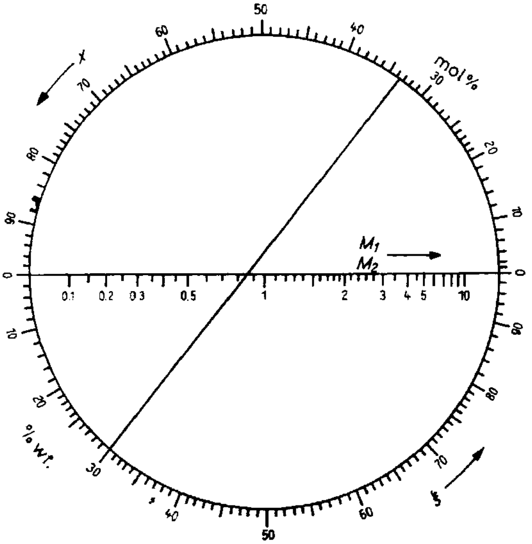


Fig. 22
Nomogram for conversion of mol% to wt.% and vice versa (Baehr)

When dealing with systems of isotopes it is customary to express the concentrations in atomic percentages. Natural water, for instance, is composed as follows (see Table 38):

99.9844 atomic % ^{1}H	99.757 atomic % ^{16}O
0.0156 atomic % D	0.039 atomic % ^{17}O
	0.240 atomic % ^{18}O
100.000 atomic % of hydrogen	100.000 atomic % of oxygen

In a paper as well as in a book Späth [17] has dealt with possibilities of denoting and representing binary systems.

4. Physical fundamentals of the separation process

4.1 Principles of simple and countercurrent distillation

The reader is reminded that the word distillation can be translated as "separation drop by drop" (see Chap. 2). It can therefore be used as a collective term for processes in which mixtures of mutually soluble liquids can be separated by evaporation and condensation of the liquid, the condensed part becoming richer in the most volatile component. The word gives no indication of the technique adopted in the separating process. The terms "simple distillation" and "countercurrent distillation", however, define the mode of operation (Fig. 23). In a strictly physical sense distillation need not produce any separation; we also speak of distillation when a pure liquid is evaporated, the vapour is condensed and the condensate is removed.

The exchange of material can be described by the following basic equation:

$$m = K \times a_{\mathrm{eff}} \times \Delta x_{\mathrm{m}} \tag{15a}$$

(in words: transition current = transition coefficient times effective area of phase interface times driving force).

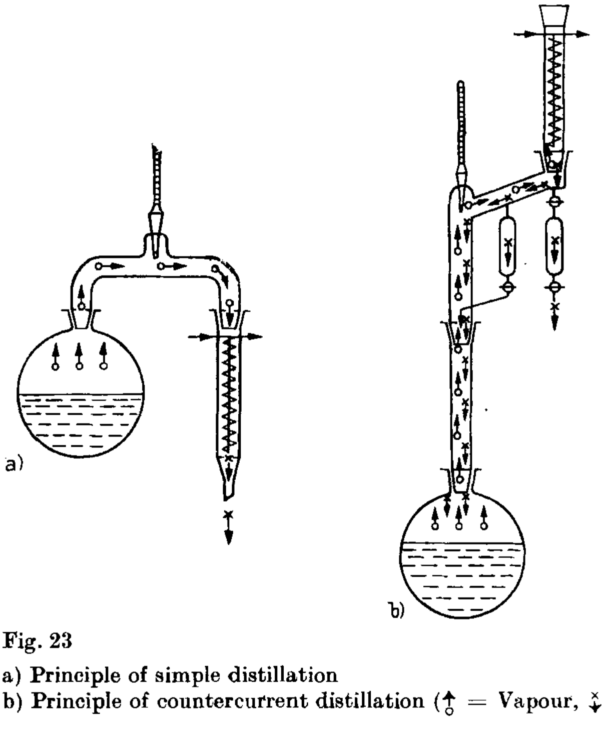


Fig. 23

a) Principle of simple distillation

b) Principle of countercurrent distillation ($\underset{\circ}{\uparrow}$ = Vapour, $\overset{\times}{\downarrow}$ = Liquid)

The exchange of material takes place by diffusion through the phase interface. It depends on the diffusion constant, D, the diffusion paths, b, concentration, x, and the phase interface area, a_{eff}, per unit of length.

The driving force results from the differences of the concentrations in the two phases of the system ($y - x$). At thermodynamic equilibrium they are saturated, the driving force becomes zero and the exchange of material taking place at non-equilibrium ceases.

In *simple* distillation the molecules emerging from the evaporating surface move uniformly until they reach the condensing surface. In *countercurrent* distillation part of the condensed vapour, termed "reflux", returns to the boiler, meeting in its passage the rising vapour. Provision is made for intimate contact between the liquid and vapour in a tube, or "column", between the boiler and condenser. Thus, while simple distillation consists merely of evaporation and condensation, in countercurrent distillation there is an exchange of material and heat between the two phases in the column. This exchange tends towards an equalization of temperature between the phases and to an alteration in the composition of the phases so that equilibrium is approached (Fig. 24).

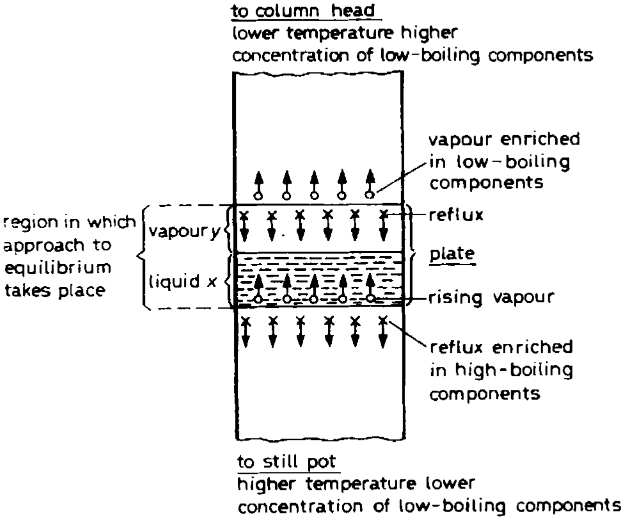


Fig. 24
Separating process on a plate in countercurrent distillation

The nature of this equilibrium is invariably such that as the concentration of a component increases in the liquid, it also increases in the vapour (or in a certain limiting case, remains constant; it never decreases). As the first vapour reaches the condenser at the beginning of a distillation it condenses completely to a liquid of the same composition and starts to return through the column. Now this vapour, at the start of the distillation, is in equilibrium with the contents of the boiler, or still-pot, and contains a greater proportion of the lighter components; thus it cannot also be in equilibrium with its own condensate. The vapour in equilibrium with this condensate would contain still more of the lighter components [1]. The exchange between the vapour and its condensate will therefore be in the direction that brings the vapour into equilibrium with a lighter liquid than the contents of the still-pot, and this will enrich the vapour in the lighter components. Correspondingly the liquid will be enriched in the heavier components.

This exchange continues as the liquid travels down the column and as the distillation proceeds, until a steady state is reached. There is then a gradient in the concentration of liquid and vapour in the column so that each contains more of the lower-boiling material at the top than at the bottom of the column. The concentration gradient is accompanied by a corresponding temperature gradient, with the lowest temperature at the top of the column. This is the principle of the fractionating column.

The exchange of material and heat is a physical process taking place at the interface between the two phases, and the surface area for exchange should therefore be as large as possible. This surface may be supplied by the empty column, by packing or by elements in the column such as plates, wire gauze or rotating components (chaps. 4.3 and 7.3).

The separation is dependent on numerous factors, in the first place on the properties of the components of the mixture, and further on the characteristics of the column and its contents and on factors related to the method of operation.

As a rule it can be assumed that two components of a liquid mixture having a difference in boiling point of more than 50 °C can be separated to a fair extent by simple distillation. For this reason simple distillation is chiefly used on liquid mixtures containing high-boiling or even non-volatile constituents in small amounts. Examples that can be quoted are the removal of dissolved, non-volatile substances in the distillation of water, and the purification of solvents from high-boiling contaminants. An exception is formed by the so-called Engler distillation [2], used for determining the boiling range of mixtures (such as gasolines) having boiling points up to 200 °C, where successive components usually differ but little in volatility. Simple distillation is used here with a view to obtaining easily reproducible conditions. Mixtures with a narrow boiling range cannot be separated by simple distillation.

As regards the mode of operation, batch distillation and continuous distillation are distinguished:

- batch distillation; simple or rectified (countercurrent) distillation in which a given charge is partly or completely distilled
- continuous distillation; simple distillation or rectification in which the feedstock is uninterruptedly passed into the apparatus and the separated different products are continuously removed from the process.

Countercurrent distillation enables components to be separated having differences in boiling point of about 0.5 deg C, whilst this figure can be as low as 0.05 °C if extremely efficient columns are employed, as in the separation of isotopes. By the use of selective methods and, in difficult cases, by combination with other methods of separation such as extraction, countercurrent distribution and gas chromatography, separations have been performed with mixtures previously regarded as inseparable.

In the following sections the complex processes taking place in countercurrent distillation will be discussed further (cf. Kuhn and Kuhn and Ryffel [3]).

Before every distillation, whether simple or countercurrent, a series of points must be considered prior to starting the calculations. A plan of work for judging a separation problem is given in Table 4.

More detailed instructions for carrying out distillations are given in section 4.14. Information about the assembly of apparatus and the starting of the process is given in sections 9.3 and 9.5, respectively.

Table 4

Plan of work for judging a separation problem

Criterion	Point to be decided or calculated	See Section
1. Difference in boiling point	Simple or countercurrent distillation	4.1 4.7.5.1
2. Vapour pressure curves	Optimum pressure in distillation	4.4 4.6.2 5.3 5.4
3. Equilibrium curve	Theoretical plate number and conditions of distillation	4.6—4.7.4
4. Required separating effect	Choice of separating method and calculation of conditions in distillation	4.7.5 4.8 4.9 5. 6.
5. Required throughput	Choice of apparatus, calculation of dimensions and heat balance	4.11 4.12 5.1 5.2 7.
6. Separating ability of the column	Testing the column	4.10
7. Automation	Measuring and regulating devices	8.

4.2 Fluid and interface dynamics

4.2.1 Wetting columns

The thermal separation of material makes use chiefly of four types of column:

plate columns (chap. 7.3.3)
columns for falling film distillation (chap. 5.4.3)
columns with various elements (chap. 7.3.4)
packed columns (chap. 7.3.2)

All these types have as a common characteristic the countercurrent of the two fluid phases. Due to the geometries of the various columns, however, marked differences are found in the way the flows pass the column. The last three types can be classified as "wetting columns" since thin-film formation is their outstanding feature and the two closed phases move against each other without mutual penetration. It is characteristic of the plate column, on the other hand, that more or less dispersed gas bubbles penetrate through the liquid and combine again on the next plate. (Fig. 25). Suitable model liquids for a study of the material exchange in countercurrent columns are freons and inorganic chlorides with a dilute iodine solution [3a]. Radionuclides have also been used to study liquid currents, *e.g.* ^{82}Br in a column for the distillation of butadiene [3b].

The basic feature of a column with stationary or rotating elements is that the elements are regularly arranged. Sulzer's packing is a wire gauze insert for falling film distillation which gives rise to a prolonged zigzag path for exchange while in the spray column (Spraypak) the liquid phase is dispersed due to the kinetic energy of the vapour, the latter moving through the packing as a closed stream. This compari-

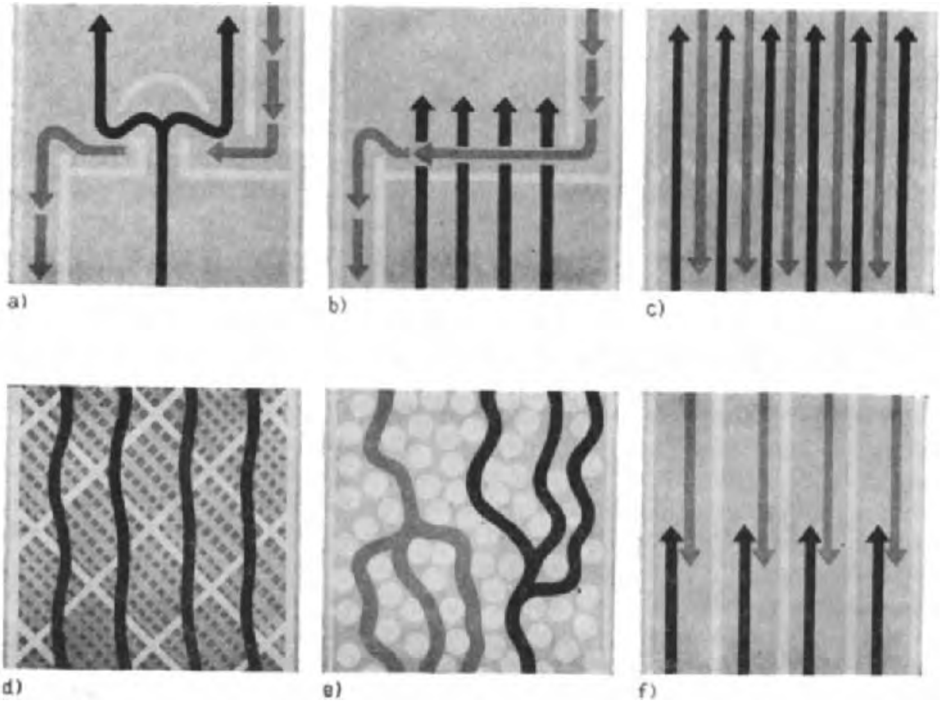


Fig. 25
Phase flow diagrams for various column types (Stage)

a) Bubble-cap column
b) Sieve-plate column with guided liquid
c) Sieve-plate column with non-guided liquid
d) Spraypak column
e) Packed column
f) Falling-film column

son already gives an idea of the problems involved in packed columns. The random arrangement of the packing leads to non-uniform, changeable flow of the fluid phases, whereas in the other types of columns the currents move along regularly arranged channels.

In packed columns a non-uniform distribution (maldistribution) is to be expected both in the vapour and in the liquid phase. In the liquid it occurs for these reasons [4]:

a) The liquid flows more readily from the packing units toward the column wall than in the opposite direction. Vapour condensation on the wall due to heat loss may enhance this process. This form of maldistribution is called wall flow (chap. 4.8.1).

b) The distributing effect of the packing units themselves is insufficient so that a channel formed by chance persists (channelling) (chap. 4.8.1).

c) The packed column contains packing layers which tend to give the liquid stream some preferred directions. This is also called channelling. Such layers may be due to the method of filling or the shape of the packing units.

d) The column is not in an exactly vertical position.

e) The reflux is unevenly distributed initially.

Hence we have:

$$\text{maldistribution} = \text{channelling} + \text{wall flow}.$$

Wall flow depends on both separating length and column diameter. With a ratio of $d_K/d_{FK} \approx 20$ a fixed wall flow of 10 to 20% is established, which in turn is influenced by the ratio of separating length to column diameter.

The relative effect of maldistribution is the greater the more separating stages a column has. A maldistribution of, say, 10% reduces the plate number of a column with 100 plates to 30 while a column of 10 plates is only reduced to 9. Since also in industry the trend is toward more and more efficient columns the question of the maldistribution of the fluid phases is gaining importance.

While it is relatively easy to cope with the problems of vertical column positioning and the distribution of the liquid research is concentrating on getting better insight into the distribution of the fluid phases during the separation process. The increase of both column diameter and separating length results in a relative decrease of column efficiency. Thus, *e.g.*, the radial extension and the distribution of a liquid from a point source in passing through a layer of Raschig rings were investigated experimentally by Bemer and Zuiderweg [4a]. The parameters varied were wettability and ring size, effective separating length and liquid load. Measurements by Farid and Gunn [4b] of radial and axial dispersion coefficients in packed columns of 0.1 and 0.3 m diameter for packings of spheres and Raschig rings of sizes 1.27 and 3.80 were made such that the influence of wall flow could be eliminated.

In all cases, the maldistribution in a column causes a reduction of the plate number since the local molar ratio of vapour to liquid is disturbed. This influence was best estimated theoretically by Huber and Hiltenbrunner [5]. They envisaged a quadrangular model column partitioned along its long axis with the two compartments loaded differently. As a measure of maldistribution l they defined the relative deviation of the local flow density from the mean value taken over the whole cross-section:

$$l = \frac{L_l - \bar{L}}{\bar{L}}, \tag{16}$$

where L_l = liquid flow density at a given point, $\bar{L}$ = mean liquid flow density over column cross-section. The partition is interspersed with several mixing points where the two partial streams are mixed to a degree m, the mixing being associated with radial transport of matter (Fig. 26).

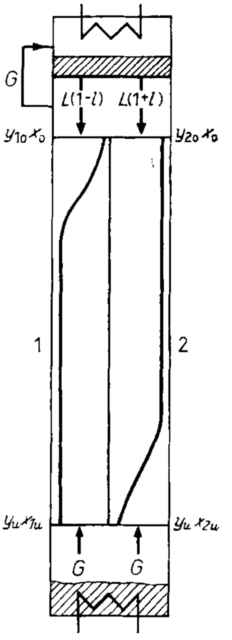


Fig. 26
Model of a column without lateral mixing (Huber and Hiltenbrunner [5])

The column is divided into two compartments by a partition. Within a compartment, the flow densities of the gas G and the liquid L are constant but they may differ from compartment to compartment. In the diagram the gas flow is equally shared by the two compartments whereas the reflux is not. l is a measure of maldistribution. Any given maldistribution can be approximated by a division into a greater number of compartments. Concentration for number of separating stages $n = \infty$.

The efficiency n_m/n_0 of a packed column then is a function of maldistribution l and degree of mixing m per separating stage:

$$\frac{n_m}{n_0} \approx \frac{1}{1 + \dfrac{l^2}{3.75 \times m}}, \tag{17}$$

where m = degree of mixing per separating stage, which indicates what proportion of the column cross-section is involved in the mixing as the material stream traverses a separating stage.

According to a model of Huber the degree of mixing m per separating stage can be estimated to be

$$m = 27 \left(\frac{d_{FK}}{d_K}\right)^2, \tag{18}$$

where d_{FK} = packing unit diameter and d_K = column diameter. For example, for $d_K/d_{FK} = 10$, $m = 0.27$; for $d_K/d_{FK} = 30$, m becomes 0.025.

In the former case the degree of mixing m is so large that even a strong maldistribution reduces the efficiency only slightly. In the latter case this does not hold any more. The example is in accordance with the empirical rule that the d_K/d_{FK} ratio should lie between 10 and 30. The true value for the plate number of a column can thus be obtained only with a d_K/d_{FK} ratio of 10:1, hence at $l \approx 0$.

The relationships between the quantities of flowing matter in the two phases and the various hydrodynamic parameters such as dynamic and static hold-up (chap. 4.10.5), longitudinal mixing and pressure drop (chap. 4.11) were studied in detail by Kafarov, Dorokhov and Shestopavlov [6]. They found a quantitative connection between dynamic hold-up and pressure drop and a dependence of the static hold-up on regions of flow. A model for the non-stationary liquid flow in the packing was elaborated on the basis of effective and dead space liquid volumes and was used for the calculation of the liquid parameters. Moreover the dependence of the longitudinal mixing coefficient on the vapour and liquid loads as well as the physical properties of the liquid were investigated. The main causes of axial mixing in packed columns were reported by Jonas [7]. The measurements of Timofeev and Aerov (chap. 7 [65]) were also made with a view to the question of the influence of column diameter on efficiency. Liquid flow and liquid-phase exchange of material in falling film distillation with various packings were studied by Zech and Mersmann [270] since it is generally impossible in physical exchange of material to measure the interface which is effective in the exchange of material between a liquid and a gas.

The separation process in a packed column can already be influenced markedly by the different surface tensions of the components of a mixture [8]. An improved method of calculating the surface tensions of vapour-liquid mixtures was developed by Bauer [8b]. It is especially suited for inclusion in programmes for the calculation of material data. If in separating a binary mixture the surface tension σ of the reflux increases (positive system) the exchange of material can proceed much faster than in systems with decreasing reflux surface tension (negative systems). In negative systems the reflux is dispersed into narrow streams and drops. However, this effect becomes appreciable only when $\Delta\sigma > 3$ dyne/cm^{-1}. Systems with interface tension differences < 3 dyne/cm^{-1} are termed neutral.

The influence of column diameter and surface tension on the HTU in packed columns in the countercurrent distillation of binary mixtures was studied by Gomez and Strumillo [8a]. They found the relation

$$\mathrm{HTU} \sim D^{0.65} \times F_\sigma^{\,0.08} \tag{18a}$$

with D = column diameter (62 – 200 mm), F_σ = quotient of $\sigma_{\text{low-boiling comp.}}$ to $\sigma_{\text{high-boiling comp.}}$, σ = surface tension.
Values for F_σ of < 1, ≈ 1 and > 1 correspond to positive, neutral and negative systems, respectively.

Ponter et al. [8c] investigated the effect of adding an interface-active substance on the efficiency of a packed column. They observed an increase in packing efficiency corresponding to a change of the wetting behaviour as determined by contact angle measurements. The additive had virtually no influence on the vapour-liquid equilibrium. These investigations were complemented by an assessment of the influence of surface tension on binary liquid systems in distillation with total reflux [271] and of the separating efficiency of packings on the basis of wetting data obtained under conditions other than material exchange [272].

In process engineering the ratio of the effective surface area of the packing to the given total surface area is called the degree of wetting B_g:

$$B_g = \frac{A_{\text{eff}}}{A} \times 100\ (\%), \tag{19}$$

where A_{eff} = wetted surface area, A = total surface area.

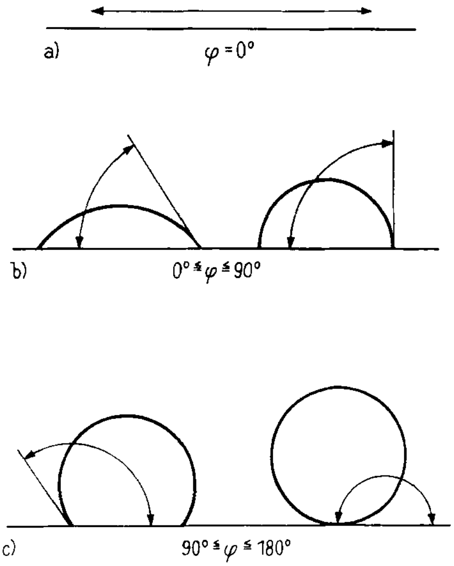


Fig. 27
Wetting of a solid by a liquid phase (φ = contact angle)

a) total wetting
b) partial wetting
c) no wettability

Numerous relations have been worked out for the determination of the degree of wetting of packing units but they differ very strongly [9]. Questions of the effective surface area of packings and practical possibilities of determining it independent of the kind of process have been thoroughly discussed by Kolev [9a]. He considered, above all, the influence of viscosity.

It seems essential that the energies of adhesion of the systems involved, the possibility of a contraction of the liquid film in negative systems and the contact angle (Fig. 27) are not taken into account in these relations. This may account for the great differences between calculated and experimental data. Combining the equations after Dupré and after Young yields the following simple relation for the work of adhesion:

$$W_{s-1} = \sigma(1 + \cos \varphi). \tag{20}$$

It is obvious from this equation that a high value of A_{s-1} requires a high surface tension and as small a contact angle as possible.

Since a system to be separated has a fixed surface tension there remains only to achieve a small contact angle by choosing the appropriate constructional material for the packing. Table 5 gives the energies of adhesion according to eq. (20) for various vapour-liquid systems [11].

Table 5

Energies of adhesion of solid-liquid systems (liquid phase: water, 20 °C)

Group	Constructional material	φ (deg)	Mean depth of roughness R_m (μm)	$W_{\mathrm{s-l}}$ (erg · cm^{-2})
Pure metals	tungsten	62	0.1···0.5	109.0
	platinum	71		96.5
	copper	84		80.4
	aluminium	85		79.2
	nickel	86		77.9
Alloys	"St. 37" steel	79	0.1···0.5	86.7
	X–10–Cr Ni Ti–18.9 steel	83		81.7
	phosphor bronze	84		80.4
Plastics	polyamide	72	< 0.1	96.3
	polyester	72		96.3
	polymethyl methacrylate	72		96.3
	polyvinyl chloride	73		94.1
	polycarbonate	77		89.2
	polystyrene	80		85.2
	polypropylene	90		72.8
	polyethylene	90		72.8
	teflon	106		52.5
Ceramics	porcelain	50	5···15	119.0
	glass	20	0.1	140.8

Obviously, the greater the energy of adhesion the greater the stability of the liquid film formed on the packing although, on the other hand, it becomes increasingly difficult to make a film of liquid form on the whole of a solid surface [11]. The wetting capacity can be increased considerably by preflooding (chap. 4.10.8) and by choosing an optimum geometry of the solid surface of the packing [9]. Titov and Zelvenskiy [10] have reported 3 methods of calculating active phase interfaces in packed columns. Graphical representations are given for the dependences of the activated surface area, the HTU value and the material exchange coefficient on the liquid rate.

Krell and Heinrich [11m] assumed that the degree of wetting can only be exactly precalculated if the contact angle of the liquid on the packing material is taken into account. They investigated Raschig rings of ceramic and PVC material of sizes between 10 and 50 mm. They varied the liquid phase so as to give contact angles φ in the range of 27 to 90°. As a result of extensive series of experiments [11n] the following relations for the calculation of the degree of wetting B_g have been formulated:

1. contact angle $0 \leqq \varphi \leqq 58°$:

$$\varphi = \mathrm{e}^{-0.105} \times \frac{\vartheta}{\sqrt{d}} - \left[\mathrm{e}^{-0.105} \times \frac{\vartheta}{\sqrt{d}} - (3.327\, d^{0.0257} - 0.00742\, \vartheta - 3.172)\right] \times \mathrm{e}^{-0.210}\, W_L, \tag{20a}$$

2. contact angle $58 \leqq \varphi \equiv 90°$:

$$\varphi = 0.489\, \mathrm{e} \left(\frac{0.0192}{\sqrt{d}} - \frac{0.39}{d} + \frac{1.245}{d^2}\right) \vartheta \times (1 - \mathrm{e}^{-0.210}\, W_L), \tag{20b}$$

where d = diameter of packing units (mm), W_L = liquid rate ($m^3/m^2 \times h$).

Relations (20a) and (20b) can be employed

- for all organic and aqueous solutions
- for all operating conditions below the point of flooding onset
- for any packing material
- for any temperature
- for all column diameters and packing heights if these recommendations are considered:

packing height < 1.000 mm: 1 redistribution of liquid for each 14 cm^2 of column cross-section
packing height > 1.000 mm: at least 1 redistribution of liquid for each 180 cm^2 of column cross-section.

The successful use of the relations has been reported e.g. by Weiß and Schmidt [110] and Schmidt [11p]. They differ from those suggested by other authors in that they allow for the constructional material of the packing and the surface roughness. The critical surface tension is not sufficient for an exact calculation of the degree of wetting.

Kwasniak [11a] studied condensation and vaporization effects in packed columns on the assumption that there is a temperature difference between vapour and liquid in each cross-section of the column. Thus the unwetted portions of the packing surfaces can be regarded as heat exchange surfaces. The packing units were of identical shapes and consisted of copper or copper-coated plastic platelets so that there resulted greatly differing heat conductivities. The platelets were arranged such that their downward surfaces remained unwetted. The two packings differed very much in separating efficiency which was due to the condensation and vaporization effects occurring in the copper packing. This demonstrates that the effect of such processes should by all means be taken into account. These considerations led Kwasniak to develop a novel regular packing consisting of zigzag strips of sheet metal which are oriented differently. Thus turbulences in the liquid and vapour phases and high degrees of wetting are achieved.

4.2.2 Film formation

The model concept of accelerated wavefree flow on flat plates was elaborated by Yilmaz and Brauer [11b] for a theoretical description of the fluid dynamic behaviour of liquid films in packing layers. Their considerations have been confirmed by measurements. Investigations of the onset of wavelike flow on acceleration yielded a diagram which is valid for the different flow states. From this it follows that, for example, film flow in packing layers is practically always laminar and wavefree. On these theoretical grounds equations have been developed for the calculation of the operating liquid contents of Raschig ring layers (see chap. 4.10.5).

A detailed study of the hydraulics of countercurrent columns for falling film distillation with an insert of corrugated sheet metal was made by Künne [11c] with air-water as test system at room temperature and normal pressure. He gives information about column dimensioning and suggests models for calculating the hydraulic resistance and the upper limiting load of the vapour phase. A method for the experimental determination of the vapour-liquid interfaces in falling film columns is reported by Antonov et al. [11h].

Marschall [11k] describes methods which allow the undisturbed measurement of the local film thickness, the wave amplitude, wave frequency and wave length as well as the inclination of the film surface as a function of time. It is interesting to note that these methods make use of the scattering of laser beams. Vorontsov [11q] made a systematic study of the effect of the types and dimensions of regular surface features providing roughness on walls with vertical film flow.

Starting from the hydrodynamic model of the liquid film generated mechanically in columns with rotating elements and using simplifying assumptions Dietz et al. [11d] deduced an equation for the calculation of film thicknesses in the range $0 <$ film thickness $<$ gap width:

$$\delta = \sqrt{\beta} + \sqrt{\vartheta \sqrt{\xi} - \frac{1}{3}\beta}, \tag{20c}$$

where

$$\beta = \frac{\varkappa^2 \mu r_i}{4 \varrho n r_A}, \quad \vartheta = \frac{\Gamma}{\varkappa r g}, \quad \xi = \frac{\mu n r_A}{\varrho r_i}.$$

δ = mean film thickness, $\varkappa = 0.304$, r_i = inner radius, ϱ = density, n = number of r.p.m., Γ = mass flow related to circumference, μ = dynamic viscosity, r_A = radius up to outer edge of brush.

The special flow processes in thin-film stills were studied by Godau [11e]. Representing the relevant parameters and mathematical relations Billet [11f] also deals with the continuous distillation from a thin film as exemplified by a Lipotherm thin-film still. Arithmetical work with the relations obtained indicates that operating with reflux can yield maximum separating results under certain loading conditions.

The possibilities of intensifying the transport of material in falling films were studied systematically by Wünsch et al. [11c]. Special consideration was given to effects due to the ripple of the film, the curvature of the phase interface, the roughness of the solid surface and the intentional disturbances of the film flow.

4.2.3 Column dynamics

On the basis of mathematical models attempts are made to precalculate the dynamic behaviour of distilling columns. According to Köhler and Schober [264] column dynamics involves these problems:

- the study of the column behaviour in time due to process disturbances (single or combined disturbances)
- the simulation of starting and stopping processes and of changes of operation (intentional or unintentional)
- the recalculation of plants during periods of nonstationary operation
- the calculation of stationary states as limits of dynamic conditions
- model calculations concerning the control of plants
- recommendations for improved designs taking into account essential effects occurring within nonstationary periods (changed vapour-liquid loads)
- the theoretical explanation of "pulsating effects" in separating plants and the calculation of variants to eliminate such effects.

Adolphi [11g] evolved a graphical method for calculating the dynamic behaviour of binary distillations which is based on the McCabe-Thiele diagram. The behaviour of packed columns with countercurrent distillation was examined by Wagner et al. [162a, b]. The behaviour of ideal and non-ideal binary and of ternary systems is reported by them. The behaviour of coupled distilling columns has also been investigated. Of course, electronic computers are employed on a large scale for column dynamic calculations (see chap. 4.15). The limiting states in the separation of binary mixtures as affected by disturbances and possibilities of removing or diminishing the latter have been examined by Wünsch [111]. He concludes that the enthalpy composition diagram may provide important information about the disturbing behaviour of separating units.

4.3 Miscibility of the components

Experience tells us that the solubility of liquids is the higher the more closely the substances are related chemically (homologous series). Regularities occurring in the mixing of organic compounds have been tabulated by Staudinger [12]. In most cases the miscibility increases with increasing temperature until we find complete miscibility above the critical mixing temperature $T_{\mathrm{m\,krit}}$. In Fig. 28 the solubility diagram of water-phenol mixtures is given as an example.

In general distillation uses completely miscible liquids since in case of phase formation a separation is carried out at first by decanting. It should be noted, however, that there is no complete insolubility. Since dissolved substances cannot be separated mechanically it is distillation which results in a separation.

Carrier vapour distillation — chiefly steam distillation — and azeotropic distillation deliberately use mixtures with no or with partial solubility. Carrier vapour distillation is employed in order to have lower vapour temperatures in the mixture while in azeotropic distillation the addition of a selected substance serves to produce an azeotrope of the added substance and one component so that the latter can be separated from the other components. It is necessary that the azeotropic distillate should be easy to separate into its components (see chap. 6.2.1). Thus in these cases it is very important to know the solubility diagram of the azeotropic mixture to achieve a phase separation by proper cooling. From Fig. 28 it can be seen, for example, that above 68.8 °C the solution is homogeneous for all concentrations whereas below this temperature demixing is dependent on the concentration.

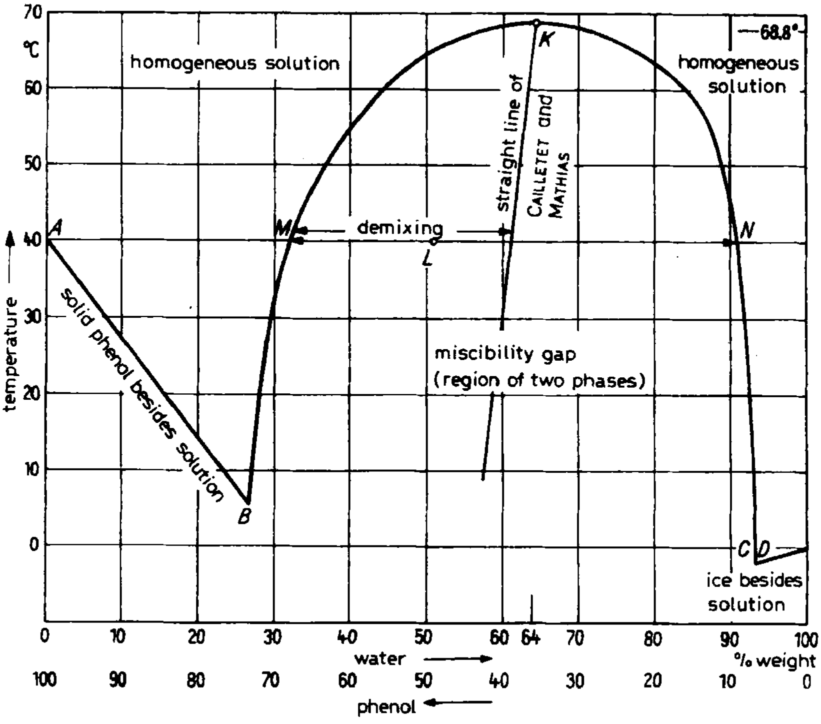


Fig. 28
Solubility diagram of the mixture water-phenol

While the solubility of two components may range from virtually insoluble to completely miscible the boiling behaviour displays greater variety. In ideal mixtures the intermolecular forces acting among like and unlike molecules are equal. If the forces between unlike molecules are smaller than those between like molecules a minimum-boiling azeotrope can be assumed, while in the converse case a maximum-boiling azeotrope will be found. Intermediate are those non-ideal mixtures the equilibrium curves of which will approach the diagonal asymptotically from above or below. Stage [13] has given a summary of the relationships involved (Table 6) and Fig. 29 shows the corresponding types of equilibrium curves. These questions will be discussed in greater detail in chaps. 4.6 and 6.2.

Hildebrand and Rotariu [14] have considered differences in heat content, entropy and activity and classified solutions as ideal, regular, athermal, associated and solvated. Despite much fundamental work the theory of binary liquid mixtures is still essentially unsatisfactory as can be seen from the systematic treatment of binary mixtures by Mauser-Kortüm [15]. The thermodynamics of mixtures is presented most instructively in the books of Mannchen [16] and Schuberth [17]. Bittrich et al. [17a] give an account of model calculations concerning thermophysical properties of pure and mixed fluids.

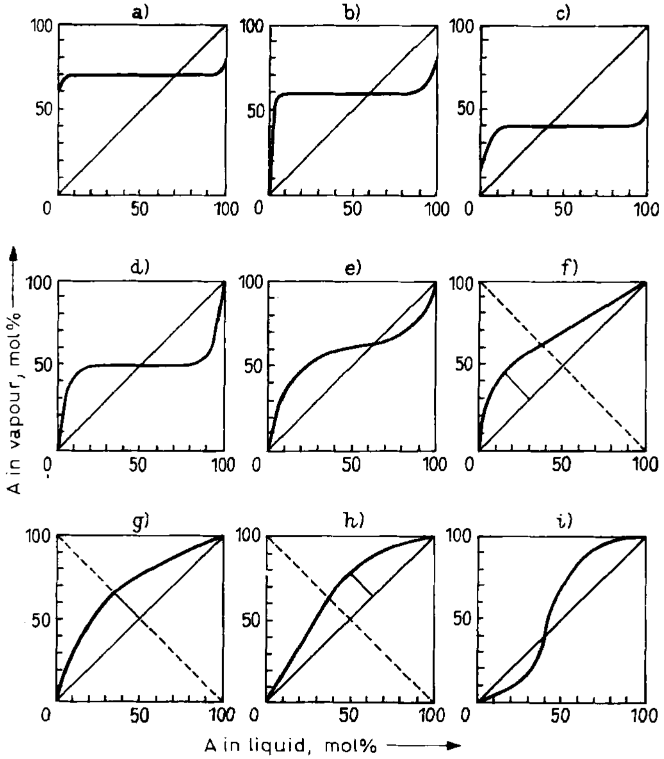


Fig. 29
Vapour-liquid equilibrium curves of binary mixtures

- a) Benzene-water
- b) Water-furfural
  (solubility of A in B < B in A)
- c) Water-n-butanol
  (solubility of A in B > B in A)
- d) Sec.-butanol-water
- e) Ethanol-water
- f) Methanol-water
- g) Benzene-toluene
- h) Acetone-acetic acid
- i) Acetone-chloroform
  Nitric acid-water

Table 6

Boiling behaviour of binary liquid mixtures

Type in Fig. 29	Solubility of the two components	Boiling behaviour	Comparative magnitudes of forces between identical ($a_{1/1}$, $a_{2/2}$) and non-identical ($a_{1/2}$) molecules
a	virtually insoluble	minimum boiling point	$a_{1/2} \ll a_{1/1}$ and/or $a_{2/2}$
b c d	partially soluble (solubility gap)	minimum boiling point	$a_{1/2} \ll a_{1/1}$ and/or $a_{2/2}$
e	completely miscible	minimum boiling point	$a_{1/2} \ll a_{1/1}$ and/or $a_{2/2}$
f	completely miscible	non-ideal, without azeotrope	$a_{1/2} < a_{1/1}$ and $a_{2/2}$
g	completely miscible	ideal	$a_{1/2} \approx a_{1/1}$ and $a_{2/2}$
h	completely miscible	non-ideal, without azeotrope	$a_{1/2} > a_{1/1}$ and $a_{2/2}$
i	completely miscible	maximum boiling point	$a_{1/2} > a_{1/1}$ and $a_{2/2}$
	completely miscible	formation of compound	$a_{1/2} \gg a_{1/1}$ and $a_{2/2}$

4.4 Vapour pressure-temperature relationship, *p*—*t*

In order to assess a separation problem we need to know the vapour pressure-temperature relationship. By plotting the pressure of the saturated vapours against the temperature we may gain some idea of the pressure at which the separation appears most promising; the abscissa is best drawn on a logarithmic or related scale (Fig. 39). The choice of the pressure depends on whether we wish to perform

a) an analytical distillation,
b) a preparative distillation,
c) a production distillation or
d) a distillation for comparison with a large-scale operation.

In general we should choose a pressure for the distillation such that, at the one extreme, the temperature in the column head is adequate for complete condensation with the cooling medium available and, at the other extreme, that the temperatures are not high enough to cause decomposition.

In analytical distillation it should be the aim to achieve a maximum separating effect; the relative volatility should therefore be as large as possible, and in an ideal mixture this is so at the pressure at which the ratio of the vapour pressures is a maximum (see chap. 4.6.2). The same applies to preparative distillation, whilst in the case of production distillation account should be taken of the increase of the volume of vapour with decreasing pressure, which may limit the throughput. In comparative distillation the pressure must be adjusted to that maintained in the larger installation.

Extensive collections of saturated vapour pressures have been given by Dreisbach [18], who also worked out the physical constants for 38 "Cox chart" families. In these tables [19] the boiling points for about 500 organic substances are quoted at 1, 10, 100 and 760 mm Hg. Stull [20] has collected the data for about 1200 organic compounds at 1, 5, 10, 20, 40, 60, 100, 200, 400 and 760 mm Hg. This collection furthermore contains figures for about 300 inorganic compounds and gives about 100 values for the region from 1 to 60 atm. Stage has published corrected saturated vapour pressures for various classes of compounds, viz. for the saturated straight-chain C_1 to C_{18} [21] fatty alcohols, for the methyl esters of the saturated straight-chain C_1 to C_{18} [22] fatty acids, for phenols [23] and the volatile components of alcoholic malts and crude spirits [24]. Extensive tables have been given by Jordan [25]. Riddick and Toops jr. [26] have provided vapour pressures and other physical data for 254 solvents, whilst Sage and Lacey [27] have tabulated vapour pressures and equilibrium curves for low-boiling hydrocarbons, H_2S and CO_2. Glaser and Rueland [28] determined the vapour pressure curves in the region of 1 to 60 atm for 33 substances, previously not investigated. The literature on vapour pressures for medium- and high-vacuum work has been reviewed by Jaeckel [29]. More recent compilations are to be found in the publication „Fortschritte der Verfahrenstechnik" and in abstract-type publications (cf. ref. chap. 1 [16]).

Although numerous data are hence already available, it may be necessary for the laboratory worker to determine vapour pressures himself. The more reliable course is to measure data experimentally, though several methods of calculation, described in section 4.4.2, can be followed.

4.4.1 Measurement of saturated vapour pressures

Fundamentally there are two methods by which saturated vapour pressures of a pure substance can be determined, namely

a) the dynamic method: the measurement of the boiling point at various pressures;
b) the static method: the measurement of the vapour pressure at various temperatures.

In the Houben-Weyl manual, Kienitz [30] gives a detailed description of how the measuring should be done. Methods and apparatus for the determination of low vapour pressures are reported by Milazzo [31]. He shows that the McLeod manometer yields very satisfactory results with pressures in the range of 10 to 10^{-5} torr.

As the experimental execution of the static method is rather difficult, particularly at high temperatures, whilst pressure control presents no difficulty with the accurate regulators now available, the dynamic method will generally be chosen. It is important that the substance to be examined should be checked for purity.

For an accurate measurement of the boiling point it is essential for the boiling liquid to be mixed thoroughly by the bubbles of vapour. The classical apparatus for measuring boiling points is Swiętosławski's ebulliometer [32]. The semi-micro form of the differential ebulliometer is depicted in Fig. 30. Besides boiling point determination, it is employed for examining the purity of substances and for studying the azeotropy of multi-component systems.

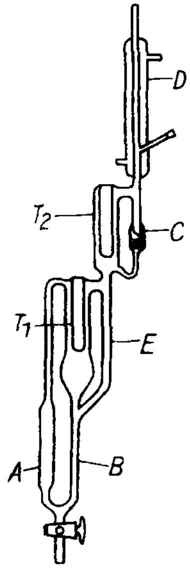


Fig. 30
Differential ebulliometer (semi-micro form for 10—12 ml) (Swiętosławski)

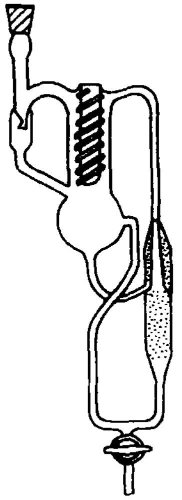


Fig. 31
Swiętosławski's ebulliometer, as modified by Olszewski, for heteroazeotropic mixtures

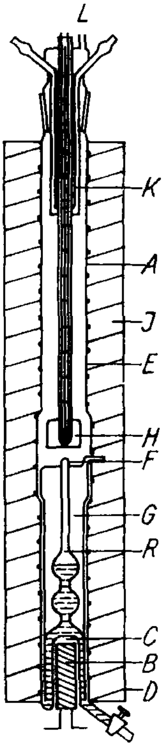


Fig. 32
Ebullioscope with heat insulating jacket, after von Weber

The substance (10—12 ml) is placed in the arms *A* and *B*. In arm *A* there is a fritted glass plug and an electric heating element. The resulting vapour entrains the liquid upwards and enters the tube T_1, where the temperature is measured. The vapour flows further along the tube T_2, where the condensation temperature is observed, and is completely condensed in condenser *D*. The liquid then returns to the boiling arm via the drop counter *C* and tube *E*. Drop counter *C* serves to measure the rate of evaporation.

A three-stage ebulliometer is used for determining the azeotropic composition of hygroscopic substances, such as pyridine bases and phenol. In this case the boiling temperature and two condensation temperatures are measured. If the charge is a pure substance or an azeotrope, all three temperatures should be the same. A further modification for boiling point determination in the case of hetero-azeotropic mixtures has been developed by Olszewski (Fig. 31).

The ebullioscope of von Weber, shown in Fig. 32, operates in a similar manner. With this apparatus vapour pressure curves in the range of 10 to 760 mm Hg can be determined, whilst it can also be employed for other purposes, for instance for the calibration of thermometers, ebullioscopic measurements, the determination of vapour-liquid equilibria and the characterization of distillate fractions, such as those from petroleum and tar [33]. The apparatus consists of a vertical boiling tube *A* of 34 mm I.D. and 500 mm length. At its lower end the liquid is heated by an electric soldering iron element *B* of variable output, which is contained in a well *C*, the outer wall of which is coated with a layer of fritted glass to prevent bumping. A collar *D*, reaching almost to the bottom, collects the bubbles of vapour, which are led together with liquid to the spray tube *R* (4 mm I.D.), where they are whirled together in two bulbs and then sprayed against the thermometer by the jet *F*. The spray tube and bulbs are surrounded by an evacuated jacket *G*; the liquid separating from the vapour at the thermometer enclosure flows back into circulation through a narrow annular space between the vacuum jacket and the boiling tube. The thermometer is immersed in a little mercury in the protecting tube *H*, which has a fused-on dropping cap diverting the downflowing condensate from the thermometer enclosure. The mercury thread is surrounded by condensing vapour. The thermometer scale is illuminated from behind and is read through the layer of condensate, estimating to 1/10th of a scale division; no difficulty will be experienced in doing this if the upper part of the ebullioscope is etched smooth before use with 1% hydrofluoric acid for 2 minutes, and is occasionally boiled out with soap solution. The apparatus, up to the condenser

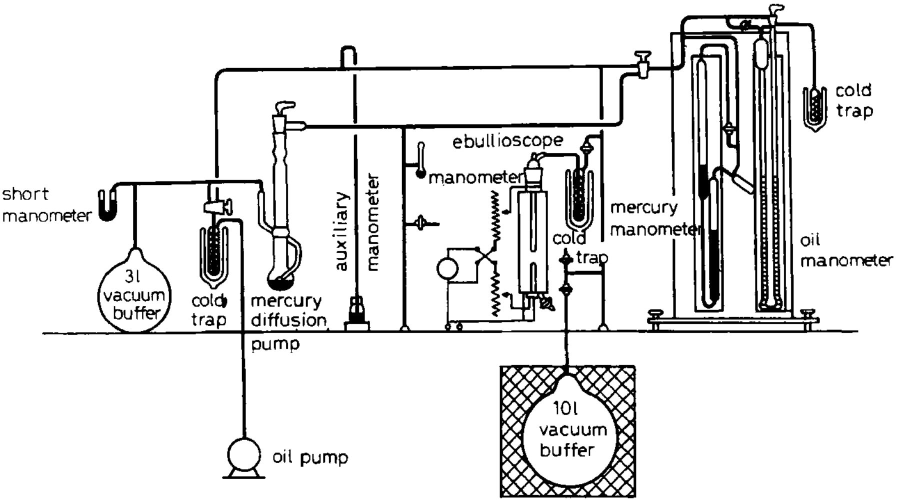


Fig. 33
General arrangement for the measurement of saturated vapour pressures with the apparatus of von Weber

K, is surrounded by an insulating jacket *J* of glass fibre provided with a narrow viewing slit; inside this jacket the tube carries a winding of thin resistance wire *E* for thermal compensation. It can be regarded as an infinitely long cylinder surrounding the measuring point, in which the source of heat is uniformly distributed. With the aid of a voltmeter and a calibration chart this heater is so regulated, with no current in the boiling element, that the predicted temperature of measurement is approximately maintained in the apparatus. Even the vapour of a high-boiling liquid will then rise up to the condenser, 250 mm above the thermometer bulb. The fourfold protection provided by the evacuated jacket, the liquid flowing back at boiling temperature through the annular space, the thermal compensation and the fibre jacket ensures an adiabatic condition in the spray tube. The liquid charge is introduced at the top through the side tube *L*, which also serves to connect the suction tube for measurements in vacuum.

The whole arrangement, provided with a manifold to which pumps, ebullioscope and manometer are connected, is shown in Fig. 33. The pressure is regulated to exactly 760 mm Hg or to any desired pressure by the methods mentioned in section 8.3. A similar device has been described by Eblin [34].

Measurements with an accuracy of ±0.003 deg. C can be carried out with an arrangement due to Herington and Martin [35], who used it for determining the vapour pressures of pyridine and its homologues in the range of 50° to 157 °C. The method of operation is shown in Fig. 34. The high degree of accuracy is attained by evaporating specially purified water in vessel *B* under the same conditions as in the boiling vessel *A*, and by calculating the pressure from the vapour temperature of the water.

A very elegant method, which, however, yields results accurate only to ±0.5 mm Hg, is described by Natelson and Zuckerman [36]. It consists in causing a drop of the liquid hanging at the end of a vertical capillary (thermometer tubing) to fall by gradually evacuating the surrounding space, the prevailing pressure at this moment being read off from a mercury manometer. For carrying out measurements on a micro-scale, with only a few milligrams of material, a procedure due to Emisch has been so modified [37], that observations can be made at pressures below 100 mm Hg. Boiling points can also be determined with minute amounts of substance by the use of Kofler's micro heating plate [38].

Radioactive isotopes may be employed in the measurement of vapour pressures at low temperatures [38]. This technique is described in detail by Nesmeyanov [39], with special reference to metals and alloys. For substances of low volatility such as iodine, naphthalene and phenol, the effusion method is also suited [40].

We will now describe some ***static*** procedures, in which the temperature is kept constant and the pressure is observed.

Vapour pressures can be determined in the range of −20° to +20 °C by a method described by Henning and Stock [41]. The apparatus is illustrated in Fig. 35.

The substance is introduced into the flask through the opening at *B*. A thermometer divided into tenths of a degree *C* is attached to the hook on *B* and the flask is placed in a cooling mixture. A vacuum pump is connected to *C*; cock *D* serves to shut off the vacuum. The riser tube *E* is placed in the mercury bath *F* of the barometer *G*. The apparatus is now evacuated and cock *D* (which has previously been tested for tightness) is closed. Flask *A* is then heated a little, so that the vapour pressure increases; heating is interrupted and cock *D* opened. This operation is repeated until all the air has been removed from the apparatus. The actual measurements can now be started. A constant temperature is established in flask *A*, and by the use of a plate glass scale — or better still a cathetometer — the difference in height of the mercury menisci in the limbs *E* and *G* is measured. This difference is the vapour pressure, in mm Hg, of the liquid tested. It is necessary to carry out a series of observations at each temperature and to take the mean figure. It is best to test the method first on a pure substance having known vapour pressure values.

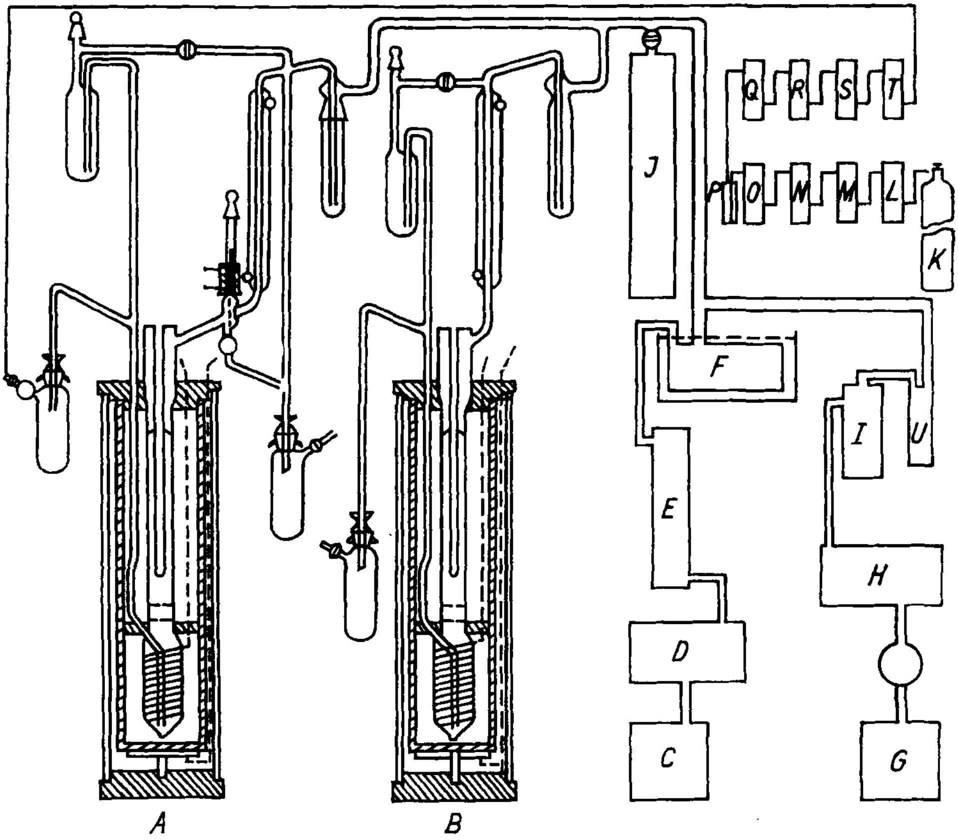


Fig. 34
Arrangement of apparatus for boiling point determination (Herington and Martin)

A = Boiling vessel for pyridine bases, *B* = Boiling vessel for pure water, *C* = Oil vacuum pump. *D* = Gas holder (30 l), *E* = Pressure regulator, *F* = Gas holder (30 l) in water bath of 400 l. *G* = High-vacuum oil pump, *H* = Vessel with P_2O_5, *I* = Mercury vapour pump, *J* = McLeod manometer, *K* = Nitrogen bottle, *L* = Solution of ammonia + ammonium carbonate on metallic copper, *M* = as L, *N* = Washing bottle with dilute sulphuric acid, *O* = 10% caustic soda, *P* = Conc. sulphuric acid, *Q* = Anhydrous calcium chloride, *R* = Silicagel, *S* = Phosphorus pentoxide, *T* = Glass wool, *U* = Cold trap

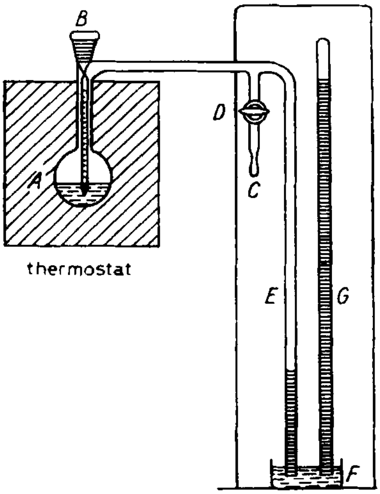


Fig. 35
Apparatus for measuring vapour pressures of volatile substances (Henning and Stock)

A = Flask for liquid with thermometer, *B* = Ground joint with hook for thermometer, *C* = Vacuum connection, *D* = Cock, *E* = Riser tube, *F* = Dish of mercury, *G* = Barometer

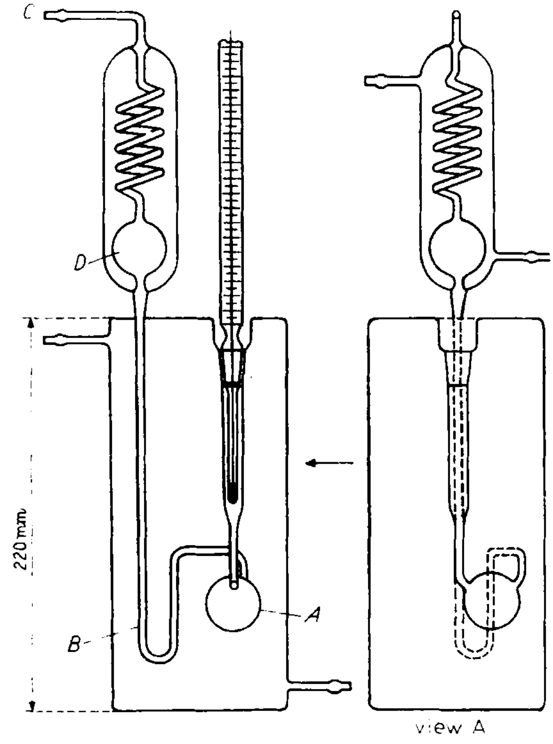


Fig. 36
Isoteniscope as modified by Schuberth

With the *isoteniscope* of Smith and Menzies [42] it is possible, by the use of an auxiliary manometer and an artificial atmosphere, to determine the vapour pressure curves of higher-boiling substances. The method gives fairly reliable results. Fig. 36 shows a modification of the apparatus after Schuberth. One of its main features is that the substance to be investigated can be distilled into the auxiliary manometer *B* and that the vacuum from *C* in the buffer flask can be so regulated by the cock that the auxiliary manometer *B* becomes adjusted to zero difference in level. The main manometer then indicates the vapour pressure of the substance exerted on the left-hand limb of the auxiliary manometer *B*. The isoteniscope is placed in a thermostat jacket *G*, so as to maintain the liquid and the auxiliary manometer at the same temperature.

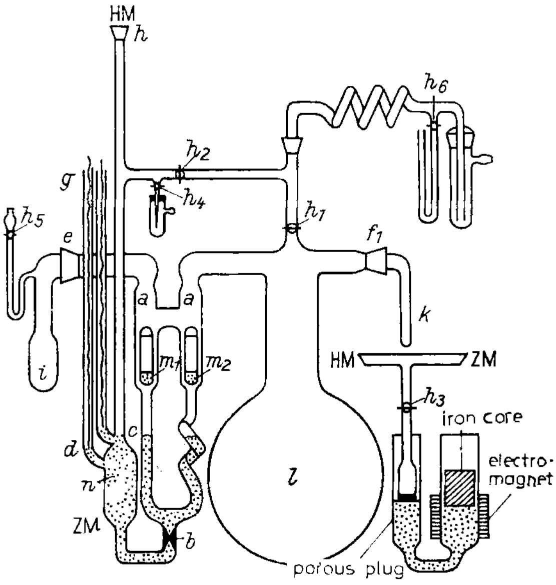


Fig. 37

Apparatus for static vapour pressure determination of Kortüm et al.

a = Conical ground joint, b = Choke, c/d = Platinum contacts, e = Ground joint, B 19, f = Ground joint, B 12, g = Leads to platinum contacts, h = To the main manometer HM, h_1/h_6 = Cocks, i = Vessel for liquid, k = Condensation vessel, l = Vapour space, m_1/m_2 = Floats, n = Storage vessel, ZM = Intermediate manometer

The determination is carried out as follows [43]. Bulb *A* of the isoteniscope tube is filled about three-quarters full with the substance in question and the isoteniscope is connected by a piece of vacuum tubing to the artificial atmosphere *C*. The thermostat bath is warmed, whereupon the whole apparatus is slowly evacuated. As soon as the pressure has fallen sufficiently the substance in *A* will begin to boil, but will again condense in bulb *D*. The downflowing condensate collects in the auxiliary manometer

B and thus shuts off the substance boiling in *A* from the air in the artificial atmosphere. When it is believed that the air has been entirely eliminated from the left-hand part of the isoteniscope, a constant temperature is established in the thermostat, and the vacuum is regulated such that the liquid in both limbs of the auxiliary manometer is at the same level. When this is the case, the thermostat temperature and the pressure indicated by the mercury manometer are read off. In order to make sure that there is no longer any air in the closed part of the isoteniscope, the evacuation and pressure adjustment are repeated. If the same result is found, the temperature is gradually raised and the pressure is changed so as to maintain the liquid levels in the U-tube at approximately the same height. An excessive outer pressure must at all times be carefully avoided, so as to prevent air from being forced back into bulb *A*. The final adjustment is best done by making small changes in the bath temperature at a constant pressure of the artificial atmosphere.

For more accurate measurements, with an uncertainty of ±0.2 mm Hg, Kortüm et al. [44] designed the apparatus shown in Fig. 37, which was employed for determining the vapour pressure diagram (*i.e.* the total vapour pressure of a mixture) of the system water-dioxane at 35 °C.

A straightforward static method for vapour pressures of aqueous salt solutions (LiCl, $MgCl_2$ and $Mg(NO_3)_2$ solutions at 20 to 90 °C) is reported by Schlünder [45].

The mass-spectrometric method of measuring low vapour pressures enables the partial pressure of a particular substance to be determined independent of any impurities.

Three different static methods were studied by Röck [46], who measured very low aniline vapour pressures (0.056 to 17.9 torr). Measurements using the Hg manometer and the aniline manometer proved to be most convenient. An autoclave of V4A steel was used by Glaser and Rüland [28] for the determination of vapour pressures up to 60 atm. and 500 °C.

4.4.2 Calculation and representation of saturated vapour pressures

If there is no opportunity to determine vapour pressures, it is possible to obtain the required data from figures published in the literature by the *method of increments*. This method, whether carried out graphically or by calculation, gives approximate results.

Péter [47] investigated the relationship between vapour pressure and molecular structure on the basis of the van der Waals pressure equation:

$$\log 1/\pi = a(1/\theta - 1) \tag{21}$$

where π = the reduced pressure P/P_c and θ = the reduced temperature T/T_c.

By calculating the constant a additively for atomic and structural increments a good agreement with experimental results is obtained. In about half the cases investigated the difference between calculated and measured values of a amounted to less than 1 per cent, and the variations in a due to temperature were small. By evaluating 73 experimental results, and by a process of averaging, the following values for the increments in a were determined.

C	−2.154	N	−0.765
H	1.139	Cl	1.356
CH_2	0.124	COOH	2.247
O	0.266	COO (ester)	0.507
OH (alcoholic)	2.327	Double bond	2.295
C_6H_5	1.708	Triple bond	4.605
		Branch in C—C chain	0.056

Knowing the structural formula of a substance, its critical temperature and critical pressure, its vapour pressure at any temperature can be calculated according to (21). The additivity of the constant a is comparable to that of the molecular refraction and the parachor. Kollár and Nagy [47a] report a method which is based on Kinney's method and enables vapour pressure curves to be calculated from structural data in a range of boiling points between 0 and 400 °C. However, the molecules should not be too polar. The vapour pressures of high-boiling complex hydrocarbons may be determined according to Smith et al. [47b] if a boiling temperature (10 or 760 torr) and the rough structure (proportion of side chains, aromatic and naphthenic groups) are known. The calculation is based on the fact that vapour pressure curves of complex hydrocarbons are similar to those of n-paraffins with the same numbers of carbons.

A similar method for *estimating the boiling point* of organic substances has been developed by Pearson [48], who employed a factor for dealing with association and justified his method on the basis of the volume and shape of the molecules. Similarly, Egloff's boiling point equation [49] allows boiling points to be calculated. If the boiling points of a compound at two pressures are known, as well as the total vapour pressure curve of a reference substance, the vapour pressure curve of the compound in question can be calculated by an application of Dühring's rule [50]:

$$(t_{1A} - t_{2A})/(t_{1B} - t_{2B}) = q \tag{22}$$

in which: t_{1A} = boiling point of the substance A in question at a pressure P_1;
t_{2A} = boiling point of the substance at a pressure P_2;
t_{1B} = boiling point of the reference substance B at a pressure P_1;
t_{2B} = boiling point of the reference substance B at a pressure P_2;
q = a constant

This rule hence states that the differences in boiling points at two pressures of two substances A and B bear a constant ratio.

Taking water as a reference compound, as has been done by von Rechenberg [51] for a number of compounds (water being a substance with very accurately known vapour pressure data), we might arrive at the following calculation:

1. Known values:

	$P_1 = 760$ mm	$P_2 = 100$ mm Hg
Acetic acid	$t_{1A} = 118.1$ °C	$t_{2A} = 63.0$ °C
Water	$t_{1B} = 100.0$ °C	$t_{2B} = 51.5$ °C

From these figures we first compute the value of q, which is used in the subsequent calculation:

$$q = \frac{118.1 - 63.0}{100.0 - 51.5} = 1.14;$$

2. Calculation of the boiling point t_{2A} of acetic acid at 200 mm:

	$P_1 = 760$ mm	$P_2 = 200$ mm Hg
Acetic acid	$t_{1A} = 118.1\,^\circ\mathrm{C}$	$t_{2A} = ?\,^\circ\mathrm{C}$
Water	$t_{1B} = 100.0\,^\circ\mathrm{C}$	$t_{2B} = 66.4\,^\circ\mathrm{C}$

$$t_{2A} = t_{1A}\, q(t_{1B} - t_{2B}) = 118.1 - 1.14(100.0 - 66.4) = 80.0\,^\circ\mathrm{C}.$$

This value agrees with that found experimentally, and further figures can be calculated in the same way. It should be observed, however, that measured data of other reference compounds in the lower pressure range are frequently very inaccurate, in which case calculation by Dühring's rule will lead to erroneous figures. An accuracy of at least ± 0.05 deg. C in the basic data should be a requirement. It is advisable to choose reference substances that are closely related in structure to the compound in question, for instance by belonging to the same homologous series. Jantzen and Erdmann [52] employed myristic acid as reference substance for calculating the vapour pressure curves of the higher saturated straight-chain fatty acids. In practice it will be found that water can be used for polar liquids and n-hexane for non-polar or weakly polar liquids. A similar method has been given by Kirejew [53].

Frequently the Antoine equation [54] is used as a vapour pressure-temperature relationship:

$$\log P = a - \frac{b}{t + c}. \tag{23}$$

This formula contains three constants depending on the nature of the substance, a, b and c, of which c is a group constant that can be taken to be 230. The use of this formula therefore entails a knowledge of the constants a and b for the compound in question, as found by experiment. Vapour pressure data are quite often quoted in this form in the literature, for instance in the tables of Dreisbach [19].

Wichterle and Linek [58] have prepared lists of Antoine constants of pure compounds to be used in electronic computers for process control. The individual parameters were calculated using an iterative procedure; standard deviations are given.

According to extensive investigations carried out by Thomson [55], the Antoine equation is the equation giving values closest to the experimental results. Constants a and b of the Antoine equation can be calculated if the boiling point of the substance at two pressures P and P_∞ is known. Constant b is given by:

$$b = \frac{\log P - \log P_\infty}{t - t_\infty}\,(t + 230)\,(t_\infty + 230) \tag{24}$$

whereupon constant a can be obtained by introducing b and c $(=230)$ into equation (23) as

$$a = \log P + \frac{b}{t + 230}. \tag{25}$$

The values for P_∞ and t_∞ can be taken from Table 7 for the individual "Cox chart families".

If the normal boiling point and the critical point of a substance are known the whole vapour pressure curve can be calculated with a universal vapour pressure formula after Riedel [56]. If data obtained at any two temperatures are known the critical point can be estimated. The formula is characterized by particular exactness. It indicates whether or not the substances associate. The method of determining boiling points as developed by Reckhard [57] is particularly suited for the vacuum distillation of multicomponent mixtures such as tars, tar oils and similar products. Two nomograms facilitate computational work. A comprehensive presentation of the methods of determining vapour pressures is contained in [59]. Othmer and Yu [60] give a survey of the application of relations with reference substances. A generalized vapour pressure equation for hydrocarbons has been established by Zia and Thodos [60a]. The mean deviation of calculated vapour pressures from those measured is about 0.38%. A critical comparison of various vapour pressure equations for a large number of substances was made by Gomez-Nieto and Thodos [60b] on the basis of the correspondence principle. A new equation using particularly the temperature of the normal boiling point besides the critical values for a given substance yielded a mean deviation of 1.43% for 7633 data from 139 substances. Employing Riedel's parameter even lowers this deviation to 1.05%.

Further results of these workers [60c, 60d] concern hydrocarbons and few inorganic substances. Westmeier and Picht [60e] made a comparative study of generalized methods for the calculation of vapour pressure. They place particular emphasis on those methods which describe the vapour pressure behaviour of polar substances with adequate accuracy.

Data on vapour pressure calculations for liquid metals and alloys (Li, Na, K, Cs, Mg, Al, Pb) are found in a paper by Waseda et al. [60f].

The *graphical methods* for determining vapour pressure generally have the advantage of being simpler and more rapid. For instance, Dühring's rule can be followed graphically by plotting the boiling points at equal pressures on linear scales along two co-ordinate axes, those of the substance A as ordinates and those of the reference compound B as abscissae. These points then lie on a straight line. Fig. 38 shows a plot of the data for acetic acid and water, mentioned above. The vapour pressure of acetic acid at a required temperature can then be found by reading off the corresponding temperature for water from this graph and then finding, on a vapour pressure curve for water (Fig. 39), what the vapour pressure pertaining to the latter temperature is. It is also possible to draw a scale for pressures in the Dühring graph (as has been done in Fig. 38), but it is then not easy to read off intermediate values.

Fig. 39 shows the normal course of vapour pressure curves, and it is evident that a fairly large number of points are needed to draw the curves accurately. Methods have therefore been sought for obtaining a linear representation. It follows from the Clausius-Clapeyron equation

$$\log P = -\frac{\Delta_V H}{R} \cdot \frac{1}{T} + c, \tag{26}$$

Table 7

Cox chart families and their focal points ϑ_∞ and p_∞

Family	Formula	ϑ_∞ °C	$p_\infty \times 10^{-6}$, mm Hg	Factor $(\vartheta_\infty + 230) \times \log (p_\infty/760)$
Aromatics with saturated side chains	C_nH_{2n-6}	1670	2.320	6621
Halogenated aromatics with saturated side chains	$C_nH_{2n-(6+m)}X_m$			
Unsaturated aromatics	C_nH_{2n-8}	1063	0.916	3985
Unsaturated halogenated aromatics	$C_nH_{2n-(8+m)}X_m$			
Naphthalenes	C_nH_{2n-12}	921.5	0.530	3274
Halogenated naphthalenes	$C_nH_{2n-(12+m)}X_m$			
Aromatic amines	$C_nH_{2n-5}N$	1750	3.800	7324
Halogenated aromatic amines	$C_nH_{2n-(5+m)}NX_m$			
Phenols	$C_nH_{2n-6}O$	2337	11.170	10697
Halogenated alkylphenols	$C_nH_{2n-(6+m)}OX_m$			
Nitrobenzenes	$C_nH_{2n-7}NO_2$	2022	3.701	8304
Halogenated nitrobenzenes	$C_nH_{2n-(7+m)}NO_2X_m$			
Aromatic aldehydes	$C_nH_{2n-8}O$	600	0.150	1905
Halogenated aromatic aldehydes	$C_nH_{2n-(8+m)}OX_m$			
Phenylethyl alcohols	$C_nH_{2n-6}O$	3300	20.000	15550
Halogenated phenylethyl alcohols	$C_nH_{2n-(6+m)}OX_m$			
Aromatic ketones	$C_nH_{2n-16}O$	2186	5.186	9263
Halogenated aromatic ketones	$C_nH_{2n-(16+m)}OX_m$			
Aromatic-aliphatic ketones	$C_nH_{2n-8}O$			
Halogenated aromatic-aliphatic ketones	$C_nH_{2n-(8+m)}OX_m$			
Aromatic ethers	$C_nH_{2n-14}O$	1850	3.400	7597
Aromatic-aliphatic ethers	$C_nH_{2n-6}O$			
Cyclohexyl-aliphatic ethers with saturated and unsaturated side-chains	$C_nH_{2n}O$ $C_nH_{2n-2}O$			
Alkylcyclopentanes	C_nH_{2n}	1450	1.550	5560
Alkylcyclohexanes	C_nH_{2n}	2076	2.076	8104
Paraffins	C_nH_{2n+2}	1240	1.300	4753
Halogenated paraffins	$C_nH_{2n+(2-m)}X_m$	1450	1.860	5693
Mono-olefins	C_nH_{2n}	1725	1.698	6548
Primary *n*-alkylamines Kp_{760} below 190°C	$C_nH_{2n+3}N$	1125	1.441	4424

Table 7 (Continuation)

Family	Formula	ϑ_∞ °C	$p_\infty \times 10^{-6}$, mm Hg	Factor $(\vartheta_\infty + 230) \times \log (p_\infty/760)$
Primary n-alkylamines Kp_{760} 190°–350°C	$C_nH_{2n+3}N$	1270	1.709	5029
Aliphatic ethers	$C_nH_{2n+2}O$	1579	2.525	6370
Aliphatic ketones	$C_nH_{2n}O$	3293	6.929	13950
Nitroparaffins	$C_nH_{2n+1}NO_2$	1350	2.000	5404
Aliphatic nitriles	$C_nH_{2n-1}N$	2025	3.461	8250
Aliphatic esters	$C_nH_{2n}O_2$	1639	3.800	6913
Aliphatic alcohols	$C_nH_{2n+2}O$	12150	128.200	64718
Aliphatic acids Kp_{760} below 142°C	$C_nH_{2n}O_2$	364	0.060	1125
Aliphatic acids Kp_{760} above 145°C	$C_nH_{2n}O$	1458	9.060	6881
Halogenated aliphatic acids	$C_nH_{2n-m}O_2X_m$			

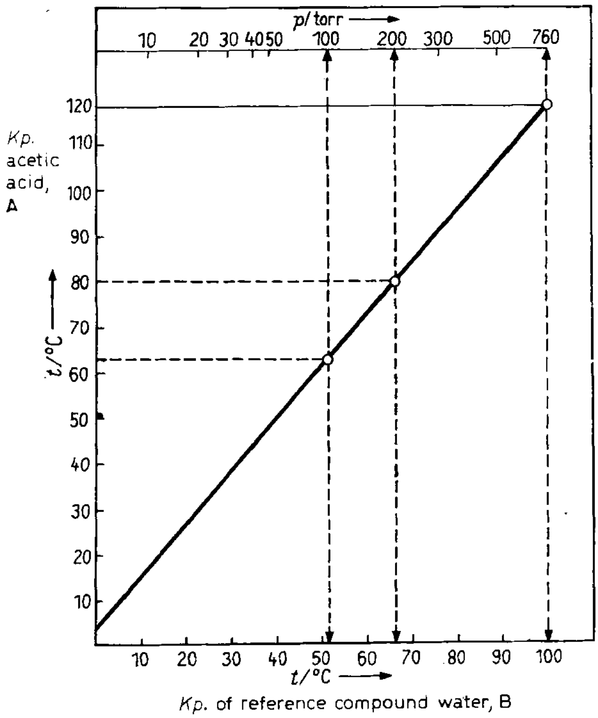


Fig. 38
Plot of boiling points of acetic acid and water following Dühring's rule

(in which R is the gas constant, T the absolute temperature, $\Delta_V H$ the heat of evaporation and c a temporarily unknown integration constant), that a plot of log P against $1/T$ should give a straight line.

Fig. 40 shows such a plot for a number of substances. The slope of these various lines is obviously a measure of the heat of evaporation. Rewriting the Clausius-Clapeyron equation as

$$\log p_2 = \frac{\Delta_V H_1}{\Delta_V H_2} \log p_1 + c \tag{27}$$

the logarithm of the vapour pressure of a substance 2 may be plotted against the logarithm of the vapour pressure of a substance 1. This also yields a straight line. The slope of this line is now determined by the ratio of the two heats of evaporation. Hence it is appropriate to use n-heptane as reference substance for hydrocarbons and water for associating substances, such as acids and alcohols, since these substances have large heats of evaporation. On the basis of eq. (27) Ohmer et al. [63] have prepared a nomogram and corresponding tables by means of which vapour pressure data, latent heats and other physical parameters can be determined.

If the boiling point and heat of evaporation of a substance are known the diagram of Bergholm-Fischer [65] which is given by Wittenberger [64] can be used. Besides the $1/T$ vs. log p plot it has, in its upper part, a kcal scale.

A method in which the logarithm of the vapour pressure is plotted along a "substance axis", thereby yielding radiating lines has been given by Hoffmann and

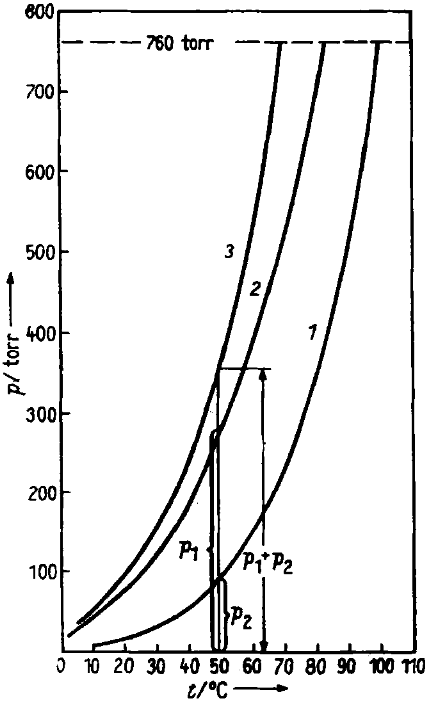


Fig. 39
Vapour pressure curves

1 = water, *2* = benzene, *3* = summated curve for water and benzene

Florin [66] and is based on the well-known Cox charts [67]. In these diagrams, which can be drawn for classes of substances — the so-called "Cox chart families" — all straight lines for the vapour pressures lead to a point (P_∞, T_∞) having a definite position for each class of substance. In this case it is therefore sufficient to know the boiling point at a certain pressure, to plot this point and connect it to the above mentioned "focus" in order to obtain the whole vapour pressure line. In Table 7 the 21 Cox chart families indicated by Dreisbach have been collected, together with their focal points T_∞ and P_∞. Fig. 41 shows a Cox chart for the alkylbenzenes.

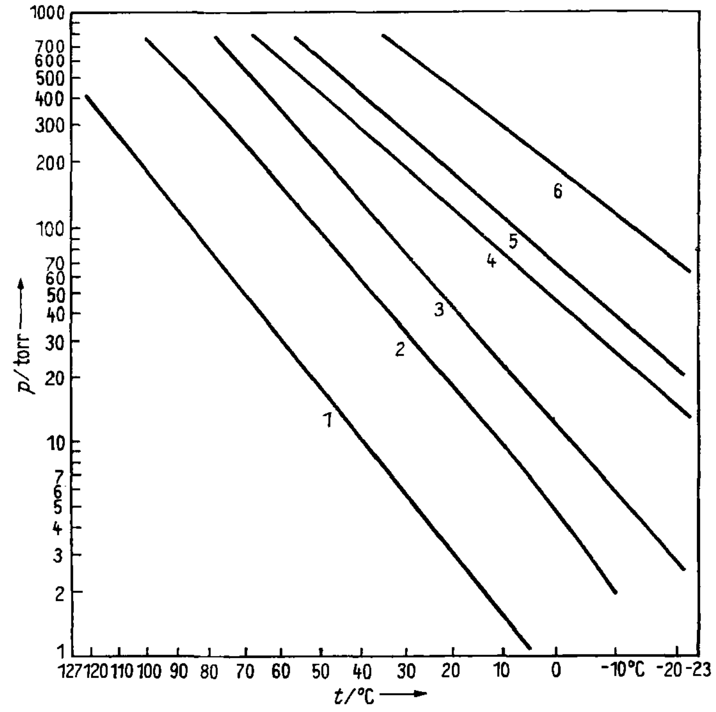


Fig. 40

Linear vapour pressure representation in the co-ordinate system $\log p$ against $1/T$

1 = propionic acid, *2* = water, *3* = ethanol, *4* = n-hexane; *5* = acetone, *6* = ether

At first Cox plotted $\log p$ against $1/\vartheta$ and obtained a straight line at an angle with the ordinate. According to the p-values of the ordinate the experimental temperature values for water were plotted on the abscissa. Davis [68] and Calingart and Davis [69] developed the Cox chart further, plotting $\log p$ vs. $1/(\vartheta + 230)$. Such a Cox chart may be considered to be the graphical representation of the Antoine equation (18) with $c = 230$. However, this group constant applies only to aliphatic hydrocarbons [70].

It is important that a Cox chart should be drawn on a sufficiently large scale. In order to represent the temperature with an accuracy of 1° up to 200 °C, the dimensions of the diagram have to be about 0.95 × 1.5 m. Dreisbach [19] gives detailed directions for constructing a Cox chart, in order that the values determined may have an accuracy sufficient for laboratory practice:

Ordinates (pressures) — Divided logarithmically; the eight divisions from 0.1 to 10^7 mm Hg should have a total length of 56 inches.

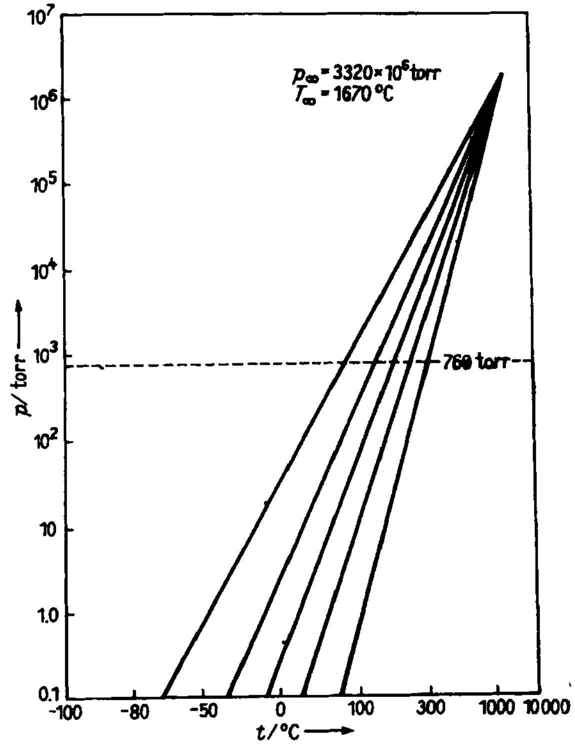


Fig. 41
Cox diagram for the family of the alkylbenzenes

Abscissae (temperatures) — The region from —100° to 10.000 °C should occupy a width of 38.75 inches. The temperature scale may be calculated by means of the formulae

$$t = \frac{230L}{33.17 - L} \quad \text{or} \tag{28}$$

$$L = \frac{33.17t}{230 + t} \tag{29}$$

(t = temperature, °C, and L = length in inches).

The zero point in the middle lies about 17.25 inches from the left-hand point for —100 °C, and the value of L is the positive or negative distance from this zero point. It is advisable to subdivide the temperature scale according to the directions given in Table 8.

Table 8

Temperature subdivisions for a Cox chart

Temperature range I (°C)	Subdivision at every
−100 to 200	10°C
200 to 600	50°C
600 to 2000	100°C
2000 to 4000	500°C
4000 to 10000	1000°C

Further subdivision:

Temperature range II	−100/0°C	0/200°C	200/600°C	600/1000°C	>1000°C
Subdivision 1	10°C	10°C	50°C	100°C	subdivision yields no useful values
Subdivision 2	10 × 1°C	5 × 2°C	5 × 10°C	2 × 50°C	

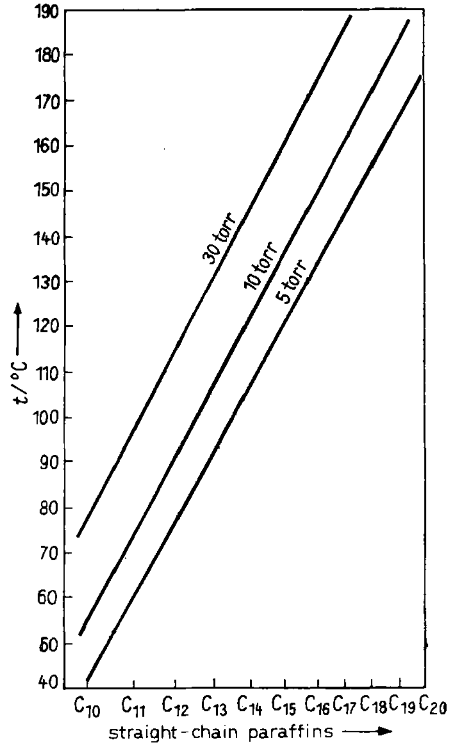


Fig. 42
Isobars for the homologous series of n-paraffins, $C_{10}-C_{30}$

Finally a method that is specially suited for homologous series will be described. It consists in plotting the boiling points as ordinates on a linear scale and the carbon-numbers of the components as abscissae on a logarithmic scale. The isobars at various pressures are then drawn in the diagram, as has been done in Fig. 42 for the straight-chain paraffins C_{10}—C_{20} at pressures of 5, 10 and 30 mm Hg. This method allows values to be interpolated, and data for members below C_{10} and above C_{20} to be found by extrapolation. It can also be used with advantage for giving an indication, during a laboratory distillation, of the molecular weight range in which distillate is situated.

There are many more methods of determining vapour pressure data which aim at obtaining higher accuracy. They are to be found in the publications of Hoffmann and Florin [66], Faldix and Stage [70], Stage and Juilfs [71] and in [59]. It is up to the practical worker to choose the one method most suited to the given conditions. It should be pointed out that all these methods are approximations and that high accuracy is obtained only by exact measurement.

4.5 Equation of state and *px*-diagrams

A liquid contains molecules moving at different velocities. For those moving fastest it is easiest to penetrate the liquid surface, thus escaping into the space above the liquid as vapour (evaporation). For the conversion of the liquid particles into vapour heat of conversion is required, which is removed from the liquid, the latter cooling down. If heat of evaporation is supplied from outside evaporation is achieved more quickly and the liquid begins to boil.

Hence, vapour is a gas near its boiling or dew point. In distillation usually only saturated vapours occur which are associated with their liquid phase, with equal numbers of molecules going over from the liquid to the gaseous phase and vice versa in the equilibrium state. An unsaturated vapour is formed only when the saturated vapour is no longer associated with the liquid and is heated beyond the saturation temperature or is expanded. Then it cannot take up more molecules from the liquid phase according to the increased temperature.

The *general equation of state* (31) can only be regarded as an approximation and a limiting case for gases near the dew point at high pressures with the molecules associated, i.e., it applies only to ideal gases and, strictly speaking, not to saturated vapours which normally occur in distillation.

The van der Waals equation seeks to account for this:

$$\left(p + \frac{a}{V_{\mathrm{mol}}^2}\right)(V_{\mathrm{mol}} - b) = \mathbf{R}T. \qquad (30)$$

Here a and b are constants, b and a/V_{mol}^2 considering the covolume of the molecules and the intermolecular forces of attraction, respectively. p is the pressure exerted by the gas on the walls of the vessel, and V_{mol} is the molecular volume. But even the van der Waals equation of state does not apply exactly to any particular substance since the intermolecular forces do not obey so simple a law as assumed in this latter equation. A fifth-order equation formulated by Planck provides an equation of state which approaches the real behaviour of gases and vapours most closely.

Obviously, calculations with third and fifth-order equations are difficult to carry out and thus the simple gas equation based on the laws of Gay-Lussac and Boyle-Mariotte:

$$pV = p_0V_0 \cdot \frac{T}{273.16}$$

or

$$pV = \boldsymbol{R}T \tag{31}$$

is generally used in the practice of distillation, it being assumed to represent conditions with sufficient accuracy. A gas approaches the more closely to its ideal state, the lower its pressure and the higher its temperature.

If into the formula $\boldsymbol{R} = p_0V_0/273.16$ we introduce the values for normal conditions, namely $p_0 = 760$ mm Hg (1 atm) and $V_0 = 22.414$ l (volume of one mole of gas at 0 °C), R becomes

$$1 \times 22.414/273.16 = 0.0821 \text{ atm/°C}.$$

For an arbitrary number Mz of moles of a gas or vapour we hence obtain the equation

$$pV = Mz \cdot 0.082T. \tag{32}$$

(In large-scale work one frequently uses a corresponding formula for kg-moles instead of g-moles.)

To calculate the volume of vapour from a substance at a definite pressure and temperature, the following formula can be employed:

$$V = \frac{Mz \times 0.082 \times T \times 760}{p}. \tag{33}$$

At normal pressure (760 mm = 1 atm) and for one mole of substance formula (33) simplifies to

$$V = 0.082T \tag{34}$$

(V in litres, p in mm Hg, Mz referred to g-moles).

The density of the vapour under normal conditions is given by

$$\varrho_\mathrm{D} = M/22.4 \text{ g/l}, \tag{35}$$

where M is the molecular weight.

At another pressure and temperature this becomes

$$\varrho_\mathrm{D} = \frac{M}{22.4} \cdot \frac{p}{760} \cdot \frac{273.16}{273.16 + \vartheta} \tag{36}$$

or

$$\varrho_\mathrm{D} = \frac{Mp}{T} \times 0.01605 \tag{37}$$

The weight of a certain volume of vapour is then simply

$$m = V \cdot \varrho_D. \tag{38}$$

As we have seen it is the intermolecular forces that influence the solubility of the components. This, in turn, determines the other *properties of binary mixtures* which are summarized in Fig. 43 after Thormann [72].

With practically *no solubility* the two components and the vapours arising from them behave as if either of them were there alone at the same temperature (Fig. 43, column 1). This applies to carrier vapour distillation (chap. 6.1).

According to Dalton's law the total pressure of a gas mixture is equal to the sum of the pressures that each gas would exert at the same temperature in the same vapour space:

$$p_{ges} = p_1 + p_2. \tag{39}$$

This leads to the *composition of the vapour of insoluble mixtures*, referred to the lowest-boiling component, in mole per cent:

$$y_1{}^* = \frac{p_1}{p_{ges}} \times 100 \text{ (mol\%)}. \tag{40}$$

In order that one may obtain the *partial pressures* (Fig. 43, series I) for such calculations of vapour compositions, both vapour pressure curves are plotted and the summated curve for the two partial pressures is drawn, as has been done for water and benzene in Fig. 39. At 760 mm a boiling point of 69.0 °C is found for the mixture. According to formula (40) the composition of the vapour is

$$y^* = \frac{534}{760} \times 100 = 70.2 \text{ mol\%},$$

a figure that can be converted by the nomogram of Fig. 22 to 91.0% by weight.

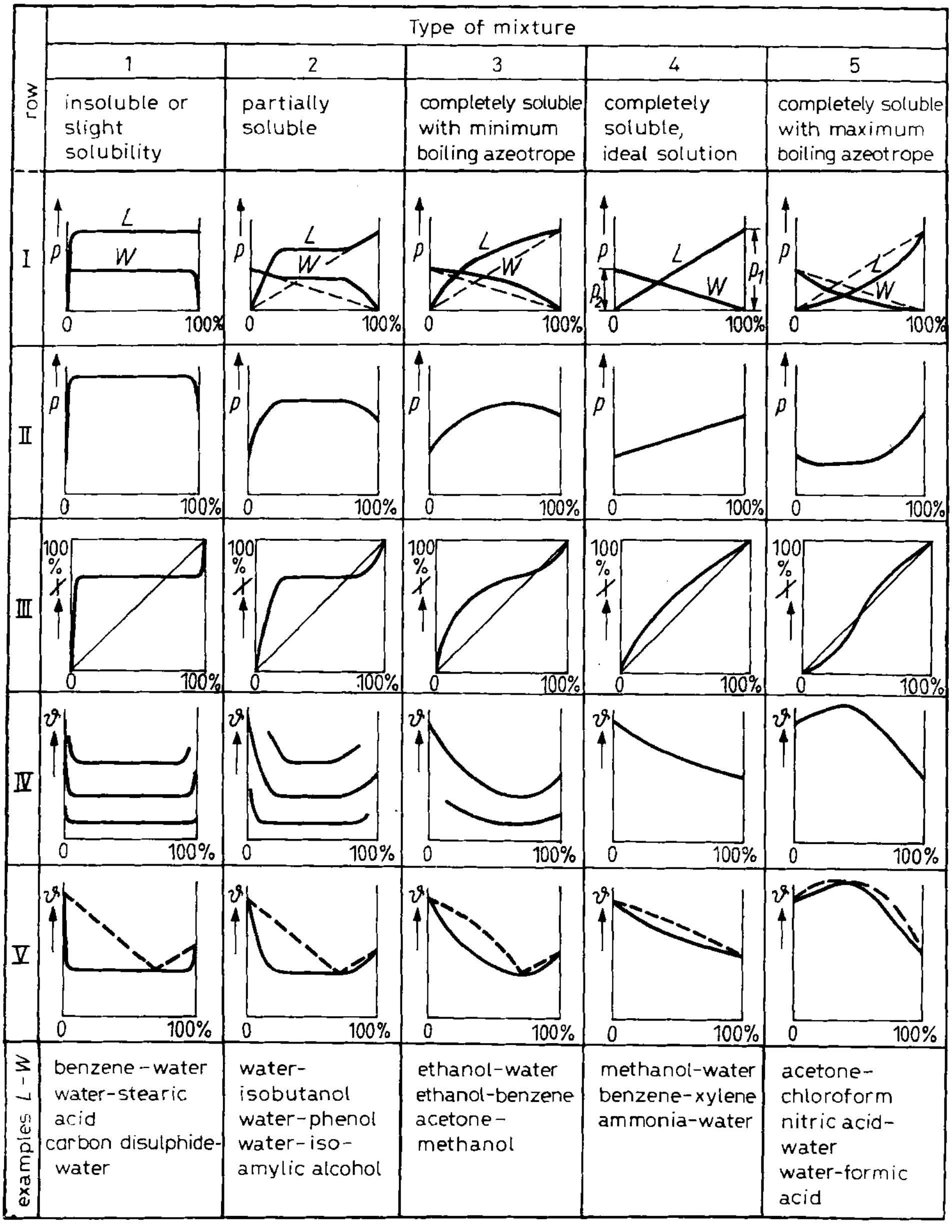
If we consider rows I and II of Fig. 43 where the diagrams show the composition of the mixture in mol% referred to the low-boiling component (see also Fig. 29) we find these relationships:

Row I

Partial pressures of the low boiling component L and the high-boiling component W (px-diagram) at constant temperature

At constant temperature the vapour pressure of a mixture depends on the composition only. If the intermolecular binding forces between like molecules are greater than those between unlike ones there is only a weak tendency for the components to mix. The mixing is accompanied by heat consumption, which results in a decrease of the heat of evaporation required. Thus the volatility increases and the vapour pressure is higher than what would correspond to an ideal mixture (Fig. 43, row I, columns 1 to 3). The deviations from the ideal behaviour can be formally expressed in terms of the activity coefficient ε so that Raoult's law takes the form $p_1 = p^* \times x_1 \times \gamma$ (see also (70)).

Column 4 presents those ideal mixtures with complete solubility (equal binding forces between like und unlike molecules) which are mixed without heat consumption



row	Type of mixture 1	2	3	4	5
	insoluble or slight solubility	partially soluble	completely soluble with minimum boiling azeotrope	completely soluble, ideal solution	completely soluble with maximum boiling azeotrope
examples I - V	benzene-water water-stearic acid carbon disulphide-water	water-isobutanol water-phenol water-iso-amylic alcohol	ethanol-water ethanol-benzene acetone-methanol	methanol-water benzene-xylene ammonia-water	acetone-chloroform nitric acid-water water-formic acid

Fig. 43
The properties of binary mixtures as a function of the concentration of light component

Row I: Partial pressures at constant temperature for light and heavy components
Row II: Total pressure at constant temperature
Row III: Equilibrium curve
Row IV: Temperature at constant pressure (boiling point curve)
Row V: Temperature of constant pressure (dew point curve)

and thus have their partial pressures proportional to the liquid concentrations. The partial pressures are then calculated by Raoult's law:

$$p_1 = \frac{x_1 \times p_{*1}}{100} \text{ mol\%}, \tag{41}$$

$$p_2 = \frac{(100 - x_1) \times p_{*2}}{100} \text{ mol\%}, \tag{42}$$

where p_{*1} and p_{*2} are the vapour pressures of the pure components at the given temperature.

If the binding forces between unlike molecules are stronger than those between like ones the mixing is an exothermic process and due to increased solubility the heat of evaporation of one component in the mixture is greater than that of the pure component. This hinders the formation of vapour and causes a lowering of the vapour pressure. Row I, column 5 in Fig. 43 shows mixtures with minimum pressure as examples of this.

Row II

Total pressure of the mixture at constant temperature (px-diagram)

The total vapour pressure is simply the sum of the partial pressures. In insoluble mixtures the total pressure is independent of the composition; in partially soluble mixtures this holds for the concentration range in which insolubility occurs. Thus in columns 1 to 3 we always find a maximum vapour pressure lying above that of an ideal mixture, the total pressure of which yields a straight line (column 4). Conversely, the example of column 5 displays a minimum pressure lying below the values for ideal behaviour. The vapour pressure curves which are convex upwards and concave upwards are termed positive (maximum pressure) and negative (minimum pressure), respectively [73, 17]. Adding formulae (41) and (42) together gives the total pressure for an ideal mixture:

$$p_{\text{ges}} = p_1 + p_2 = \frac{x_1 \times p_{*1} + (100 - x_1) \times p_{*2}}{100}. \tag{43}$$

For a mathematical interpretation of the mixing behaviour further methods of calculation are described in Matz [73], Kortüm and Buchholz-Meisenheimer [74], Bošnjaković [75] and, above all, in Schuberth [17].

4.6 Boiling point diagram, $\vartheta - x$, equilibrium curve, $y^* - x$

While we have studied the properties of binary mixtures at constant temperature so far we shall now examine the behaviour of these mixtures at constant pressure. The conditions are those found in distillation, which is normally an isobaric process tending to establish equilibrium between the liquid and vapour phases. A *boiling point diagram* shows the boiling points and the equilibrium compositions of binary mixtures at constant pressure (Fig. 43, rows IV and V). In a coordinate system with ϑ as the ordinate and x_B as the abscissa are plotted the boiling point curve *a* and the dew point curve *b* whose ends coincide. Fig. 44 represents the boiling point diagram for benzene and toluene. In conditions represented by points above the dew point curve *b* the mixtures are entirely unsaturated vapour, while those on curve *b* are saturated vapour. Between the two curves, points represent liquid in equilibrium with vapour, while below the boiling curve *a* only liquid is present. If a mixture with the composition x_B is heated, it begins to boil at the temperature ϑ, and the vapour has the composition y^*; the liquid x_B and the vapour y^* are in equilibrium at the temperature ϑ. The boiling point diagram is determined experimentally in the same way as the equilibrium curve (see Chap. 4.6.3) and may be similarly used to determine the number of separating stages required. Fig. 59 shows the equilibrium curve for benzene and toluene as obtained from the values of the boiling point diagram.

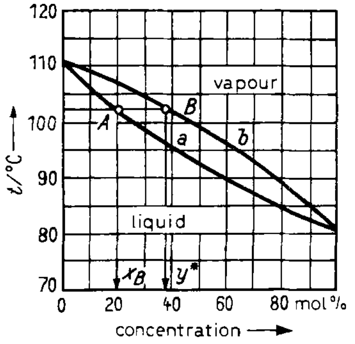


Fig. 44
Boiling point diagram for benzene-toluene solutions at 760 torr

Here points A and B coincide. The boiling point diagram has the advantage that in distillation processes the concentration of the top product can be read off through the top temperature. When plate columns are used the boiling point diagram allows the continuous checking of the bottom concentrations via the column temperature gradient. Bottom temperatures may also serve to determine the most suitable feed plate or draw-off plate for side streams.

Florin [76] gives a method of calculating the boiling point diagram of an ideal multicomponent mixture. Only few points are determined but in addition the slopes of the curve at these points need to be calculated.

In rows IV and V of Fig. 43 we find the boiling point diagrams for various kinds of mixtures. In columns 1, 2 and 3 the boiling temperature is below the bubble point of the pure components (minimum-boiling mixtures) over a wide range of concentrations whereas, on the other hand, column 5 displays a range with boiling temperatures above those of the pure components (maximum-boiling mixtures). The dew point and boiling point curves coincide at the azeotropic compositions.

The equilibrium curve reveals the relationship between the concentration of the liquid, x_B, and the corresponding vapour concentration, y^*, in equilibrium. Thus the equilibrium curve provides the basis for the calculation of separating stages by the McCabe-Thiele method [77] which is no doubt most commonly used due to its simplicity. Row III of Fig. 43 gives the equilibrium curves for the various mixtures. For insoluble mixtures the equilibrium curve is a straight line (column 1) intersecting the diagonal at a point where the vapour and liquid concentrations are equal. It is impossible then to enrich the vapour in low-boiling component at higher liquid concentrations x_B; on the contrary, the vapour will then contain less of the low-boiling component than the liquid. Hence, in insoluble or partially soluble mixtures the distillate vaporizes with the same composition over a wide range and only near the points 0 and 100% do transition concentrations occur (columns 1 and 2). The concentration of the vapour is lower than that of the liquid, x_B, above and below the azeotropic point for mixtures with maximum (column 3) and minimum (column 5) vapour pressure, respectively. Column 4 shows the curve of an ideal mixture; y^* is always greater than x_B.

4.6.1 Calculation of vapour-liquid equilibria

It is a simple matter to obtain the equilibrium curve of an ideal or an almost completely insoluble mixture by calculation, and for partially soluble mixtures the calculation is fairly straightforward. For non-ideal but completely miscible systems calculation is less accurate and takes rather longer, and where some degree of precision is required equilibrium data should be obtained experimentally. However, considerable experience is needed if reliable equilibria are to be measured, and the procedures are time-consuming, particularly if materials have to be purified.

In the last few years many contributions dealing with the calculation of phase equilibria have been published. It would lead us too far to mention all of these, particularly since this subject is exhaustively treated by Schuberth [17] and Hála et al. [78]. Their books include extensive bibliographies. Of particular interest in this context is a remark made by Späth (cf. chap. 3, ref. [17]) about a simplification in representing and evaluating vapour-liquid equilibria.

The trend is toward precalculating the data for multicomponent mixtures with digital computers on the basis of equilibrium measurements on binary mixtures [79]. The reason is that enough such data are available [105, 106] whereas measurements on multicomponent mixtures are exacting and time-consuming. At the international symposium "Distillation 1969" at Brighton [6] no less than 7 papers were devoted to the precalculation of phase equilibria on the basis of the material properties of the pure components. There were treated equilibrium data for electrolytes and non-electrolytes, consistency tests for non-electrolytes, and methods of precalculating activity coefficients. In many cases the Wilson equation [80] has proved to be useful. According to Donth and Weichmann [81] iterative methods can be used to obtain equilibrium data of binary solutions from $p - x$ (or $T - x$) data. The most important relations as formulated by Margules, Redlich-Kister, van Ness, van Laar (Scatchard-Hamer), Wilson, Heil and Renon-Prausnitz (NRTL = non-random two-liquid) are discussed by Krug, Haberland and Bittrich [82]. Schuberth [17] considers the Renon-Prausnitz assumption to be quite promising. It avoids the disadvantage of a three-parameter Wilson equation whose application, as a matter of principle, is restricted to non-demixing liquid systems. The NRTL relationship provides a connection between Wilson's model and Scott's theory. In an excellent survey article Onken and Gmehling [83a] suggest ways of precalculating vapour-liquid equilibria. It is no problem any longer to include even complex non-idealities in column calculations. In most cases the results could be more accurate if the data input were more complete. The survey therefore explains the UNIFAC method and mentions the Dortmund data bank (DDB). The efficiency of the method is illustrated by some examples. Onken [83c] reports recent developments in equilibrium calculations and Bittrich [83f] gives an excellent account of the proceedings of the section on "Vapour-liquid equilibria" of the Sixth CHISA Congress, 1978. The state of the field of modelling phase equilibria of binary and multicomponent systems is presented by Hauthal [83g] in a survey of improved methods of approximation and precalculation.

A purely phenomenological description of the effects occurring in high-pressure vapour-liquid equilibria was given by Wichterle [83b] in the first part of a series of papers.

The work was continued by Wichterle et al. [83d] and resulted in a generalized method of calculating and predicting vapour-liquid equilibria at high pressures.

The practical application of molecular thermodynamics to the calculation of phase equilibria is illustrated by Prausnitz [83c].

In further papers the calculation of high-pressure vapour-liquid equilibria and the use of the UNIQUAC equation for the calculation of multicomponent mixture equilibria are reported [83c].

The equilibrium curves of *ideal mixtures*, which are exemplified by chemically related substances and particularly by near homologues, may be calculated by various procedures. Some of these will be outlined to explain the basic method.

In order to obtain the equilibrium composition of the vapour from the vapour pressure data for the pure components, we must apply Raoult's law. This law states that the partial pressure of a component is equal to the product of the mole fraction of this component and its vapour pressure at the existing temperature.

Raoult's law:

$$p_1 = p_{*1} \cdot x_1 \qquad (x_1 \text{ as a mole fraction}) \tag{44}$$

or

$$p_1 = \frac{p_{*1} \cdot x_1}{100} \qquad (x_1 \text{ in mol\%}). \tag{45}$$

For the second component we have, similarly

$$p_2 = p_{*2}(1 - x_1) \qquad (x_1 \text{ as a mole fraction}) \tag{46}$$

$$p_2 = p_{*2}\,\frac{100 - x_1}{100} \qquad (x_1 \text{ in mol \%}). \tag{47}$$

The total pressure p_{ges} is obtained from the partial pressures p_1 and p_2 by

$$p_{\text{ges}} = p_1 + p_2 = p_{*1} \cdot x_1 + p_{*2}(1 - x_1) \tag{48}$$

$$p_{\text{ges}} = p_1 + p_2 = \frac{(p_{*1} \times x_1) + p_{*2}(100 - x_1)}{100} \qquad (x_1 \text{ in mol \%}). \tag{49}$$

Since, now, the equilibrium composition of the vapour, y^*, is equal to the ratio of the partial pressure of component 1 to the total pressure p_{ges} we find that

$$y^* = \frac{p_1}{p_1 + p^2} = \frac{p_{*1} \cdot x_1}{p_{*1} \cdot x_1 + p_{*2}(1 - x_1)} = \frac{p_{*1} \cdot x_1}{p_{\text{ges}}}. \tag{50}$$

This will be illustrated by an example. We wish to calculate the equilibrium curve at 760 mm pressure for the mixture benzene-toluene, by Raoult's law. We first plot the vapour pressures values on as large a scale as possible and then derive the vapour pressures of both components at definite temperatures (Table 9).

Table 9

Vapour pressures of benzene and toluene at various temperatures

Temp. °C	p_* benzene	p_* toluene	$p_{*1}/p_{*2} = \alpha$
80	748	294	2.54
90	1 013	408	2.46
100	1 335	555	2.41
110	1 739	747	2.33

By a rearrangement of formula (48), the composition of the liquid is obtained as

$$x_1 = \frac{p_{\text{ges}} - p_{*2}}{p_{*1} - p_{*2}} \cdot 100 \text{ mol\%}. \tag{51}$$

With the values for 90 °C this formula gives us

$$x_1 = \frac{760 - 408}{1013 - 408} \cdot 100 = 58.18 \text{ mol\%}. \tag{52}$$

By introducing this value of x_1 into formula (49) we find the corresponding equilibrium vapour composition

$$y^* = \frac{1013 \times 58.18}{760} = 77.55 \text{ mol\%}. \tag{53}$$

Further figures can be calculated in the same way. The more data that are available, the better can the equilibrium curve be drawn. It is evident that this calculation can be carried out not only for normal pressure, but also for any pressure in question, say for 20 mm Hg. In that case the figure 20 must be introduced for p_{ges}, and the temperatures have to range between the boiling points of components 1 and 2 at this pressure. It is useful to arrange the data as shown in Table 10.

Mention should also be made of the graphical determination of equilibrium curves, which, however, is far more cumbersome than the arithmetic method. Details may be found in Thormann [72] and Rosengart [84].

Table 10

Calculation of the equilibrium curve for the normal fatty acids C_{10} and C_{11} at $p_{ges} = 20$ torr

ϑ (°C)	p_{*1} (torr)	p_{*2} (torr)	x_1 (mol%) by formula (50)	y^* (mol%) by formula (49)	$p_{*1}/p_{*2} = \alpha$
161.5	20	11.0	100	100	1.819
163	21	11.9	83.9	93.4	1.765
164	22	12.5	78.9	86.8	1.760
165	23	13.2	69.4	79.8	1.742
166	24.1	13.9	59.7	71.9	1.733
167	25.2	14.5	51.3	64.7	1.736
168	26.4	15.2	42.8	56.5	1.735
169	27.5	16.0	34.7	47.15	1.717
170	28.7	16.9	26.3	37.7	1.696
171	30.0	17.4	20.6	30.9	1.723
172	31.4	18.0	14.95	23.45	1.743
173	32.6	18.8	8.70	14.3	1.733
174.5	35.0	20.0	0	0	1.750

For ideal binary mixtures the course of the equilibrium curve can be computed by employing a combination of Raoult's and Dalton's laws:

$$\frac{y^*}{1 - y^*} = \frac{p_1}{p_2} = \frac{x \cdot p_{*2}}{(1 - x)\, p_{*2}} = \frac{x}{1 - x} \cdot \alpha \tag{54}$$

which reduces to

$$y^* = \frac{\alpha x}{1 + x(\alpha - 1)} \tag{55}$$

and again yields the vapour composition as a molecular fraction. In order to give the composition in mol% , formula (55) can be modified (with x in mol%) to

$$y^* = \frac{100\alpha}{100/x + \alpha - 1}. \tag{56}$$

In these formulae we have employed the fraction $\alpha = p_{*1}/p_{*2}$, which we denote as the *separation factor* (section 4.2.6) or the *relative volatility*. In the case of ideal mixtures α can be taken as being approximately constant between the two boiling points (see Table 10). (At constant temperature it is absolutely constant in an ideal mixture.) The figures for α calculated from p_{*1} and p_{*2} for benzene-toluene mixtures in Table 9 are seen to lie between 2.54 and 2.33, while the arithmetic average is 2.43. One may also calculate a geometric mean from the two terminal values of α (*i. e.* those corresponding to the boiling points of the components) by

$$\alpha_m = \sqrt{\alpha_1 \cdot \alpha_2} \tag{57}$$

or

$$\log \alpha_m = \frac{1}{2} (\log \alpha_1 + \log \alpha_2) \tag{58}$$

the figure obtained being almost the same as the arithmetic average, provided the terminal values of α are not too different. The geometric mean is preferred. This figure for α is now introduced into equation (57) or (58), and the vapour concentration y^* calculated for particular values of x. In the case of the benzene-toluene example we thus obtain the figures shown in Table 11 (column I).

Table 11

Calculation of equilibrium concentration y^* for benzene-toluene with $\alpha = 2.43$

x (mol %)	I y^* calculated by		II y^* determined from		Determination by Kirschbaum [103]
	Formula (53) or (54) (mol%)	Difference (mol%) from determination	Ideal equilibrium curve $\alpha = 2.4$	Difference (mol%) from determination	
10	21.2	−0.4	20.0	+0.8	20.8
20	37.8	−0.6	37.2	±0.0	37.2
30	51.1	−0.4	51.0	−0.3	50.7
40	61.8	+0.1	61.0	+0.9	61.9
50	70.8	+0.5	70.8	+0.5	71.3
60	78.7	+0.4	78.4	+0.7	79.1
70	85.0	+0.7	84.8	+0.9	85.7
80	90.7	+0.5	91.0	+0.2	91.2
90	95.6	+0.3	95.6	+0.3	95.9

The nomogram of Orlicek and Pöll (Fig. 21) may also be used for the determination of equilibria of ideal mixtures [85]. The left-hand vertical scale gives the molecular fraction in the liquid phase (x_B), the right-hand scale the equilibrium composition of the vapour phase (y^*). Let us again use the system benzene-toluene as example. For $x = 50$ mol% and $\alpha = 2.4$ a figure of 70.8 mol% is read off for y^* on the right-hand scale, as shown by the line drawn in the nomogram; this figure agrees reasonably well with that found by calculation. The nomogram is valid for molecular fractions. When it is used, it should be noted that if α or Q lies above unity, the unenclosed figures on scales X and Z should be employed; if the figure for α or Q (central scale) is less than 1, the figures enclosed in circles against scales X and Z should be used. The circular diagram after Voorwijk [86], which is based on formula (53), also enables equilibrium data to be determined very quickly.

We have so far confined ourselves to the treatment of binary mixtures, partly in view of the fact that multicomponent mixtures may sometimes be regarded as composed of a number of binary mixtures. Methods of calculation for mixtures of three substances, with complete solubility and with a miscibility gap, have been described in detail by Thormann [72] and Matz [73]. Hollo and Hollo and Lengyel [87] are concerned with problems of vapour-liquid equilibria of ternary and quaternary systems. They examined three non-ideal quaternary systems using new apparatus and a new computing method which shortens experimental work considerably. Quaternary equilibrium data can be obtained by means of a double orthogonal projection.

To meet the particular requirements of the petroleum industry Umstätter and Flaschka [88] have developed a method of obtaining equilibrium diagrams from the vapour pressure curves of the components which, in turn, may be mixtures of various substances. By considering the heats of evaporation and dilatation the accuracy of the calculation is greatly increased. The method is reported to be applicable to azeotropic mixtures as well.

A Fortran programme has been elaborated by Williams and Henley [89] for the computation of multicomponent vapour-liquid equilibria. To take into account real behaviours a number of subprogrammes are available which enable fugacities to be calculated by means of the virial equation, the Redlich-Kwong relation or according to Chao-Seader. Activity coefficients may be considered following Wilson, van Laar or Hildebrand. The state of the art of precalculating vapour-liquid equilibria in multicomponent mixtures was surveyed by Hála [89a]. Lu and Polak [89b] discussed the special requirements for the calculation of phase equilibria at low temperatures (20 K to room temperature).

4.6.2 Volatility, separation factor α and activity coefficient γ

By the volatility F we denote the tendency of the liquid to pass into the vapour phase. It is expressed as the ratio of the partial pressure to the mole fraction in the liquid at a given temperature:

$$F_1 = \frac{p_1}{x_1}, \qquad F_2 = \frac{p_2}{x_2}. \tag{59}$$

The relative volatility of a binary mixture is defined as

$$\frac{F_1}{F_2} = \frac{\dfrac{p_1}{x_1}}{\dfrac{p_2}{x_2}} = \frac{p_1 \times x_2}{p_2 \times x_1}, \qquad F_1 > F_2. \tag{60}$$

For ideal mixtures the volatility is independent of composition and equal to the vapour pressure of the pure material. According to Raoult's law we have, for the low-boiling component 1 of an ideal mixture,

$$p_1 = p_{*1} \times x_1 \tag{61}$$

and for the high-boiling component 2,

$$p_2 = p_{*2} \times x_2 \quad \text{or} \quad p_2 = p_{*2}(1 - x_1). \tag{62}$$

That is, the partial pressure of a component is equal to the product of the vapour pressure of the pure component and the concentration of the same component in the liquid, expressed as a mole fraction.

According to eq. (39) the equilibrium concentrations in the vapour are

$$y_1{}^* = \frac{p_1}{p_{\mathrm{ges}}} \quad \text{and} \quad y_2{}^* = \frac{p_2}{p_{\mathrm{ges}}}.$$

Substituting eqs. (61) and (62) into these latter equations we have

$$y_1{}^* = \frac{p_{*1} \times x_1}{p_{\mathrm{ges}}} \quad \text{and} \quad y_2{}^* = \frac{p_{*2} \times x_2}{p_{\mathrm{ges}}}. \tag{63}$$

The quotient of eqs. (59) is found to be

$$\frac{y_1{}^*}{y_2{}^*} = \frac{p_{*1} \times x_1}{p_{*2} \times x_2} \quad \text{or} \quad \frac{y_1{}^* \times x_2}{y_2{}^* \times x_1} = \frac{p_{*1}}{p_{*2}} = \alpha. \tag{64}$$

This expression for the separation factor α, however, is identical with (60) so that the relative volatility of an ideal mixture may be expressed much more easily by the ratio of the vapour pressures of the pure components, where $p_{*1} > p_{*2}$.

The relative volatility can be determined from the boiling points of the components. By starting from Trouton's rule, with $K = 20.5$ ($= \Delta_V H/T$ cal/°C) and the Clapeyron equation, Rose [91] obtained a relationship that can be used for purposes of orientation, between the boiling points and the separation factor of two normal liquids:

$$\log \alpha = 8.9 \frac{T_2 - T_1}{T_2 + T_1}. \tag{65}$$

Melpolder and Headington [90] developed the following more accurate formula, giving errors of 0 to 6.2%, the vast majority of which, however, lie below 1%.

For normal pressure:

$$\log \alpha = \frac{\vartheta_2 - \vartheta_1}{T} (3.99 + 0.00119397T). \tag{66}$$

For pressures above or below atmospheric (10—1500 mm Hg):

$$\log \alpha = \frac{\vartheta_2 - \vartheta_1}{T} \left(7.30 - 1.15 \log p + \frac{T}{179 \log p}\right) \tag{67}$$

$(\vartheta_2 - \vartheta_1)$ deg. C = boiling point difference of components;
TK = boiling point of mixture;
p torr = distillation pressure.

Equation (66) is represented graphically in Fig. 45, which covers the range from −100° to +300°C for the boiling points of the mixtures.

In order to check the validity of the separation factor Rose and Biles [90] tested a column, arranged as in Fig. 88, with finite reflux ratios between 9.2 and 15.8. In the case of the mixture n-heptane-methylcyclohexane they found a good agreement with phase equilibrium measurements for an average value of $\alpha = 1.074$. The calculation from the experimental figures was performed by means of the formula

$$\alpha = \frac{v + x_E/x_B}{v + (1 - x_E)/(1 - x_B)}. \tag{68}$$

This method is very suitable for calculating the value of α for ideal and non-ideal mixtures from test data obtained with various column packings. It is also applicable to multicomponent mixtures.

It is only in the case of ideal mixtures that the difference in boiling point of two components is a consistent measure of the ease of separation. If the mixture is not ideal the dependence of α on the pressure gives a valuable pointer for the solution of a problem in separation.

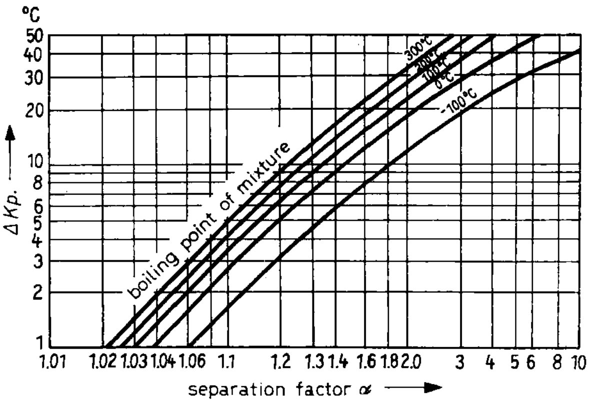


Fig. 45
α as a function of the boiling point difference $\Delta Kp.$, with the boiling point $Kp.$ of the mixture at 760 torr

If α becomes unity ($\log \alpha = 0$) a separation of the two components by distillation is not possible. Only selective methods of separation (section 6.2) can then lead to a solution of the problem. The larger the value of α, the higher does the hyperbola of the ideal equilibrium curve lie and the easier is the separation.

As a rule, particularly in homologous series, the value of α rises with decreasing temperature, so that the separation of a mixture should become easier in vacuum. This is also the conclusion at which Hawkins and Brent [92] arrived after extensive distillation tests; the columns were just as efficient under vacuum as at 760 mm pressure and it is only the increase in relative volatility in vacuum that facilitates the separation. As an example, according to Tsypkina [93] the number of theoretical plates required for the separation of anthracene-carbazole and of pyrene-fluoranthrene dropped by more than 50% if the distillation was performed at 60—100 mm Hg. There are mixtures for which α remains constant over a wide range of pressures, for instance chloroform-carbon tetrachloride and n-heptane-methylcyclohexane, and such mixtures are the most suitable for testing columns (see section 4.10.3). In some cases, however, α increases with increasing temperature, an example being the mixture 2.4-dimethylpentane-2.2.3-trimethylpentane; such mixtures can be separated more easily under pressure. In theory it would sometimes be separated more easily under pressure. In theory it would sometimes be preferable to employ isothermal distillation, in other words to keep the still temperature constant and progressively lower the pressure.

In the case of non-ideal mixtures eq. (64) has to be corrected by introducing the *activity coefficient* γ:

$$\alpha = \frac{p_{*1} \times \gamma_1}{p_{*2} \times \gamma_2}. \tag{69}$$

Since, according to (40), $y^* = \frac{p_1}{p_{ges}}$ (Dalton's law) or $p_1 = p_{ges} \times y^*$ we have

$$\gamma_1 = \frac{p_{ges} \times y_1^*}{p_{*1} \times x_1}; \qquad \gamma_2 = \frac{p_{ges} \times y_2^*}{p_{*2} \times x_2}. \tag{70}$$

For an azeotropic composition this becomes, since $y_1^* = x_1$,

$$\gamma_1 = \frac{p_{ges}}{p_{*1}} \text{ and } \gamma_2 = \frac{p_{ges}}{p_{*2}}. \tag{71}$$

A plot of γ vs. x_1 gives curves which are an immediate and clear quantitative measure of the degree of deviation from Raoult's law (Fig. 46).

For ideal mixtures the activity coefficient is unity. The deviations of γ from 1 are a measure of non-ideal behaviour. If the vapour pressures of both components are higher than what would correspond to Raoult's law ($p_1 = p_{*1} \times x_1$), γ_1 and γ_2 will be greater than 1 ($\log \gamma > 0$). This situation is referred to as a positive deviation from Raoult's law. If the deviation is sufficiently great the mixture is a minimum-boiling azeotrope (with minimum vapour pressure). Conversely, a great negative deviation ($\log \gamma < 0$) implies a maximum-boiling azeotrope (with minimum vapour pressure). Very great deviations from Raoult's law result in the breaking up of the mixture into two separate liquid phases and thus in the formation of a heterogeneous azeotrope. The latter displays the same behaviour as a homogeneous azeotrope (see chap. 6.2) [94].

A knowledge of activity coefficients and their dependence on the composition of a mixture is necessary, above all, to identify liquid mixtures as belonging to certain groups. Further, for example, the reliability of measured equilibrium data may be checked see p. 100. The determination of activity coefficients is also gaining importance for calculations concerning azeotropic and extractive distillations involving ternary systems. The methods of calculating the activity coefficients of such systems were thoroughly dealt with by Kortüm and Buchholz-Meisenheimer [74] and Schuberth [17].

The value of the activity coefficient γ of a mixture is determined experimentally by isothermal partial pressure measurements (Fig. 37). Substituting the measured value of p into eq. (70) yields the γ values as functions of x for a constant temperature (see chap. 4.4.1). The activity coefficients of systems forming azeotropes should be determined according to the method of Carlson and Colburn [95] as illustrated by Orlicek-Pöll [85]. In a graphic method reported by Orlicek [96] exact values may be derived from the course of the curve representing the total pressure.

Measuring data for vapour pressures and phase equilibria can be checked for thermodynamic consistency by means of the activity coefficient. The data for x and p or x and y^* are used to calculate the activity coefficients after eqs. (70) and (71) and log γ is plotted as a function of x. The curves thus obtained are compared with those derived from the van Laar [97] or the Margules [98] equation [17, 78]. Fig. 46 gives an example based on measurements made by Gelbin [109]. If the vapour-liquid equilibria have associations in the vapour [98a] these have to be taken into consideration so that activity coefficients may be obtained which fulfil the requirement of thermodynamic consistency.

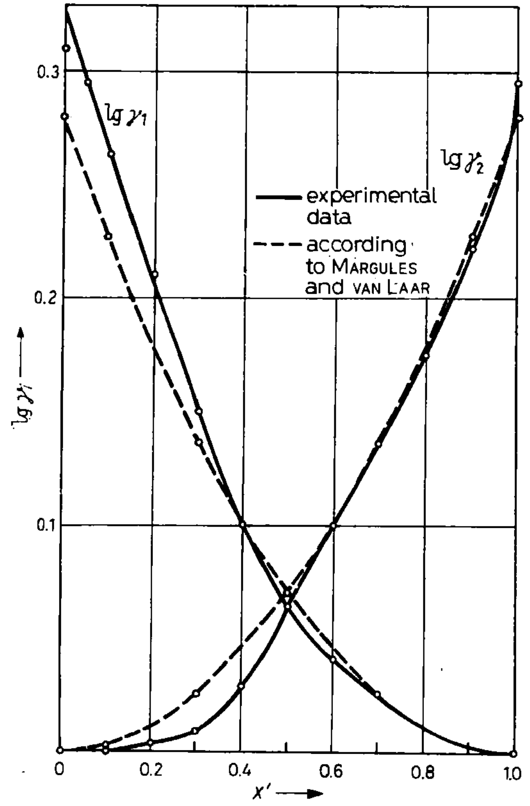


Fig. 46
Activity coefficients in the system methanol-water [109]

4.6.3 The experimental determination of equilibrium curves

The phase equilibria of binary and multicomponent mixtures are essential for the determination of the plate number required for a separation and of other distillation requirements.

The vapour-liquid equilibria published up to 1933 have been collected in the book of Landolt and Börnstein [99]. Equilibrium data are also to be found in books by Perry [100], Yu Chin Chu [101] and Chu, Wang, Levy and Paul [102].

Stage and coworkers published a number of tables containing phase equilibrium data. Figures for the lower hydrocarbons, H_2S and CO_2 are to be found in the book by Sage and Lacey [27]. Jacobs [104] gives the plots of eqnilibrium curves for 50 mixtures. Kogan and Fridman present an ample amount of tabulated data in their handbook [105]. The 1966 edition contains the equilibrium data of 1765 binary mixtures, 359 ternary mixtures and 32 multicomponent mixtures as well as an introduction into the experimental investigation and the checking of phase equilibria. The whole subject of vapour-liquid equilibria has been discussed extensively by Hála et. al. [78]. Part I of this work deals with the thermodynamics of solutions of non-electrolytes, part II with the laboratory technique for the measurement of phase equilibria, part III contains literature references for 1232 investigated systems.

One of the most extensive compilations of phase equilibrium data at normal pressure was published by Hála et al. [106] in 1969. PPDS, which is intended to be a long-term project, will be able to provide distillation data on a large scale [106a]. It is noteworthy that Renon has edited an international journal entitled "Fluid-Phase Equilibria" since April 1977, which is published by the Elsevier Publishing Company.

In laboratory practice, nevertheless, we frequently encounter mixtures for which the phase equilibria have not been measured so that the question arises what apparatus will be suitable to obtain the desired data. We distinguish between isothermal methods and circulating methods with constant pressure. The principle of the latter method consists in evaporating a binary mixture and allowing phase equilibrium to become established at a certain pressure, whereupon the temperature and the compositions of the contents of the still pot and of the liquefied vapour are determined. An excellent introduction into the technique of measuring as exemplified by the boiling behaviour of fatty acids is given by Müller and Stage (Refs. chap. 1 [39]). It is also possible to carry out the determination isothermally, the pressure that is established at a constant temperature being measured. Static methods of determination have the advantage of requiring small amounts of substance. Kortüm and Freyer [107] report a straightforward method of determining isothermal vapour pressure diagrams of binary and ternary mixtures of liquids. A versatile arrangement for passing the mixture through the thermostat is described by von Weber [108]. Gelbin [109] compared various methods of determination.

It is particularly important to know the *course of the equilibrium curve* accurately near its beginning and end; for this reason as many points as possible should be determined between 0 and 10 mol% and between 90 and 100 mol%. In general the equilibrium vapour concentration y^* is measured at the following compositions x_B of the liquid:

1, 3, 5, 10 and every 5% up to 95, 97, 99 mol%.

The number of points depends, of course, on the nature of the mixture and the use to which the data are to be put; in the case of ideal mixtures, intermediate points in the central region may be omitted.

To determine these values in a fairly simple apparatus about 250 to 500 ml of the mixtures are placed in flask a (Fig. 47) and the liquid is heated to boiling. The vapour liquefies in condenser b, and the condensate returns to flask a as long as tap c is kept closed. The temperature established is read off on thermometer d. After equilibrium has become established a sample of about 0.1 to 0.2 ml is taken at tap c. At the same time a sample of the flask contents is taken through tap e. The determinations are continued until three successive concentrations are the same. When measurements are carried out in vacuum a sampling device (which is of course also suitable for normal pressure) may be used to ensure that the sample is not contaminated with tap grease. The compositions are determined by measurement of the refractive index, with the aid of a calibration curve (n_D^{20} — per cent wt.), which has previously been prepared for mixtures of the pure components. Another criterion, such as density or freezing point may be adopted instead of the refractive index if required. The series of determinations is usually started with the lowest content, x_B, of low-boiling component. After each measurement enough of the low-boiling component is added to give the next intended concentration; the amount added need not be very exact, since the position of the point is not critical.

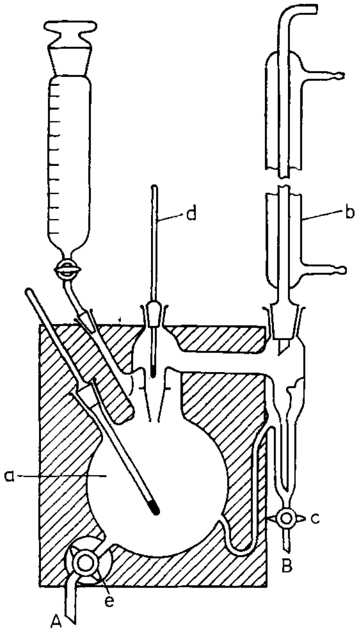


Fig. 47
Othmer's phase equilibrium apparatus
A = Sampling point for liquid
B = Sampling point for condensed vapour

Care is necessary to guard against the following sources of error in equilibrium determinations:

1. superheating of the liquid;
2. the occurrence of a concentration gradient in the flask contents;
3. partial condensation above the flask;

4. entrainment of droplets by the vapour;
5. total evaporation of sprayed liquid;
6. the disturbance of equilibrium by the withdrawal of excessively large samples;
7. contamination of the samples during withdrawal.

Attempts have been made to reduce these sources of error by modifications in apparatus design and by standardizing the conditions of operation. The ideal method would be to determine compositions of the flask contents and condensate without removing samples. Recently, flow refractometers have been used for this purpose (see section 8.5). According to Stage et al. [110] the time required to attain equilibrium with their circulation-type apparatus amounted to less than 10 minutes, as against several hours for the usual Othmer apparatus [111]. It is at all events advisable to employ as large a charge as possible, in order that the samples taken shall not affect the equilibrium.

If one of the components has a very high vapour pressure (as in the system methanol-methyl formate), or if the refractive indices differ but little, a satisfactory method for determining compositions is by gas chromatography. This method will be particularly useful for measuring the equilibrium concentrations of multicomponent mixtures and requires very small samples [112]. Gillespie [113] has investigated the possibility of eliminating entrainment and superheating by the use of a Cottrell pump. This principle seems promising, since apparatus so equipped (for instance that of Röck and Sieg [114], Figs. 48 and 49) gives thermodynamically sound results.

A heating coil b, directly immersed in the liquid in the still pot produces a regular stream of vapour bubbles. The rising bubbles stir the contents thoroughly and entrain an appreciable amount of liquid along the Cottrell tube *c*, so that a mixture of vapour and liquid is ejected onto the temperature measuring point *f*, which is provided with a spray guard *e* (Fig. 48). The vapour and liquid phases there separate; the liquid flows downwards, passing the sampling chamber *g*, and returns to the flask, whilst the vapour passes through a settling chamber, is totally liquefied in condenser *i*, flows through the receiver *k* and finally also returns to the still pot. In the improved apparatus shown in Fig. 49 the vapour space *h* and the Cottrell pump *d* are surrounded by a vacuum jacket for the prevention of partial condensation. The outer wall of this jacket is maintained at the temperature of ebullition by means of a circulating thermostat. By this means an error in the equilibrium composition of the vapour resulting from partial condensation or the evaporation of sprayed liquid is avoided. The hydrostatic pressure head due to the Cottrell pump and still pot has no influence on the temperatures and pressures measured, provided the experiment is properly performed. The mixture nowhere comes in contact with valves or ground joints, so that contamination is excluded. The ratio between the volumes of the distillate receiver and the still pot is smaller than 1:20.

Apparatus equipped with a Cottrell pump has also proved suitable for systems with relatively high volatilities ($\Delta Kp. > 100\,^{\circ}\mathrm{C}$) [115]. The improved Labodest circulating apparatus makes use of a Cottrell pump and electromagnetic valves with Teflon cones for sample withdrawal [112]. Its microscale construction is designed along the same lines and requires only 100 ml charge (Fig. 50). The sources of error

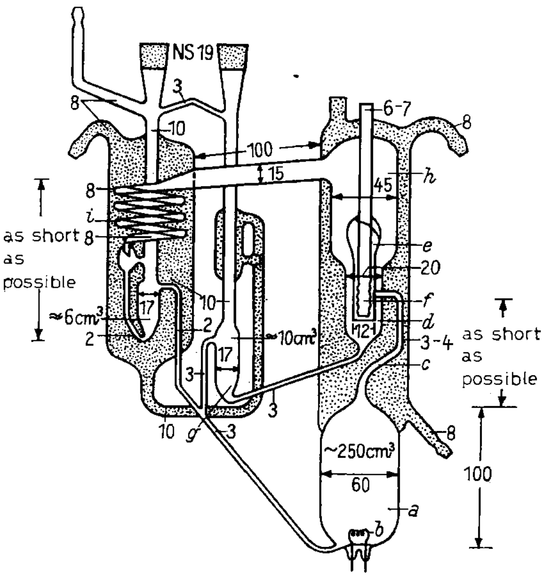


Fig. 48
Circulation-type apparatus of Röck and Sieg (dimensions in mm; internal diameters given).

a = Boiler, *b* = Heating coil, *c* = Cottrell tube, *d* = Cottrell pump, *e* = Spray guard, *f* = Temperature measuring point, *g* = Sampling vessel, *h* = Vapour space, *i* = Condenser, *k* = Receiver

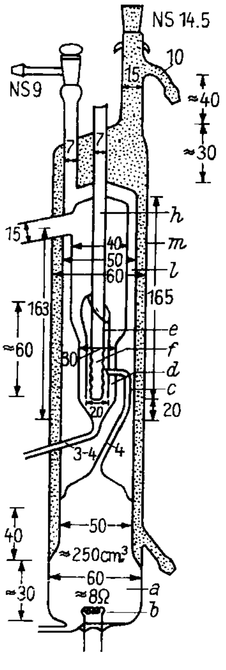


Fig. 49
Heated part of Röck and Sieg's apparatus with vacuum jacket (designations as in Fig. 48)

l Vacuum jacket, *m* Thermostat jacket

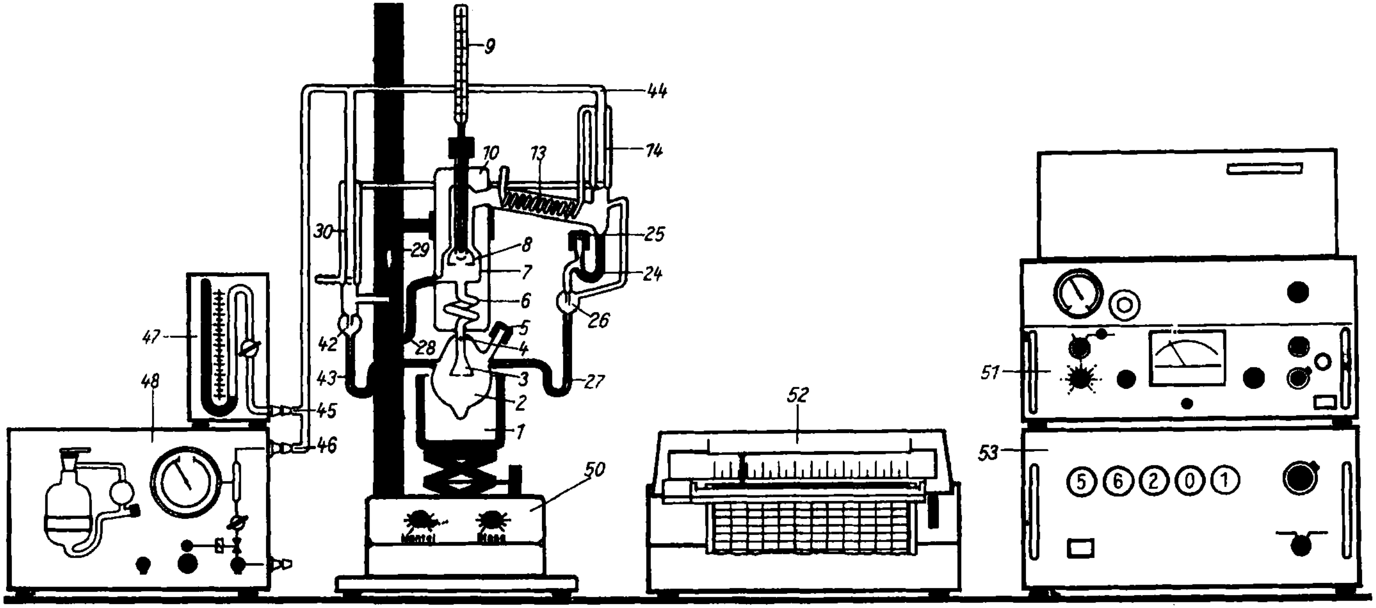


Fig. 50
Labodest circulation-type apparatus with Cottrell pump

Micro-scale version with laboratory recorder (*52*), device for gas chromatography (*51*), electronic integrator (*53*), control panel (*50*) and vacuum controller (*48*)
(Manufacturers: Fischer, Labor- und Verfahrenstechnik, Bonn—Bad Godesberg)

mentioned on p. 93 have been practically eliminated in this type of apparatus. The same holds true for the equilibrium apparatus after Schuberth [116] the latest design of which, named G 15, is shown in Fig. 51. The apparatus of Raffenbeul and Hartmann [116a] which is also of the Gillespie type allows quite accurate routine measurements. It is practically free from the disadvantages mentioned above and enables both isothermal and isobaric measurements to be made.

The connection between the still pot and the vapour space is provided by the Cottrell tube. The tube mounted on top of the still pot is essentially that of the G 13

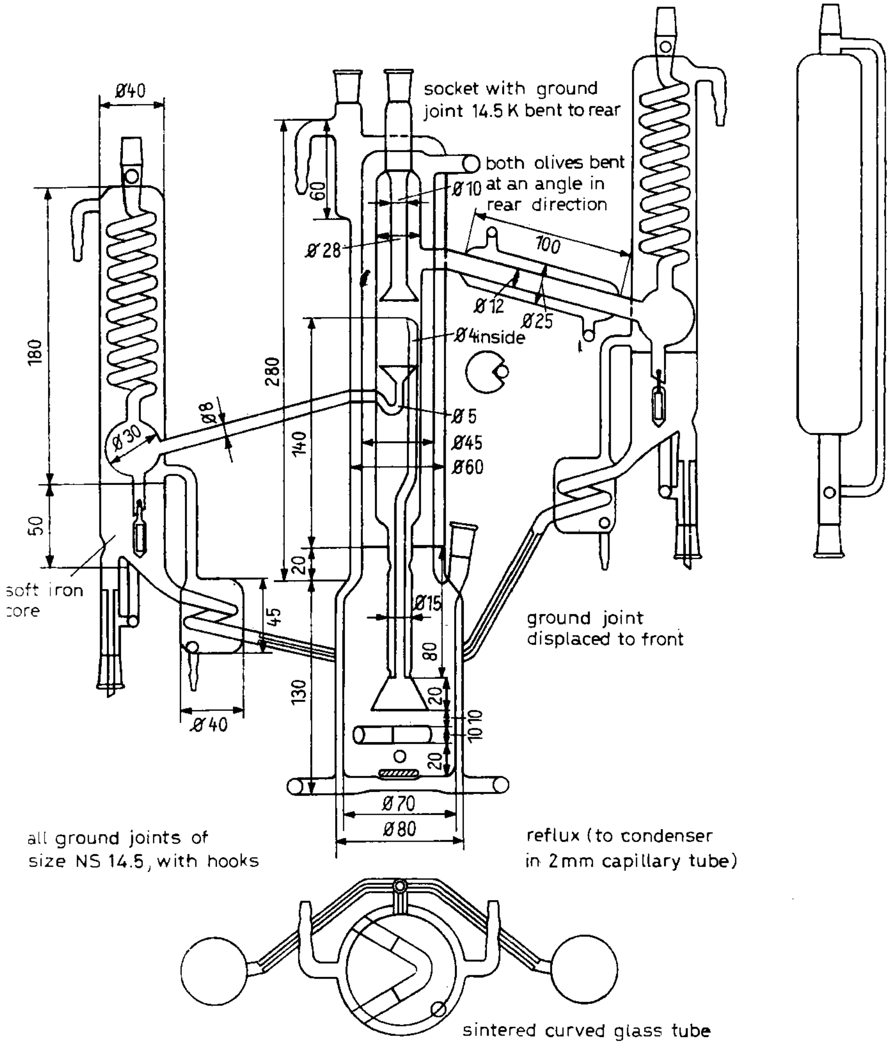


Fig. 51
Constructional sketch of the G 15 equilibrium apparatus (Schuberth)

apparatus. The heat required for the evaporation of the liquid is supplied by a heater which consists of a curved glass tube carrying a heating coil. The tube surface is sintered in order to avoid boiling delays. The tube is placed at a height above the bottom which allows the operation of a Teflon-coated magnetic stirrer under it ensuring better mixing of the liquid. Due to the shape of the curved tube the production of vapour bubbles is most intense at the centre of the equilibrium space since the heat flow density is highest where the tube is most curved. Samples are withdrawn by means of suspended rods which are operated electromagnetically. The totally condensed vapour or the cooled liquid flows down these rods. The use of the rods in contrast to the suspended funnels of the older apparatus is advantageous in that two ground glass joints are saved in each withdrawal unit. Another characteristic of the G 15 apparatus is the joining of the reflux capillary tubes (3 mm) for condensate and liquid outside the central part. The mixing of the two reflux streams thus brought about prevents too great concentration fluctuations being set up at the inlet of the equilibrium space, which might disturb the equilibrium. All the other details of the apparatus are identical with those of its forerunners.

A microscale apparatus for isothermal phase equilibrium determinations in multicomponent systems with sample volumes as small as 2 ml is described by Wichterle and Hála [117]. The equilibrium apparatus developed by Neumann and Walch [118] for low-temperature measurements was used to study the system CO_2—CH_4. The development of new low-temperature phase equilibrium apparatus and work on binary and ternary systems were reported by Lu and Polak [89b]. Details of the improved Labodest circulating apparatus with a view to measurements on mixtures with a miscibility gap were given by Stage and Fischer [118a]. Schmidt [118b] suggests that equilibrium measurements for rapid determinations should be combined with a gas-chromatographic vapour space analysis.

Kumarkrishna Rao et al. [119] used the equipment shown in Fig. 52 for measurements on the systems benzene-n-hexane and benzene-cyclohexane at pressures up to 18 atm. It is also possible, however, to place an ordinary glass apparatus inside a pressure vessel. Jost et al. [120] built a circulating apparatus of glass with an adiabatic jacket into a 20-litre autoclave.

A glass apparatus described by Slocum [120a] is reported to be applicable to vapour pressure and vapour-liquid equilibrium measurements at temperatures from −50 to 250 °C and pressures from 0 to 70 bar. An extensive description of methods and apparatus for the measurement of isothermal vapour-liquid equilibrium data at high pressures (4.5···110.4 bar) is given by Gransø and Fredenslund [120b]. Thus, these authors together with Mollerup [120c] measured the vapour-liquid equilibrium data of the systems C_2H_6/N_2, C_2H_4/N_2, C_3H_8/N_2 and C_3H_6/N_2 isothermally in the temperature range from 200 K to 290 K. The pressures involved extended to 216.32 atm.

For measuring equilibria down to 1 mm Hg pressure Lydersen and Hammer [121] developed an apparatus that is rotated, so as to produce evaporation from a constantly renewed, downflowing film and to ensure good mixing of the boiling liquid and the condensate (Fig. 53). This arrangement was employed, for instance, for determining phase equilibria of the system di-n-butyl phthalate-di-n-butyl sebacate at 1 mm pressure.

A method of equilibrium determination involving the entrainment of saturated vapour by a current of an inert gas was described by Junghans and von Weber [122]. The method was used in measurements on the binary mixture ethyl benzene-styrene. Polymerization was avoided by adding an inhibitor. The *entrainment method* has the great advantage of proceeding isobarically, the varying partial pressures p_1 and p_2 being made up to the exterior pressure by the partial pressure p_3 of the carrier gas

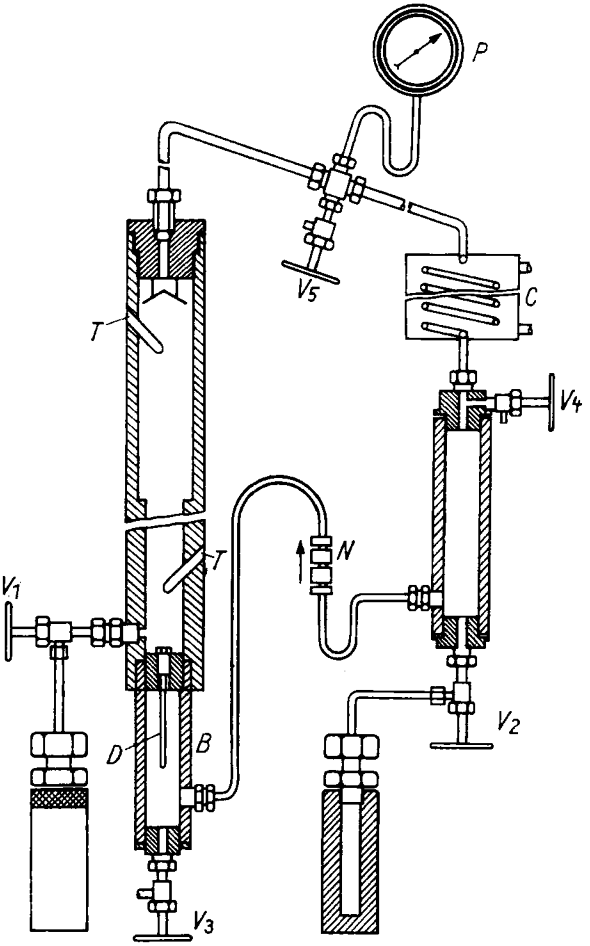


Fig. 52
Equilibrium apparatus of Kumarkrishna Rao et al. for measurements up to 15 atm

V_1 = Valve for liquid samples, V_2 = Valve for vapour samples, V_3 = Drain valve, $V_4 - V_5$ = Valves for admitting air, B = Evaporator, D = Perforated copper tube, T = Thermo-wells, C = Condenser, P = Manometer, N = Safety valve (nitrogen), and the total mixture then passing isothermally through the thermostat (Fig. 54).

The use of radioactive substances for equilibrium determinations may offer appreciable advantages [123]. Thus, *e.g.* ^{35}S has been used [124].

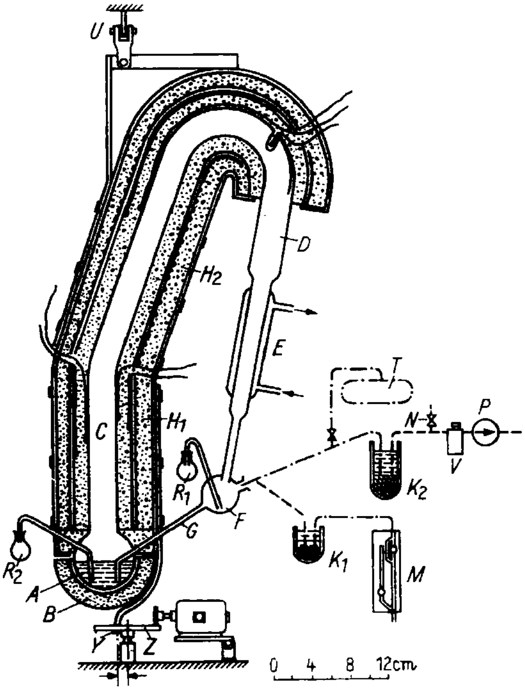


Fig. 53
Equilibrium apparatus of Lydersen and Hammer for pressures up to 1 mm Hg

A = Flask (6 cm dia.), B = Heating jacket, C = Connecting tube, D = Air condenser, E = Water condenser, F = Receiver, G = Capillary connecting tube, H_1/H_2 = Electrically heated aluminium cylinders, K_1/K_2 = Dewar vessels containing solid CO_2, M = McLeod manometer, P = Vacuum pump, N = Valve, T = Buffer vessel, V = Pressure regulator, R_1/R_2 = Sampling vessels, Y = Shaft, Z = Rotating table

Though very careful work has been done in the past, it will be noted that there is often a considerable spread in the results found by investigators. A large number of comparative measurements have therefore been performed recently, with the object of finding the sources of error and of providing exactly reproducible data.

The equilibrium between liquid and vapour in binary systems with the association of the components in both phases was discussed by Trybula and Bandrowski [124a]. They reported measurements on the mixtures acetic acid-acrylic acid and formic acid-acrylic acid as illustrations of their method (see also Refs. chap. 6 [29a]).

Experimentally determined equilibrium data may be checked for thermodynamic consistency by methods described by Kortüm et al. [44], Carlson and Colburn [95], Redlich and Kister [125] and others [126]. Redlich and Kister showed that the criterion of thermodynamic consistency for a set of isothermal measurements could be expressed by

$$\int_0^1 \log (\gamma_1/\gamma_2) \cdot \mathrm{d}x_1 = 0, \tag{72a}$$

in which γ_1/γ_2 is calculated from equilibrium data as

$$\log \gamma_1/\gamma_2 = \log \frac{y_1 \cdot x_2}{y_2 \cdot x_1} - \log \frac{p_{*1}}{p_{*2}} \tag{72b}$$

where γ = the activity coefficient;
y = the concentration in the vapour phase;
x = the concentration in the liquid phase and
p^* = the vapour pressure of the pure component.

If, in accordance with equation (72a), $\log \gamma_1/\gamma_2$ is plotted against x_1, the areas above and below the x-axis must be equal if the isothermal data are thermodynamically reliable. As an example, Fig. 55 shows this relationship for the system chloroform-ethanol at 45 °C. The difference between the areas amounts to only 1.6%. Herington [127] extended this method to ternary systems and isobaric data.

Bittrich [128] studied the possibilities of checking the consistency of equilibrium measurements. He assessed the more important methods suggested in the literature. Herington's graphic method of "symmetric areas" [6] allows individual data to be

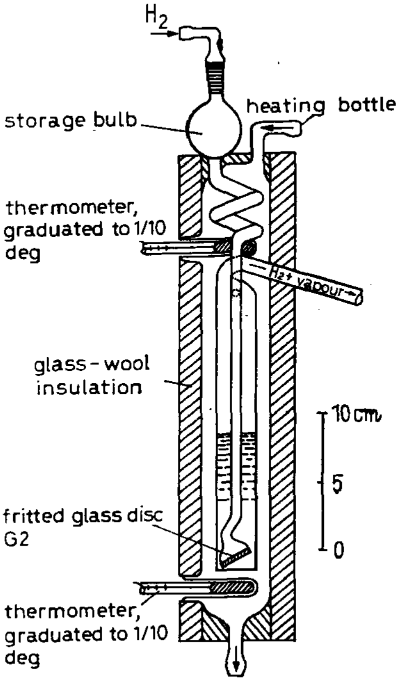


Fig. 54
Equilibrium apparatus employing the entrainment method (Junghans-Weber)

checked in limited concentration ranges of binary and ternary systems. Starting from the Gibbs-Duhem equation Tao [129] established a relation for checking the consistency of multicomponent equilibria. Chapter 6 of Schuberth's book [17] offers a thorough discussion of the techniques of measuring activity coefficients and the methods of checking binary systems for consistency.

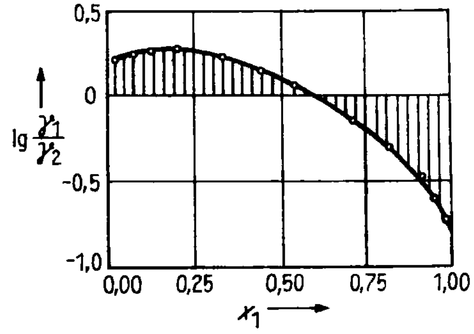


Fig. 55
Redlich and Kister's criterion of thermodynamic consistency applied to data for the system chloroform-ethanol ($t = 45\,°C$)

4.7 Number of theoretical plates (separating stages)

It has already been pointed out in the historical summary in chapter 2 that, together with the development of the various types of column, there arose the need to compare their separating efficiencies. By *separating efficiency* we imply the amount of distillate, having a definite concentration, obtained under predetermined conditions of distillation in unit time from a mixture of a certain composition. At first the tests were carried out on a charge consisting of 50% w. of benzene and 50% w. of toluene, under definite distillation conditions, a plot being subsequently made of the distillation temperature against the amount of distillate. The course of such curves was compared, and it was thus possible to show trends in a qualitative manner, for instance that the separating efficiency is dependent on the length of the column and on the load. More accurate information is obtained if a physical characteristic of the distillate such as the refractive index is determined and is also plotted against the amount of the overhead; the boiling point alone is frequently not a sufficient criterion of the purity of a substance. These methods are very suitable for comparing various columns, but do not allow the column and distillation conditions required for a certain separation to be calculated beforehand. For this reason the following criteria for separating efficiency were proposed:

1. The yield of distillate of a certain purity [130].
2. The amount of the transition fraction between two concentrations of distillate.
3. The slope of the distillation curve in the transition region [131].
4. The amount of residue [132].

The last two criteria, in particular, are suitable for comparing separating efficiencies in the batch distillation of binary mixtures. The concept of the *pole height* was then developed [131]; this is obtained from the slope of the distillation curve at the point where the distillate contains exactly 50 mol% of the low-boiling component (Fig. 56).

It was not, however, until the concepts of the theoretical stage and the transfer unit had been introduced that it became possible to express in numerical terms the efficiency of a column and the difficulty involved in a separation. A *theoretical* (or ideal) *plate* (or stage) is defined to be such a section of a column that the vapour leaving it upwards (towards the next higher theoretical plate) and the liquid leaving it downwards (towards the next lower theoretical plate) are in thermodynamic equilibrium (Fig. 24).

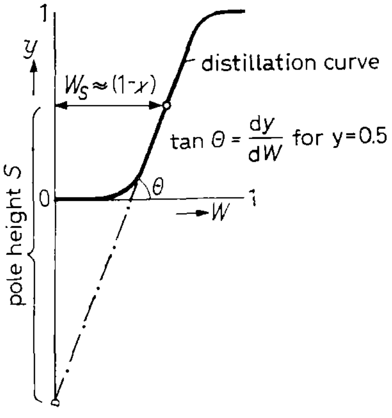


Fig. 56
Definition of pole height in batch distillation (after Bowman and Cichelli)

To make this matter clear we will consider the development of the plate column. The simplest apparatus for distillation consists of a still pot for evaporating the liquid together with a still head for condensing the vapour and collecting the distillate (Fig. 57a). We have here a single theoretical stage, since the vapour rising from the still pot attains thermodynamic equilibrium with the still pot contents. In order to obtain a higher separating effect, Adam (see chapter 2) applied the method of placing several stills next to one another, the following still in each case being heated by passing into it the vapour from the preceding one. A certain amount of reflux is produced by condensation in the connecting tubes. We can, now, place the consecutive stills above each other and then obtain the well-known plate column (Fig. 57b).

For a further explanation a diagrammatic plate column has been shown in Fig. 58; together with an equilibrium curve representing the processes taking place in the column graphically. We shall postulate that the operation is performed at total reflux, as in the case of equilibrium determinations, that is to say, no distillate is taken off. In the still pot we have a mixture x_1, containing 10 mol% of the low-boiling component 1. The vapour y_1^* formed from the still pot contents at equilibrium has a concentration of 25 mol%. If this vapour is condensed we obtain the liquid x_2 on the second plate. (The still pot is regarded as the first plate.) The vapours rising from the still pot evaporate part of the low-boiling constituents from the second plate liquid, the vapours y_2^* leaving this plate having a concentration of 50.4 mol%. These vapours condense on plate 3, so that the liquid on this plate again has the same com-

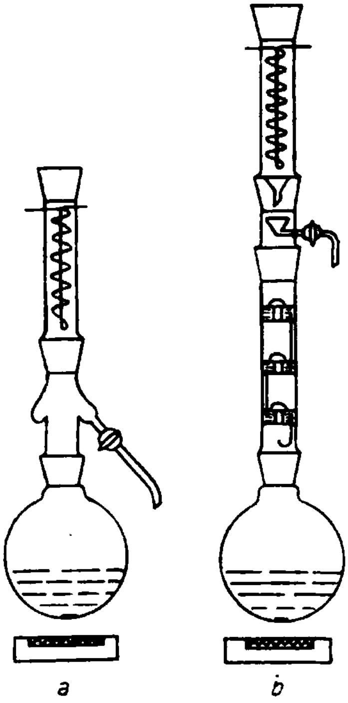


Fig. 57
Development of the plate column

a) Simple apparatus with one separating stage;
b) Plate column with 3 actual plates

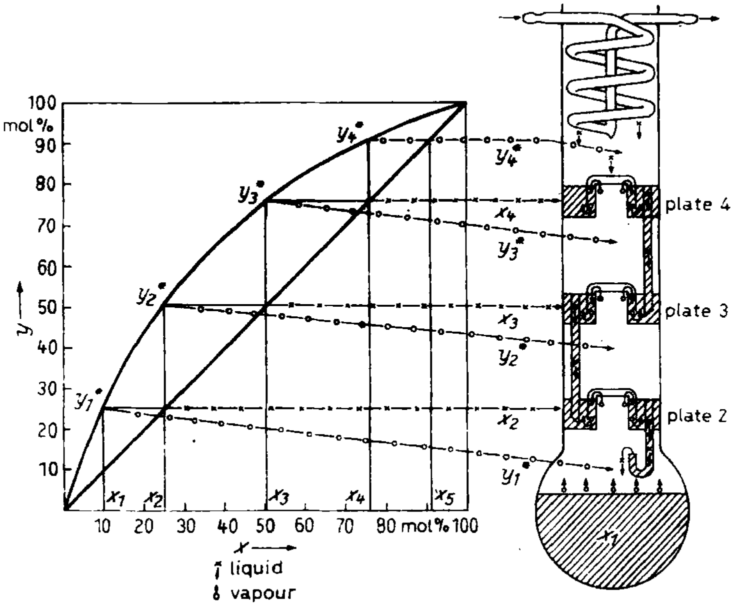


Fig. 58
A column with ideal plates and its behaviour as shown by the equilibrium curve

position $x_3 = 50.4$ mol%. The vapours rising from plate 3 then have the composition $y_3 = 76$ mol%, and so on. If the vapour $y_1{}^*$ rising from plate 4 is condensed, we obtain a distillate with a concentration of 91 mol%.

Hence, in order to enrich the charge having 10 mol % of the low-boiling component to a distillate with 91 mol% concentration, we must employ a total of 4 theoretical stages, constituted by the still pot (one stage) and a column of 3 ideal plates. In the following we shall speak of theoretical stages instead of theoretical plates, as the former term best express the progressive enrichment taking place both in plate columns and packed columns.

The concept of theoretical stage has been adopted for packed columns and several other separating procedures. It allows the efficiency of apparatus to be characterized. The distance required to achieve an equilibrium step $y^* - x$ is called HETP (height equivalent to a theoretical plate). Mathematically, we have

$$(y_1{}^*)_{z+\mathrm{HETP}} - (x_1) = \Delta x \tag{73}$$

or

$$\frac{\left(\dfrac{y_1{}^*}{y_2{}^*}\right)_{z+\mathrm{HETP}}}{\left(\dfrac{y_1{}^*}{y_2{}^*}\right)_z} = \alpha, \tag{74}$$

where z is the coordinate of length. For apparatus of length l, the relation will be

$$\mathrm{HETP} = \frac{l}{n_{\mathrm{th}}}.$$

The number of theoretical plates is a function of numerous apparatus and operating parameters. Thus, it has not been possible yet to precalculate the HETP value for a packed column on the basis of mathematical considerations alone. So far, only empirical relations have been established resulting from a large number of experimental tests (chap. 4.2, 4.8).

In practice plates do not have an efficiency of 100%, like the ideal plate, but of about 50 to 90% only. This is partly because the mixing of vapour and liquid does not produce complete equilibrium in the time available, and partly because the vapour entrains droplets of liquid to the next plate, particularly at high vapour velocities.

The term *reflux ratio* denotes the ratio between the amount of liquid R flowing back to the column after condensation, and the quantity E drawn off as distillate:

$$\text{Reflux ratio } v = R/E$$

If no distillate is taken off, we obtain an infinite ratio:

$$v = \lim_{E \to 0} R/E = \infty$$

We may express the reflux ratio graphically in the following way. The amount of vapour D removed from the still pot is the sum of reflux and distillate:

$$D = R + E \tag{75}$$

This applies to each component, as is expressed by the formula

$$D \times y = R \times x_B + E \times x_E. \tag{76}$$

By introducing (77) into (78) we obtain

$$y = \frac{R \times x_B}{R + E} + \frac{E \times x_E}{R + E}. \tag{77}$$

If the right-hand member of (77) is divided by E we find

$$y = \frac{R/E}{R/E + E/E} + \frac{E/E \times x_E}{R/E + E/E} \tag{78}$$

and by introducing v for R/E this becomes

$$y = \frac{v \cdot x_B}{v + 1} + \frac{x_E}{v + 1} \quad \text{(operating line)}. \tag{79}$$

This linear equation relates the composition of the vapour to the composition of the liquid at any level in the column (on the assumption of adiabatic operation) and represents the operating line $a - c$ (Fig. 59). If the molar heats of vaporization differ markedly this has to be taken into account when using the McCabe-Thiele method.

Differences in the molar heats of vaporization may appreciably influence the theoretical plate number, particularly near the minimum reflux ratio or with low volatilities of the components and high column efficiency. The graphical method would be greatly complicated by the calculation and plotting of the resulting curved operating lines. However, a modification by Fischer [134] makes the McCabe-Thiele method easy to handle. Billet [135] derived equations for the determination of operating lines for binary mixtures with different molar heats of vaporization of the components. A method which allows the immediate calculation of the number of theoretical stages for ideal binary mixtures at a finite reflux ratio and considers the different heats of vaporization was evolved by Thum [136]. Neretnicks et al. [137] introduced a factor N for each substance such that all substances will have the same heat of vaporization in the new system of units. Thus, a simple transformation enables straight operating lines to be plotted in McCabe-Thiele diagrams for systems with greatly differing heats of vaporization. In cases of constant relative volatility the transformation needs to be carried out at a few points only.

If plotted on the same diagram as an equilibrium curve, that is on scales of vapour composition *versus* liquid composition, equation (79) becomes a straight line with gradient $v/(v + 1)$, and an intercept on the y-axis, when $x = 0$, of $x_B/(v + 1)$.

At an infinite reflux ratio, or total reflux, the gradient is unity and the intercept zero:

$$\lim_{v \to \infty} y = 0; \tag{80}$$

$$\mathrm{tg}_\alpha = \frac{v}{v + 1} \tag{81}$$

so that the operating line is then the 45° line, as employed in Fig. 59.

We now have all the material available for the graphical calculation of distillation conditions by the McCabe-Thiele method. This is one of the most used and simplest methods for the calculation of batch and continuous distillations of binary mixtures. It involves the simplifying assumptions that the molar heats of evaporation of the components and their mixtures are identical, and there are no heat losses from the column; the consequence ist that the vapour and liquid flow rates, in moles per unit time, are constant throughout any section of the column, provided there is no addition or withdrawal of material.

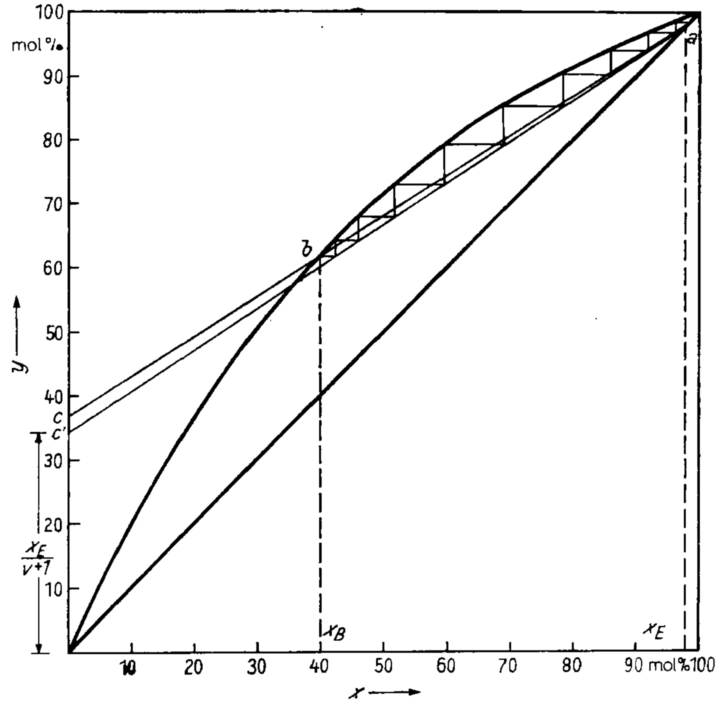


Fig. 59
Equilibrium curve for the system benzene-toluene at 1 atm, showing the construction of the operating line and the method of stepping off plates in the McCabe-Thiele method

So far all our considerations have applied to plate columns. In these, exchange occurs during the passage of the vapour through the layer of liquid on the plate, where the two attain something falling short of equilibrium. The changes in concentration and temperature are repeated from plate to plate, so that the process actually takes place in steps. Matters are different in a packed column. In this case there is a continuous exchange between the liquid film on the packing and the vapour flowing past it. The vapour nowhere remains so long that it can establish equilibrium with the liquid. Therefore we have a progressive enrichment caused by many elementary separating stages. For this reason there has been introduced a concept known as the height of a transfer unit (HTU) for packed columns; this will be discussed in section 4.8.

In laboratory practice, nevertheless, we can apply to packed columns the simpler methods of calculating separating stages for plate columns, as long as the relationship between the two is clear and we realize that such calculations are merely good approximations without theoretical justification. An analogy between the two types of column can be pictured if we imagine a plate column and a packed column of the same dimensions, in which separations are carried out under identical conditions. If both columns give the same separating effect it is reasonable to say that they contain the same number of separating stages.

4.7.1 Calculation of separating stages by the McCabe-Thiele method in batch operation

Let us keep to the mixture benzene-toluene as a practical example. It is our purpose to enrich a mixture of 40 mol% benzene to 98 mol%.

We construct the equilibrium curve (Fig. 59) and through the point $x_B = 40$ mol% draw a parallel to the ordinate, intersecting the equilibrium curve at the point b. The line parallel to the ordinate through the point $x_E = 98$ mol% intersects the diagonal at a. By joining a and b we obtain an operating line, which when continued intersects the vertical axis at c ($y = 37$).

According to eq. (79) we have

$$v_{\min} = \frac{x_E}{y} - 1 \tag{82}$$

$$v_{\min} = \frac{98}{37} - 1 = 1.65. \tag{83}$$

This figure, 1.65, is the *minimum reflux ratio*, at which an infinite number of plates would be required for separation. Since in this case points x_E, x_B and y^* lie on the operating line the minimum reflux ratio may also be expressed as [103]

$$v_{\min} = \frac{x_E - y^*}{y^* - x_B}, \tag{84}$$

where y^* refers to point b, at which the operating line a — c intersects the equilibrium curve,

$$v_{\min} = \frac{98 - 62}{62 - 40} \approx 1.65. \tag{85}$$

If the selected reflux ratio is less than $v = 1.65$ a distillate composition of 98 mol% cannot be reached. Increasing the reflux ratio beyond this value leads to finite plate numbers which are the smaller the higher the selected ratio. In our example we choose a reflux ratio $v = 1.85$. The operating line intersects the ordinate at

$$y = \frac{98}{1.85 + 1} = 34.4. \tag{86}$$

The intersection, c' (Fig. 59), is connected with a, yielding the operating line which corresponds to the distillation conditions chosen. Now we construct steps between b and a, moving alternately from the operating line to the equilibrium curve and back. We find 10 theoretical plates.

We can show how the number of separating stages varies when the reflux ratio is increased. Fig. 60 represents the equilibrium curve with a number of different operating lines and Table 12 gives the number of stages found for each reflux ratio.

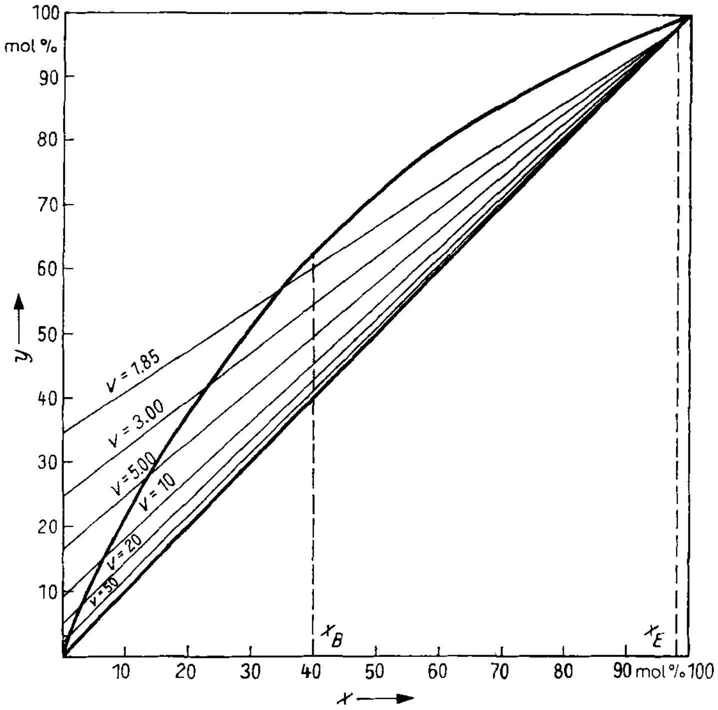


Fig. 60
Operating lines for various reflux ratios with $x_E = 98$ mol%

It will be seen that in this case there is not much object in increasing the reflux ratio above, say, 5; the saving in separating stages becomes so small that it is scarcely worth while.

In a batch separation the concentration of the still pot contents gradually changes owing to the removal of low-boiling component with the distillate; the value of x_B shifts towards zero. Let us assume that we have distilled down to a concentration x_B of 10 mol% and let us again carry out the above calculation. We then obtain the data shown in Table 13 where they are compared with those found for the beginning of the distillation.

The number of separating stages has purposely been kept constant in order that we may find how much the reflux ratio must be increased to produce the same separation. If we had kept the reflux ratio constant at 1.85, the concentration x_E would have fallen with the change in composition of the boiler contents.

In the case of a batch distillation it is therefore not sufficient to determine the conditions of distillation at the start; it is necessary to consider what the final composition of the contents of the still pot is to be, or what is the highest reflux ratio that one is prepared to use, considering the total time required. Suppose that we adopt $v = 25$ as the limiting reflux ratio, that $x_B = 80$ mol% and that we keep x_E and the number of theoretical stages constant at 98% and 10 respectively. The data found for a reduction of the still pot concentration from 80 to 5 mol% are then as shown in Table 14.

Table 12

Separating stages required for the separation of the mixture benzene-toluene in batch operation ($x_B = 40$ mol%; $x_E = 98$ mol%; $v_{\min} = 1.65$)

v chosen	Intercept on ordinate $y = x_E/(v+1)$	Number of theoretical stages n_{th}
1.85	34.4	10.0
3.00	24.5	7.0
5.00	16.4	6.0
10.00	8.9	5.5
20.00	4.7	5.0
50.00	1.9	5.0
∞	0.0	4.5

Table 13

	x_B	x_E	v (minimum)	v (chosen)	n_{th}
At start of distillation	40	98	1.65	1.85	10
At the later stage	10	98	7.10	8.80	10

Table 14

Reflux ratios for the mixture benzene-toluene with $x_B = 80$ to 5 mol%, $n_{\text{th}} = 10$ and $x_E = 98$ mol%

x_B	Minimum reflux ratio	Reflux ratio chosen
80	0.58	0.65
60	0.94	1.09
40	1.65	1.85
20	3.46	3.90
10	7.10	8.80
5	13.00	25.00

If we plot a graph of the selected reflux ratio against x_B (Fig. 61), it will be seen that when the concentration falls below 10% every reduction in x_B entails a very large increase in the reflux ratio. In practice we might start with a reflux ratio of 2 and increase it to 5 as the top temperature rises, and later to 10. It must be decided in each case whether a further increase in the reflux ratio is justified, bearing in mind that the amount of the transition fraction becomes greater the less closely one adheres to the optimum conditions.

On the basis of the Raleigh equation von Weber [138] developed a diagram from which the concentration of the liquid in the still pot after distilling a charge B_0 down to a residue B_i can be read off for ideal mixtures if α is known. A method of calculating the stepwise countercurrent distillation of ternary systems was evolved by Vogelpohl [139]. A mathematical model was constructed by Domenech et al. [139a]. A procedure, partly mathematical and partly graphical, has been developed by Billet [140] for batch countercurrent distillation of binary mixtures, with which one can calculate the reflux ratio, the yield, the still pot concentration and the quantity of mixed vapour flowing through the column as a function of the time of distillation.

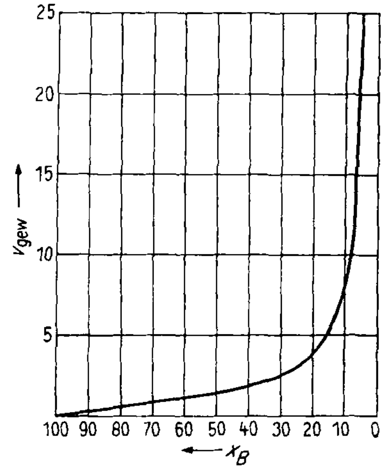


Fig. 61
Dependence of the reflux ratio on the still pot concentration x_B with x_E = 98 mol% and 10 separating stages

With a view to the high purification of liquids by means of batch distillation Wilcox [140a] derived special equations for distillations which aim at achieving very high distillate purities.

Just as the concentration of the liquid in the still pot decreases during a batch distillation, so also does the proportion of the low-boiling component in the *operating hold-up* of the column (see section 4.10.5).

4.7.2 Calculation of separating stages by the McCabe-Thiele method in continuous distillation

Although distillations in a laboratory are for the greater part done batchwise, cases occur in which a continuous procedure is preferable or even essential (see section 5.2.2). As opposed to batch distillation, in which the concentrations of the still pot contents, the distillate and the hold-up are changing all the time, continuous distillation is characterized by constant conditions throughout. A mixture to be distilled is preheated to a certain temperature and introduced into the column a—d at some point along its length; this column yields an overhead product E and a bottom product A (Fig. 62). The apparatus operates in such a way that

$$Z = E + A \tag{87}$$

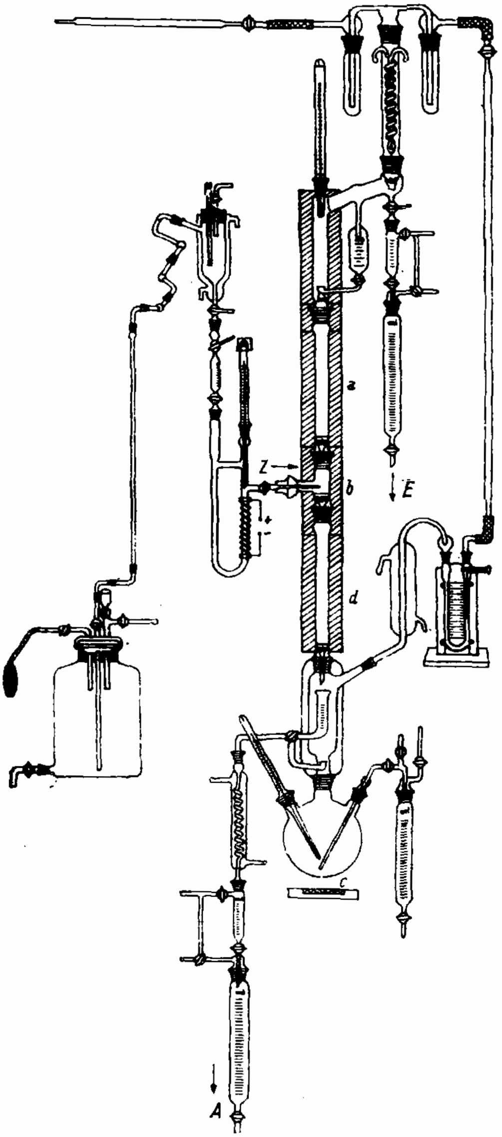


Fig. 62
Destinorm apparatus, Model IIIv, for continuous fractional distillation in vacuum

and hence

$$x_Z \times Z = x_E \times E + x_A \times A \tag{88}$$

where Z = the amount of feed in unit time,
E = the amount of top product in unit time,
A = the amount of bottom product in unit time.

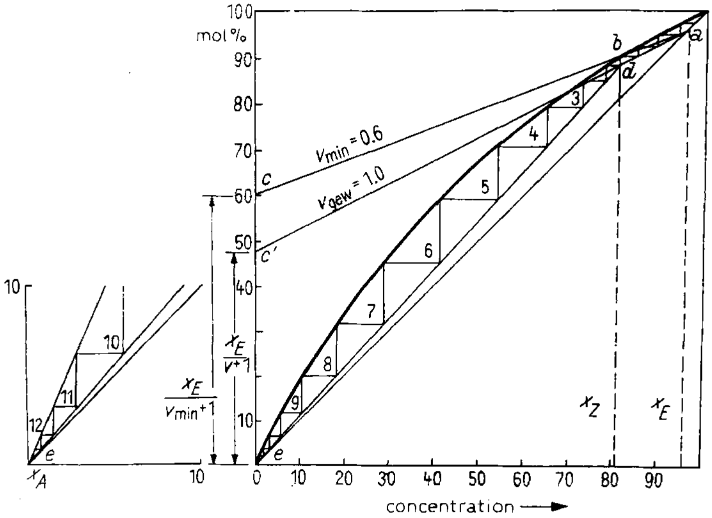


Fig. 63
Equilibrium curve for a binary mixture of the normal fatty acids C_6 and C_7 at 20 mm pressure (calculated), determination of the number of separating stages in continuous distillation

Let us assume that we wish to separate a mixture of the C_6 and C_7 normal fatty acids, the mixture containing 81 mol% of the C_6 component, and that we have to determine the number of separating stages necessary to obtain a top product of 96 mol% and a bottom product of 0.5 mol% concentration. The distillation pressure is to be 20 mm Hg. The equilibrium curve for this mixture has not yet been measured; it was calculated by formula (58) with $\alpha = 2.10$ (Fig. 63).

First we draw an operating line through the points a ($x_E = 96$ mol%) and b ($x_Z = 81$ mol%); this intersects the y-axis at 59.8 (point c). The minimum reflux ratio is hence, according to formula (82)

$$v_{\min} = x_E/y - 1 = 96/59.8 - 1 = 0.6. \tag{89}$$

In order that the number of separating stages needed shall not be too high, a reflux ratio of 1 is chosen, which gives an intercept on the y-axis equal to

$$y = \frac{96}{1+1} = 48. \tag{90}$$

The chosen operating line $a - c'$ hence starts from the point 48 on the y-axis; it intersects the vertical through $x_Z = 81$ mol% in the point d. From $x_A = 0.5$ mol% a vertical line is drawn, meeting the diagonal at e. We join points e and d; this straight line is the operating line for the lower column section. Starting at d, we now draw in the steps for the separating stages on the upper column section between the equilibrium curve and the operating line $d - a$; this gives us slightly less than 4 stages. Going downwards from d, we draw further steps between the equilibrium curve and the lower operating line $d - e$, which gives us 13 stages. If the equilibrium curve has been constructed on a small scale (say 25 × 25 cm), or if the curve is very flat, it is useful to draw the part between 10 and 0 mol% again on a larger scale, so as to obtain greater accuracy.

The separation requires a total of 17 stages, of which 13 have to be in the lower column section and 4 in the upper. The way in which these 17 theoretical stages may be realized is described in sections 4.10.9 and 7.3.

The above-mentioned determination of the minimum reflux ratio for a continuous distillation assumes that the mixture to be separated is fed in at its boiling (bubble) point. In this case the amount of reflux in the lower column section is increased by the amount of the feed, *i.e.*

$$R' = R + Z. \tag{91}$$

If the temperature of the feed is lower, condensation of a quantity of vapour will take place, this amount being determined by the quantity of heat necessary to bring it to its boiling point. This may be expressed by a correction factor e, which modifies equation (91) to

$$R' = R + eZ \tag{92}$$

in which e has the value

$$e = 1 + \frac{Q_{Kp.} - Q_Z}{\Delta_V H}.$$

$Q_{Kp.}$ here denotes the heat content of the feed at its boiling point, Q_Z that at the actual feed temperature and $\Delta_V H$ the molar heat of vaporisation. Consequently the abscissa of the point g (Fig. 64) has the value

$$x'_Z = \frac{x_Z}{e}. \tag{93}$$

The straight line $g - d$ then intersects the upper operating line in the point b. The minimum reflux ratio thus becomes lower. If the mixture is fed in at its boiling point, e becomes 1 and the points b and f have the same abscissa x_Z [103]. If the feed consists partly of vapour a construction by Cavers [142] allows the McCabe-Thiele diagram to be used also.

On the basis of the McCabe-Thiele graphical method Pohl [143] has derived a numerical procedure for calculating the conditions of the lower column section for mixtures containing a very low concentration of the light component. The equilibrium curve can then be approximated by a straight line. Horvath and Schuberth [144] developed a method for dealing with high concentrations in the top product (say 99.99%) and low concentrations of the bottom product. A high degree of accuracy is obtained by plotting the McCabe-Thiele diagram on logarithmic co-ordinates. The arithmetic determination of the theoretical plate number and the parameters for the continuous separation of ideal mixtures will be treated in detail in chap. 4.15.

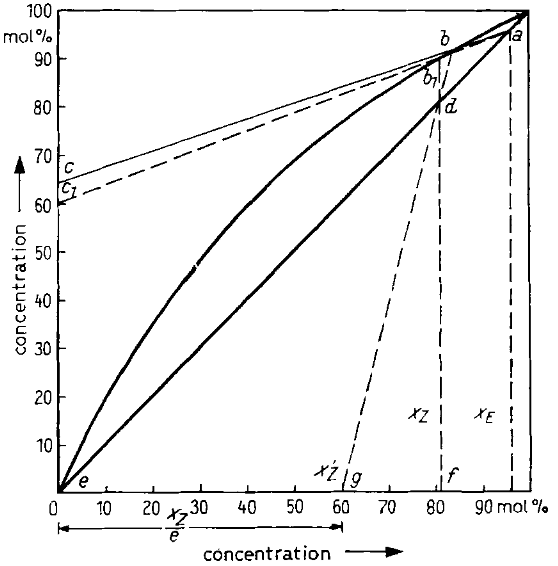


Fig. 64
Influence of the feed temperature in continuous distillation

4.7.3 Determination of separating stages by the McCabe-Thiele method for equilibrium curves with an inflection point or an azeotropic point

If an inflection point occurs in the equilibrium curve of a mixture, as in the case of the system methanol-water, the number of separating stages is found as described in sections 4.7.1 and 4.7.2, but in determining the minimum reflux ratio the upper operating line may have to be drawn as a tangent to the equilibrium curve (Fig. 65). If the upper operating line $a-c_1$ were drawn as described previously from the point a through the point b_2, three points of intersection with the equilibrium curve would result, at b_1, b_2 and b_3. Then if the reflux ratio were increased by a small amount, an infinite number of separating stages would still be required even to reach a residue composition at about b_1. The true minimum reflux ratio is derived by drawing the tangent from a to the equilibrium curve and extending it to c, so that a slight increase in the reflux ratio leaves a clear path for the steps from a to b_4, with the operating line between the equilibrium curve and the 45° line. Because the operating line for minimum reflux may be determined by the distillate composition and the tangent from it to the equilibrium curve, and not by the feed composition, we then find that the minimum reflux ratio is independent of feed composition over a wide range. Thus Fig. 66 shows the dependence of v_{min} on the feed concentration x_Z for the system ethanol-water, with a constant distillate composition of 81.6 mol% (92.0% wt.) of ethanol; v_{min} remains constant at 1.3 between $x_Z = 7.5\%$ and 65.3 mol%.

If the equilibrium curve lies below the diagonal from the origin, and above it after the intersection, we have a mixture with a maximum boiling point, that is

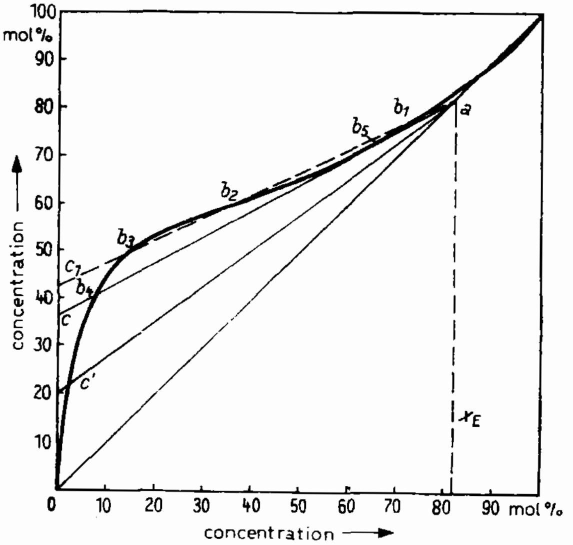


Fig. 65
Determination of minimum reflux ratio for an equilibrium curve with an inflection point

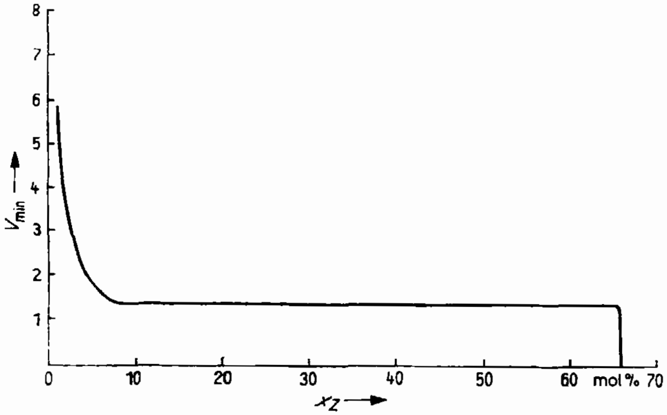


Fig. 66
Dependence of v_{min} on x_Z in the continuous distillation of an ethanol-water mixture at 760 torr with $x_E = 81.6$ mol%

to say, the boiling point of the azeotrope lies above those of the pure components. An example is the mixture nitric acid-water, for which the data are as follows (Fig. 29i):

$Kp._{760}$ nitric acid	86.0 °C
$Kp._{760}$ water	100.0 °C
$Kp._{760}$ azeotrope with 37.8 mol% of nitric acid	122.0 °C

A graphical method for the determination of the distillation conditions for this system is given by Flatt [145].

4.7.4 Determination of separating stages for flat equilibrium curves and for equilibrium curves close to operating line

If the mixture in question has a very flat equilibrium curve, as may occur when the boiling points are close together (an example being the system m-cresol-p-cresol, Fig. 67), it becomes very difficult to construct the separating stages accurately in the regions of low x_B and high x_E values. As a makeshift one can draw the equilibrium curve on a large scale, say 2 by 2 metres, and enlarge the regions from 0 to 10 and from 90 to 100 mol% still further, the portions of the curve then being practically straight lines (compare Fig. 63).

A similar situation occurs when a relatively high equilibrium curve has a shape such that the space between the curve and the upper operating line, where the steps are to be constructed, is narrow. This kind of curve denotes a close approach to azeotrope formation as in Fig. 68. Owing to the nearly asymptotic approach of the curve to the diagonal (and still more so to the operating line) the number of steps to be drawn is so that accuracy becomes poor.

For an infinite reflux ratio Stage and Schultze [146] describe a method involving the construction of a differential curve. The difference $y^* - x_B$ is plotted against x_B

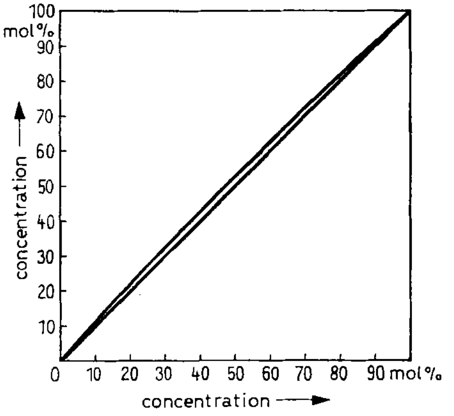


Fig. 67
Equilibrium curve for the mixture m-cresol-p-cresol at 30 torr

on as large a scale as possible. This gives us a differential curve, as shown in Fig. 69 for the system benzene-n-heptane. From this diagram a curve for separating stages *versus* concentration is constructed. Starting with a very low concentration of the still pot contents — say 0.16 mol% — we read off the enrichment $y^* - x_B$ from the differential curve to be 0.28. This value is added to 0.16 and we thus obtain the figure of 0.44 for the concentration of the liquid in the second stage. Against this value we again read off the enrichment (0.70), add it to 0.44 and so find the concentration in the next stage to be 1.14. This procedure is followed up to, say, 99.98 mol% and gives us the curve for separating stages against concentration (Fig. 70). The number of stages with infinite reflux ratio is now obtained by drawing lines vertically from the points x_B and x_E to the last-mentioned curve, reading off the corresponding numbers of

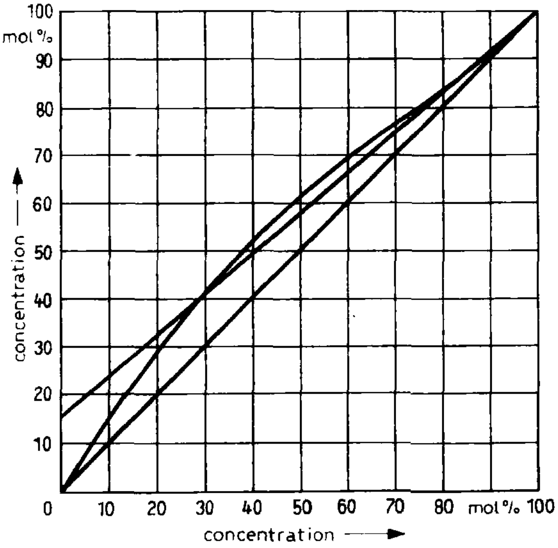


Fig. 68
Equilibrium curve for the system toluene-n-octane at 760 torr, having a close approach to azeotrope formation

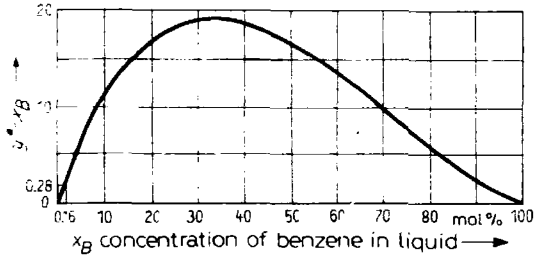


Fig. 69
Differential curve according to Stage and Schultze for the system benzene-n-heptane

separating stages and finding the difference between them. Fig. 70 shows that, for enriching a charge of 25 mol% benzene to 85 mol%, 11.2−6.6 = 4.6 separating stages are needed with an infinite reflux ratio.

Instead of x_B, other characteristic quantities may be plotted as abscissae, for instance the density of the refractive index, the figure for the charge and the distillate being entered and the difference of the corresponding ordinate values determined. Fig. 71 gives the curve for separating stages against refractive index for the test mixture n-heptane-methylcyclohexane [147].

For *finite reflux ratios*, Schäfer [148] evolved a method involving two nomograms and two diagrams.

The method is particularly suited to determining series of plate numbers. It makes use of the approximate hyperbolic relation between plate number n and reflux ratio v as employed by Fischer:

$$(n - n_{\min}) \times (v - v_{\min}) = (n - n_{\min}) \times (v - v_{\min}). \tag{95}$$

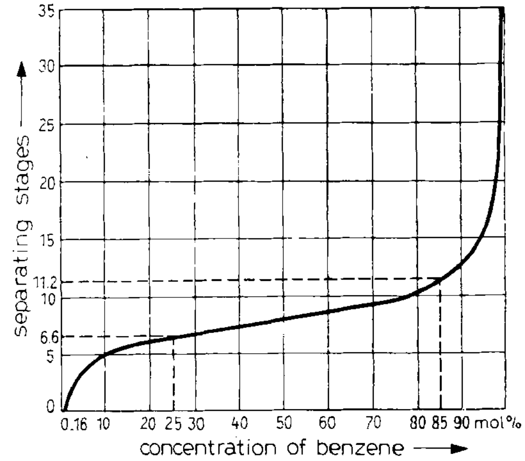


Fig. 70
Curve for separating stages against concentration after Stage and Schultze for the system benzene-n-heptane

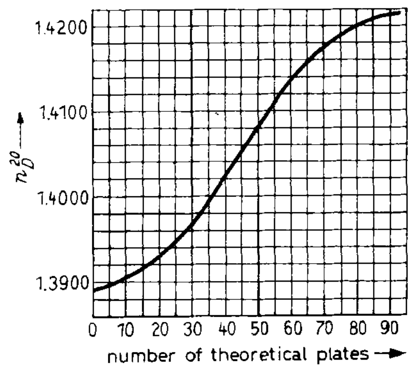


Fig. 71
Curve of separating stages against refractive index for the system n-heptane-methylcyclohexane

Fischer himself describes a method for which, unlike Schäfer's, one nomogram suffices [149]. Further graphical and semi-graphical methods are found in a compilation by Stage-Juilfs [71].

By the "method of the separating factor" according to Matz [150] plate numbers can be calculated for ideal mixtures with batch and continuous operation even if the x_E-values are in the range from 99 to 99.8%.

4.7.5 Methods for determining the plate number in batch distillation arithmetically

So far we have chiefly considered graphical and semi-graphical methods, as they are best suited for clarifying the idea of a separating stage. Numerous procedures have, however, also been developed for determining the conditions during distillation arithmetically.

The graphical methods have the advantage of being based on the equilibrium curve of the mixture, so that they are applicable to non-ideal systems. The methods based purely on calculation as a rule postulate an ideal system.

4.7.5.1 Determination of the plate number from difference in boiling point

In order to gain a rough impression of the relation between differences in boiling point and the required number of separating stages, the values for binary hydrocarbon mixtures at normal pressure, given by Hilberath [151], are quoted in Table 15.

A better indication is obtained if we consider the desired purity of the low-boiling component as well. From a diagram published by Bragg and Lewis [152] the minimum number of plates may be read off directly against the difference in boiling point of equimolar, ideal binary mixtures (Fig. 72).

For given differences in boiling point the number of plates needed can also be calculated by the following formula, which, however, does not consider the other con-

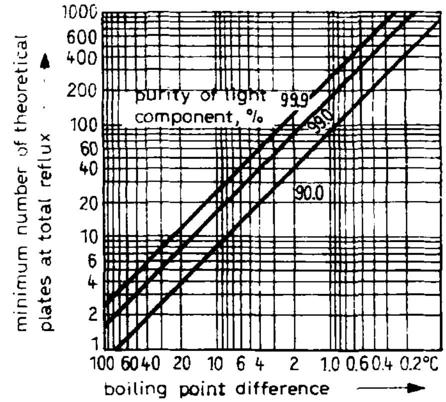


Fig. 72
Minimum plates versus boiling point difference and distillate purity (Bragg and Lewis)

ditions of distillation such as reflux ratio, pressure and hold-up:

$$n_{\text{th}} = \frac{T_2 + T_1}{K(T_2 - T_1)} \tag{96}$$

where T_1 and T_2 = boiling points of the low- and high-boiling components,
K = a constant. (By putting $K = 2.5$, 3 and 4 we obtain the maximum, optimum and minimum number of separating stages respectively.)
n_{th} = number of theoretical stages.

Table 15

$\Delta\ Kp._{760}$ °C	Number of separating stages required
1.5	100
3.0	55
5.0	30
7.0	20

With equations derived by Strangio and Treybal [152a] the distillation conditions (v and n_{th}) for multicomponent mixtures may also be estimated if constant α-values and gaseous or liquid feed are assumed.

4.7.5.2 Calculation of the plate number with the aid of the fractionating factor and the Rose formulae

The use of formula (96) is equivalent to the calculation of the number of stages for ideal mixtures from the relative volatility α and the fractionating factor Fr. The *fractionating factor* is a value found empirically by Cook as the result of numerous experimental distillations:

$$Fr = \alpha^{n_{\text{th}}} = \frac{x_{E1} \cdot x_{B2}}{x_{E2} \cdot x_{B1}} \tag{97}$$

in which x_{B1} and x_{B2} are the concentrations of low- and high-boiling components, respectively, in the liquid in the still pot;

x_{E1} and x_{E2} are the concentrations in the distillate of low- and high-boiling components, respectively;
n_{th} = the number of theoretical plates.

Fr has a value of 10.000 for a sharp separation, in which the low-boiling component present in the distillate amounts to 99 mol% and in the still pot to 1 mol%. For a normal separation, in which these figures are 90 mol% and 1 mol%, respectively, *Fr* works out at 1000.

$$Fr = \frac{99 \times 99}{1 \times 1} = 9801 \approx 10.000 \tag{98}$$

$$Fr = \frac{90 \times 99}{10 \times 1} = 891 \approx 1000. \tag{99}$$

From this we conclude that

$$\text{for a } \textit{sharp} \text{ separation } n_{\text{th}} = \frac{4.0}{\log \alpha} \text{ separating stages} \tag{100}$$

$$\text{for a } \textit{normal} \text{ separation } n_{\text{th}} = \frac{3.0}{\log \alpha} \text{ separating stages.} \tag{101}$$

Obviously the fractionating factor may also be calculated for other conditions, such as a distillate concentration of 95 mol % and a residue concentration of 1 mol %:

$$Fr = \frac{95 \times 99}{5 \times 1} = 1850 \tag{102}$$

$$\alpha^{n_{\text{th}}} = 1850 \tag{103}$$

$$n_{\text{th}} \log \alpha = \log 1850 \tag{104}$$

$$n_{\text{th}} = \frac{3.3}{\log \alpha} \text{ separating stages.} \tag{105}$$

The figures resulting from equations (100) and (101) have been listed in Table 16 and plotted in Fig. 73.

Rose [154] developed this method further. He assumed that in most separations a purity of 95 mol% may be regarded as sufficient for the first 40% of distillate and

Table 16

Number of separating stages from the empirical fractionating factor *Fr*

α	Difference in boiling points of components deg C	Required number of stages n_{th}	
		Normal separation, I (formula (101))	Sharp separation, II (formula (100))
3.0	30	5	8
2.0	20	9	13
1.5	10	17	22
1.3	7	25	35
1.25	6	30	42
1.20	5	38	50
1.15	4	50	65
1.12	3	70	80
1.07	2	100	150

that the mixture in question is an ideal system containing 50 mol% of each component. He further postulated that the hold-up is negligible and that the relationship $n = v$ can be taken as valid for a laboratory distillation. From the average vapour pressure ratio α he then derived the maximum, optimum and minimum number of stages required (Fig. 74).

$$n_{\max} = \frac{3.6}{\log \alpha} \tag{106}$$

$$n_{\mathrm{opt}} = \frac{2.85}{\log \alpha} \tag{107}$$

$$n_{\min} = \frac{2.3}{\log \alpha}. \tag{108}$$

These formulae give the following numerical values (Table 17), which have been plotted in Fig. 74.

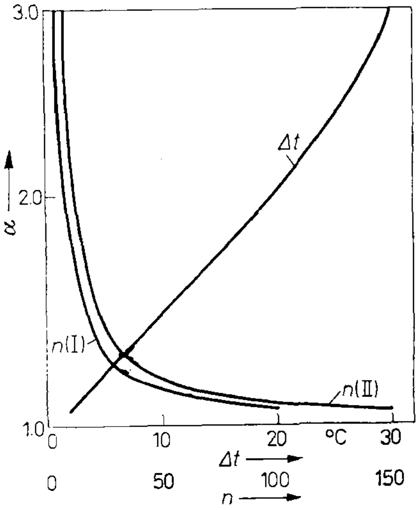


Fig. 73
Dependence of the value of α on the difference in boiling points of the components and dependence of the required plate number on the fractionating factor *Fr*

n(I) by formula (101)
$Fr = 1000$
n(II) by formula (100)
$Fr = 10000$

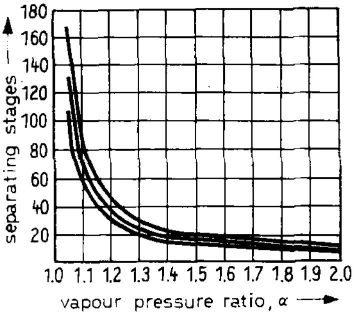


Fig. 74
Separating stages required for the standard distillation of Rose

Table 17

Number of separating stages according to Rose

α	$\log \alpha$	$n_{\min}$	n_{opt}	$n_{\max}$
2.0	0.3010	8	9	12
1.5	0.1761	13	16	20
1.25	0.0696	24	29	37
1.10	0.0414	56	69	87
1.05	0.0212	108	134	170
1.03	0.0140		203	
1.02	0.0085		335	

As regards the reflux ratio, we have previously seen that a low value of *n* can be compensated by an increase in *v*, and that higher values of *n* allow lower values of *v*. It is, however, important to remain within certain limits, since excessively low values of *n* cannot be offset by increasing *v* and very high values of *n* do not allow a proportional reduction in *v*. Rose expressed this fact by adopting the following standard values for the reflux ratio (see Fig. 75).

$$v_{\max} = \frac{3}{2} n_{\min} \tag{109}$$

$$v_{\text{opt}} = n_{\text{opt}} \tag{110}$$

$$v_{\min} = \frac{2}{3} n_{\max} \, . \tag{111}$$

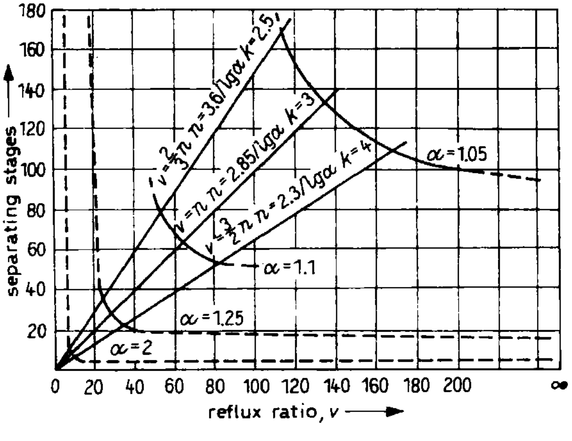


Fig. 75
Dependence of the required plate number on the reflux ratio for Rose's standard distillation

4.7.5.3 Calculation of the minimum plate number by the Fenske equation for ideal mixtures and $v = \infty$

The relative volatility of an ideal mixture can be expressed by:

$$\alpha = \frac{y_1^*/y_2^*}{x_1/x_2} \tag{112}$$

in which y_1^* and y_2^* = concentrations of the low- and high-boiling components, respectively, in the vapour;
x_1 and x_2 = concentrations of the low- and high-boiling components, respectively, in the equilibrium liquid.

If the elementary separating effect of a theoretical stage takes place in each of n_{th} theoretical stages at total reflux, we find

$$\alpha^{n_{\text{th}}} = \frac{x_E/(1 - x_E)}{x_B/(1 - x_B)}. \tag{113}$$

By taking logarithms of both sides of this formula, we obtain the Fenske equation [155] for determining the minimum number of separating stages (see section 5.1.4.2) in a batch distillation of an ideal mixture:

$$n_{\min} = \frac{\log \left\{ \dfrac{x_E(1 - x_B)}{x_B(1 - x_E)} \right\}}{\log \alpha} - 1 \tag{114}$$

or

$$n_{\min} = \frac{1}{\delta} \left[\ln \frac{x_E}{1 - x_E} - \ln \frac{x_B}{1 - x_B} \right]$$

(see chap. 5.1.4), where $\delta = \alpha - 1$.

This formula has the advantage with respect to those of Rose that it can be used with arbitrary values of x_B and x_E , though only with $v = \infty$. The Fenske formula has been converted by Melpolder and Headington [90] into a nomogram, by means of which the data required can be found quickly and easily (Fig. 76). In the nomogram the following example has been shown:

$$x_B = 15\ \text{mol\%},\ x_E = 90\ \text{mol\%},\ \alpha = 1.2;\ \text{result: } n_{\text{th}} = 22.$$

On the upper horizontal scale for x_B one first finds the point for 15 mol%, whereupon one proceeds vertically downwards to the x_E curve for 90 mol%. From this point a horizontal line leads to the slanting straight line for $\alpha = 1.2$. One then again proceeds vertically downwards to the lower horizontal scale and finds $n_{\text{th}} = 22$.

Richter [156] rewrote the Fenske equation, setting

$$\log \frac{x_E(100 - x_B)}{x_B(100 - x_E)} = K, \tag{115}$$

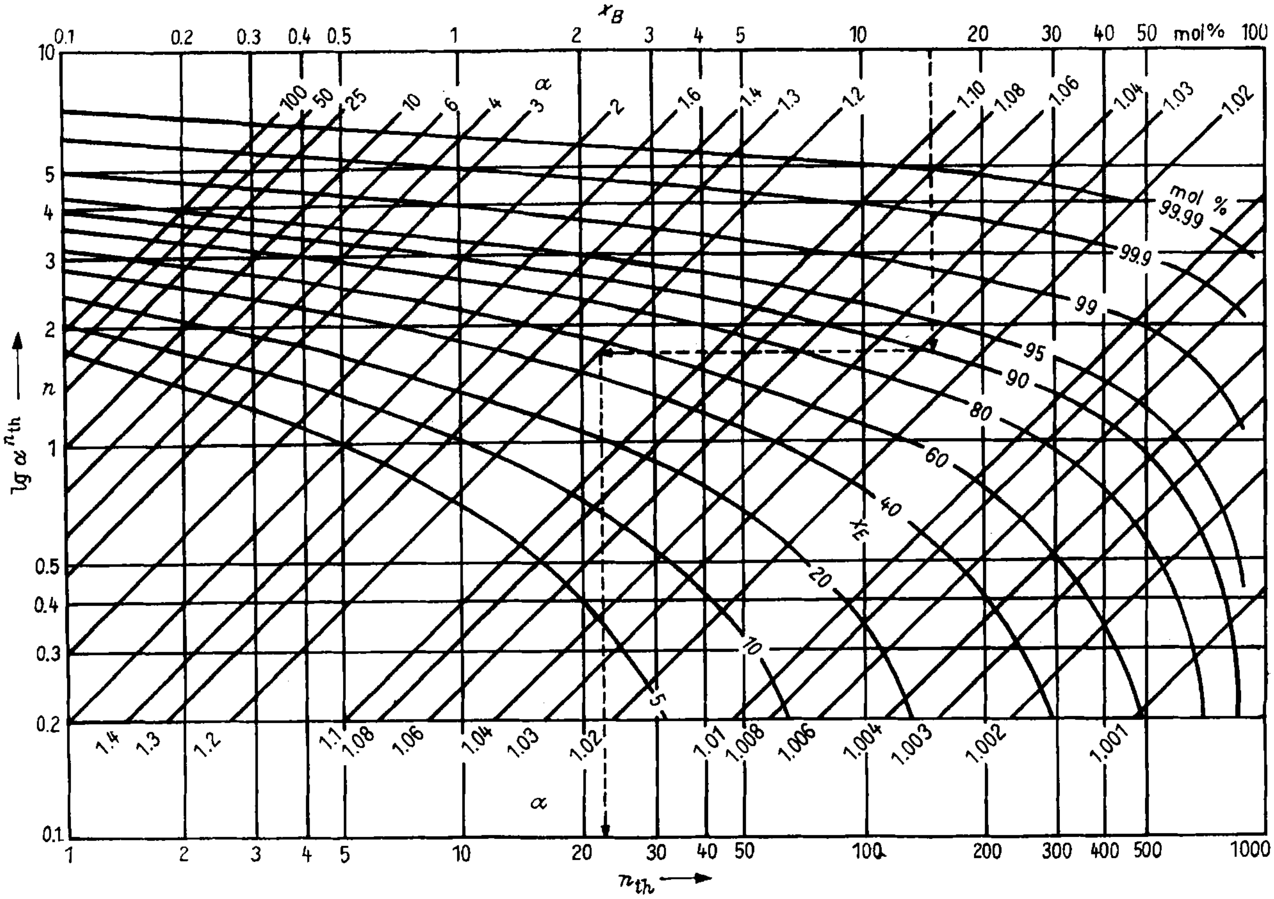


Fig. 76
Nomogram for the determination of minimum plate numbers for ideal mixtures and $v = \infty$ (Melpolder and Headington)

which yielded

$$n_{\mathrm{th}} = \frac{\mathrm{K}}{\log \alpha} - 1 \tag{116}$$

or

$$K = (n_{\mathrm{th}} + 1) \times \log \alpha. \tag{117}$$

The formulae mentioned in sections 4.7.5.2 and 4.7.5.3 can all be reduced to the fundamental type:

$$n_{\mathrm{th}} = \frac{c}{\log \alpha}, \tag{118}$$

in which the value of c depends on the conditions of distillation. The use of this formula is limited to ideal mixtures.

The *minimum reflux ratio* v_{min} required for an ideal mixture may be calculated by means of the following formula:

$$v_{\mathrm{min}} = \frac{1}{\alpha - 1} \cdot \left(\frac{x_{E1}}{x_{B1}} - \alpha \frac{x_{E2}}{x_{B2}} \right) \tag{119}$$

in which v_{min} = minimum reflux ratio,

x_{E1} and x_{E2} = mole fraction of the low- and high-boiling components in the distillate,
x_{B1} and x_{B2} = mole fraction of the low- and high-boiling components in the residue.

A relevant nomogram after Smoker is included in the book of Kharabanda [238].

4.7.5.4 Other methods and comparison

Of course, the above presentation of arithmetic methods is not exhaustive. Pohl [157] published numerical methods for ideal mixtures and batch as well as continuous operation at infinite and finite reflux ratios which make possible a rapid and relatively simple determination of the plate number. The contributions of Stage and Juilfs [71] should also be mentioned in which further accurate and approximate methods are summarized. The same applies to the book of Rose et al. [153]. Zuiderweg [158] reports a procedure which considers the operating hold-up (see chap. 4.10.5) and the magnitude of the transition fraction in batch distillation.

Finally, the calculating procedures described in section 4.7.5 have been summarized below and compared with the graphical McCabe-Thiele method for a particular example of a separation (see the summary).

It can be seen that the truly comparable methods, that is to say II and IV, I and VII, as well as VI with $v = \infty$, agree well.

Methods II and IV merely give a rough indication of the required number of theoretical stages. The maximum value of n_{th} would be chosen, the reflux ratio being increased with rising top temperature.

Summary of methods of calculation for batch distillation and comparison with the graphical McCabe-Thiele procedure (x_B = 40 mol%; x_E = 98 mol%; α = 2.4; Δ *Kp.* ≈ 30°C)

Method		v	n_{th}		Remarks	
I.	McCabe-Thiele graphical method (Table 12)	1.85	10.0	Initial state	Final state with x_E = 98 mol% and n = 10	
		3.00	7.0			
		5.00	6.0			
		10.00	5.5		x_B	v
		20.00	5.0			
		50.00	5.0		80 mol%	0.65
		∞	4.5		60 mol%	1.09
					40 mol%	1.85
					20 mol%	3.90
					10 mol%	8.80
					5 mol%	25.00
II.	Diagram Fig. 72		5.0	(x_E = 99%)	x_B = 50 mol%	
			8.0	(x_E = 99.9%)		
III.	Formula (96)		9.7	(maximum)	Purity not considered; x_B not considered	
			8.0	(optimum)		
			6.0	(minimum)		
IV.	Formulae (100) and (101)		10.0	(x_E = 99 mol%)	Residue = 1 mol%	
			7.5	(x_E = 90 mol%)		
V.	Formula (106)	8.8	9.0		x_B = 50 mol% First 40% of distillate > 95 mol%	
	Formula (107)	7.1	7.1			
	Formula (108)	6.0	5.8			
VI.	Formula (114)	∞	3.7			
VII.	Method of Zuiderweg [158], section 4.10.5	26	10.0		Corresponds to Table 14 with final condition x_B = 5 mol%	

4.8 Theory of packed columns

4.8.1 Process of separation in a packed column

By considering a plate in a column we have been led to the concept of the theoretical separating stage. What are the conditions in a packed column, which contains a regular or irregular aggregate of packing for promoting the exchange between vapour and liquid? As before, there is a countercurrent flow of the two phases between the still pot and the condenser, so that, on the one hand, there exists a tendency for equilibrium to become established by diffusion in a horizontal sense (whereby an enrichment of low-boiling fractions in the vapour takes place), and on the other hand the flow in a vertical sense tends to disturb this equilibrium. The different paths travelled by the vapour and the liquid in a packed column and in a plate column are shown diagrammatically in Fig. 77. In chap. 4.2 it was pointed out that random packing strongly influences the aerodynamic and hydrodynamic properties of a column.

In addition, the separating behaviour of a packed column cannot be completely described from a physical point of view by only one parameter, such as the HETP or the HTU value. Sizmann [159] has shown that material transfer in a packed column is the more intense the easier it is for the components to get from inside one phase to the liquid-vapour interface and from there to the interior of the other phase. Hence, two resistances to transfer, W_D and W_F, for material transport in the vapour and liquid phases, respectively, have always to be considered. The magnitudes of these resistances depend on the mean path travelled in the respective phase, the frequency of mixing at certain points along the flow path, the formation of turbulence and other factors which have been discussed in chap. 4.2. The distribution of the resistances to mass transfer for 7 different packings as determined by Sizmann is given in Table 18. It is seen that the proportion of the resistance in the vapour phase may vary from 9 to 96% of the total resistance.

By a proper choice of the packing an attempt is made to provide the optimum surface for phase contact. Channelling may be restricted by ensuring that the ratio between the diameters of the column and the packing units is more than 10:1, by the use of aerodynamically efficient packing units (such as those of saddle shape) and by repeatedly sectioning the column, so as to recombine the reflux frequently and distribute it again over the column contents. The influence of channelling on column efficiency is demonstrated by Fig. 78, which refers to measurements carried

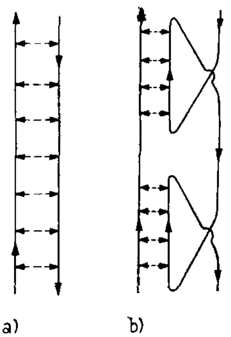


Fig. 77
Exchange of material and heat
a) a packed column
b) a plate column with 2 actual trays (↑↓ paths of vapour and liquid;
--- direction of exchange)

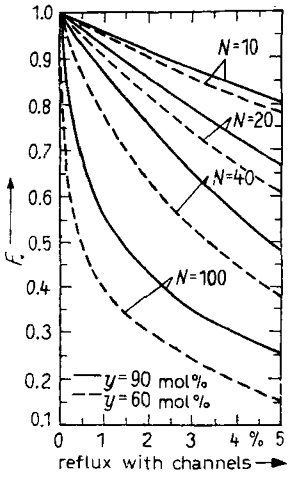


Fig. 78
Effect of channelling on column efficiency
F = Deterioration factor for number of stages, N = Number of theoretical stages, y = Liquid composition in head

Table 18

Packing data and distribution of resistance to material exchange according to Sizman [159]

Chlorobenzene-ethylbenzene was used as test mixture in a column of 1 m height and 30 mm diameter. Lower concentration of mixture, about 20 mol% of chlorobenzene; separation factor, 1.11; distillation temperature, about 110°C. Turbulent vapour flow

Packing type	Size (mm)	Material	Free column volume/ packing volume1)	Load (cm^3/ cm^2 × h)	HETP (cm)	W_D/W_F	$W_D/(W_D+W_F)$	Flooded
Raschig rings	6 × 6	glass	0.72	170	13.4	24	0.96	yes
	6 × 6	glass	0.72	170	13.8	3	0.75	no
Raschig rings	4 × 4	glass	0.70	170	10.0	0.75	0.43	yes
	4 × 4	glass	0.70	130	11.4	0.80	0.45	no
	4 × 4	glass	0.70	280	10.0	0.5	0.33	yes
Berl saddles	4 × 4	ceramic	0.54	170	6.5	1.2	0.55	yes
	4 × 4	ceramic	0.54	140	7.5	0.5	0.33	no
	4 × 4	ceramic	0.54	125	6.1	1.1	0.52	yes
Beads	4 ⌀	glass, matt	0.38	170	7.1	0.20	0.17	yes
Wire-gauze rings with one turn	5 × 5	V4A steel	0.90	210	3.2	17	0.95	yes
	5 × 5	V4A steel	0.90	185	3.3	7	0.87	yes
Wire-gauze rings with one turn	4 × 4	V4A steel	0.88	195	2.8	0.1	0.09	no
Wire-gauze rings with two turns	4 × 4	V4A steel	0.66	170	3.3	0.05	0.05	no

1) measured in a tube of 30 mm diameter

out with the mixture n-heptane-methylcyclohexane. It will be seen that a small degree of channelling has no important effect in columns with 10 to 20 theoretical stages, but is of great influence in columns with 100 stages. In the case of mixtures with a value of α above 1.07 the influence of channelling is a minor one, but when α is below 1.07 it causes the separating effect to deteriorate appreciably [160].

In spite of a frequent redistribution of the liquid it may occur that the packing is not uniformly wetted; the film itself may also have different forms. Stuke [161] has investigated this subject in detail, and has examined the influence of the nature of the packing, the properties of the liquid, the column load and the distillation pressure (with its associated temperature) on irregularities of film formation. His conclusions can be summarized as follows (see also chap. 4.2).

1. Channelling on the packing will occur principally at low loads; a large amount of liquid is distributed better on the surface of the packing.

2. The higher the density of the liquid and the lower its viscosity, the sooner will channelling take place by flow under gravity, even if the packing is fully wetted.
3. The lower the surface tension, the better the wetting of a packing unit at low loads.
4. The high separating effect to be expected with small packing can be realized only if the wetting is extremely uniform. At higher loads, irregularities in the film have a progressively unfavourable influence.
5. An unambiguous influence of the distillation pressure has not as yet been established. Some investigators have reported an optimum pressure in countercurrent distillation, others have stated that no such influence exists.

Another point of interest is the dynamic behaviour of packed columns. Heise, Hiller and Wagner [162] investigated the response of a packed column to marked disturbances of the liquid-vapour ratio in the countercurrent distillation of the ternary, almost ideal mixture ethyl acetate-benzene-trichloroethylene (see chap. 4.2, 4.15).

What has been said so far, however, by no means mentions all the complicated processes taking place in a packed column. Krell (see chap. 4.2) had previously pointed out the effects of surface energies and had summarized the factors operative in countercurrent distillation with packed columns as follows.

Factors in countercurrent distillation

1. *Properties of the mixture to be distilled*

   Average relative volatility
   Phase equilibrium
   Molecular proportions
   Solubility of the liquid components
   Density of the vapour and reflux
   Viscosity of the vapour and reflux
   Surface tension of the vapour and reflux
   Specific heat of the components
   Heat of evaporation of the components
   Wetting properties

2. *Characteristics of the column*

   Diameter
   Length of the packed portion
   Method of packing

3. *Characteristics of the packing*

   Height, diameter and wall thickness
   Nature of surface
   Solid volume
   Material, shape

4. *Factors connected with the method of operation*
   - Admission and distribution of the reflux
   - Hold-up or ratio of hold-up/charge
   - Operating pressure
   - Pressure differential
   - Surface velocity

It is apparent from this summary that countercurrent distillation is such a complex process that very great difficulties are often involved in determining the influence of a certain factor on the separation by experiment. Owing to this fact, contradictory statements are frequently encountered in the literature.

4.8.2 Determination of the transfer unit, TU

A quantitative description of the processes taking place in a packed column is therefore possible only along semi-empirical, comparative lines. Chilton and Colburn [163] introduced the concept of the transfer unit TU for packed columns, in which they took account of the fact that in a packed column, as opposed to a plate column, the exchange of material and heat occurs in infinitely small elementary stages. The factor causing the exchange of heat is the difference in temperature, and the factor producing transfer of material is the gradient in partial pressure and concentration of the substances. The dimensionless magnitude "number of transfer units" is derived from the concentration gradient represented by the space between the equilibrium curve and the operating line [73].

Let us consider an enlarged section of the McCabe-Thiele diagram for determining the number of separating stages (Fig. 79). The upper line is the equilibrium curve, the lower one is the operating line. In a plate column the liquid present on an arbitrary plate, having concentration y_1, reaches thermodynamic equilibrium with the ascending vapour, concentration y_1^*, and falls from the plate in countercurrent to a vapour

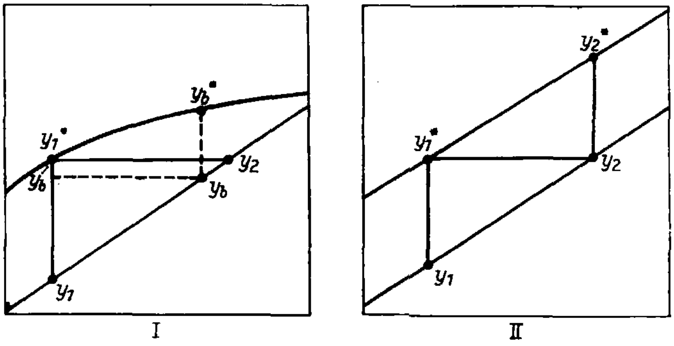


Fig. 79
Relation between number of theoretical stages n_{th} and transfer units TU
(— — — TU; ——— n_{th})
I Operating line steeper than equilibrium curve
II Operating line parallel to equilibrium curve

of composition, determined from the operating line, of y_1. The vapour y_1^* rises in countercurrent to the liquid of composition y_2. Between the plates, that is, between y_1 and y_2, no interchange takes place. Matters are different in a packed column. The rate at which material is transferred from one phase to the other is proportional to the extent to which the concentration of vapour, y^*, in contact with liquid of concentration y_1 differs from that of the equilibrium vapour, y^*, *i.e.* is proportional to $y^* - y$. Then over any arbitrary height of the column the rate of transfer will be proportional to the mean value of $y^* - y$ over that height, $(y^* - y)_m$, and a *transfer unit* is so defined that the step height is this quantity $(y^* - y)_m$, in place of the step $y_1^* - y_1$ used in theoretical plate calculations [71]. This mean quantity is shown as $y_b' - y_1$ in Fig. 79I. In general $(y^* - y)_m$ is equal to $y_1^* - y_1$ only if the equilibrium curve is parallel to the operating line (Fig. 79II); if the value of $\Delta y = y^* - y$ increases as the vapour moves up the column, the number of transfer units is smaller than the number of theoretical plates; if Δy decreases the reverse is true (Fig. 79I). Δy usually increases as vapour rises up the column below the feed in a continuous column, and decreases above the feed, and therefore for an ideal mixture at total reflux, with a distillation range equally divided about the 0.5 mole fraction, the number of theoretical plates will equal the number of transfer units; this is approximately true in the conditions of column testing. With highly non-ideal mixtures, and systems with high relative volatility at low reflux ratio the difference between the numbers of transfer units and theoretical separating stages may be large. Table 19 shows some comparisons where the difference becomes appreciable [164].

Table 19

Comparison between the theoretical number of separating stages n_{th} and the transfer unit TU

α	y_1 mol% (corresponding to x_B)	y_2 mol% (corresponding to x_E)	TU by formula (126)	n_{th} by formula (114)
1.08	10	99	119.5	119.5
1.08	50	99	61.0	59.8
2.50	10	99	10.7	10.0
2.50	50	99	6.9	5.0

On the assumption that the resistance to transfer is associated with the vapour phase only the number of transfer units is defined by

$$\mathrm{TU} = \int_{y_1}^{y_2} \frac{\mathrm{d}y}{y^* - y} \tag{120}$$

as compared with

$$n_{th} = \int_{x_B}^{x_E} \frac{\mathrm{d}x}{y^* - x}. \tag{121}$$

Corresponding to the height of a separating stage,

$$\frac{\text{column length}}{n_{\text{th}}}\ (\text{cm}) = \text{height equivalent to a theoretical plate, (HETP)}, \tag{122}$$

we can formulate the effective unit of height as

$$\frac{\text{column length}}{\text{TU}}\ (\text{cm}) = \text{height of a transfer unit (HTU)}. \tag{123}$$

The height of a transfer unit is a measure of the resistance to mass transfer. It varies but little with variation in vapour velocity [165].

Matz [73], taking account of the fact that the processes of material and heat exchange producing thermodynamic equilibrium do not proceed infinitely slowly, but in a measurable time at a finite speed, replaced the integral (120) by the expression

$$(aH) \cdot (K/w). \tag{124}$$

In this expression

(aH) = a characteristic number for the interfacial area, with
a = the interfacial area relative to the volume (m^2/m^3),
H = the column height;
(K/w) = a characteristic number for the velocity, with
K = the velocity of material transfer (m/sec) and
w = the vapour velocity (m/sec).

Starting from this expression, Matz developed equations with which the number of transfer units TU may easily be calculated for an *infinite reflux ratio:*

$$\text{TU} = \frac{1}{m-1} \ln \frac{1-y_1}{1-y_2} + \frac{m}{m-1} \ln \frac{y_2}{y_1}. \tag{125}$$

in which m = the tangent of the angle between a section of the equilibrium curve and the abscissa of the co-ordinate system, it being assumed that this section may be regarded with sufficient accuracy as a straight line.

On page 230 of Matz's book [73] detailed examples of the calculation are given both for $v = \infty$ and for a finite reflux ratio greater than the minimum value.

In the case of ideal mixtures and an infinite reflux ratio, eq. (120) can be subjected to a closed integration, which gives

$$\text{TU} = \frac{2.303}{\alpha - 1} \log \frac{x_E(1-x_B)}{x_B(1-x_E)} + 2.303 \log \frac{1-x_B}{1-x_E}. \tag{126}$$

The calculation becomes much more complex if the reflux ratio is finite [71].

A rapid graphical method, related to the McCabe-Thiele procedure, has been described by Chilton and Colburn [163]. It is applicable to all mixtures for which the equilibrium curve is known. The operating line should, however, not lie too close to the equilibrium curve in the range considered. The operating line is constructed in the usual way in the equilibrium diagram, and through the point x_B a vertical line is drawn, intersecting the operating line at y_1 and the equilibrium curve at $y_1{}^*$. This has been illustrated diagrammatically in Fig. 79 on a section of the equilibrium diagram; Fig. 79I deals with the case in which the equilibrium curve is not so steep as the operating line, Fig. 79II with the case in which the two lines are parallel.

According to Fig. 79I a transfer unit gives an enrichment in the vapour corresponding to $y_b' - y_1$, the latter being the mean of $y_b{}^* - y_b$ and $y_1{}^* - y_1$. A theoretical separating stage gives an enrichment corresponding to $y_1{}^* - y_1$. The transfer units may be drawn as steps in the McCabe-Thiele diagram if care is taken that the magnitude of the enrichment, $y_b' - y_1$, is equal to the average of $y_1{}^* - y_1$ and $y_b{}^* - y_b$. Point y_b on the operating line must hence be so chosen that

$$y_b' - y_1 = \frac{1}{2}\left[(y_1{}^* - y_1) + (y_b{}^* - y_b)\right]. \tag{127}$$

This involves a certain amount of trial and error, but does not require much time.

If the equilibrium curve and the operating line were both straight (but not parallel) lines, the method would be exact if the logarithmic mean of $y_1{}^* - y_1$ and $y_b{}^* - y_b$ were employed. In most problems, however, the inexactitude caused by a curvature of one or both of the lines and by the use of the arithmetic instead of the logarithmic mean will be of little significance.

We have chosen the simplest graphical method to illustrate the relation between theoretical plate number and number of transfer units. Further exact and approximate methods are mentioned in the papers of Stage-Juilfs [71]. In a very interesting paper Arkenbout and Smit [166] present the mathematical foundation of n_{th} and TU and go on to suggest that, according to their results, in several cases HETP is more suited to column length calculations than HTU.

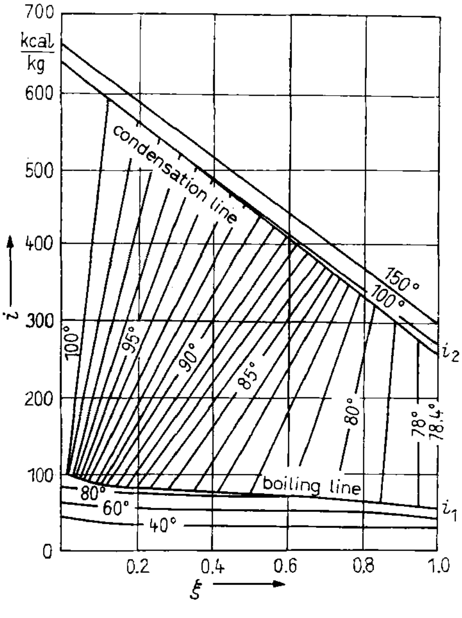


Fig. 80
Heat content versus concentration for the system ethanol-water at 1.033 atm

Two more methods should be noticed here, which are independent of the column type and hence may be used for plate columns as well as for packed columns and columns provided with other elements. Merkel's [167] method is based on the heat content-concentration diagram representing the countercurrent process, from which the changes of the liquid and vapour compositions, the amounts of liquid and vapour and the amounts of heat to be supplied and removed are seen (Fig. 80). Unfortunately, only few such diagrams are available at present so that the method has been applied to a small number of mixtures only. Therefore we shall only give the pertaining references [73, 75, 103]. The various ways of determining the theoretical plate number for the separation of binary mixtures have been unified by Bitter [261]. He gives equations for the operating lines. These provide the basis also for the graphical solution by means of the enthalpy-concentration diagram.

4.8.3 Intensity of countercurrent exchange; time required

The hold-up is an essential factor in a countercurrent distillation and has an important influence on the time required for carrying it out (see chap. 4.10.5). Whilst the theoretical plate number and the reflux ratio increase in proportion to $1/\log \alpha$, the time expended increases as the square of $1/\log \alpha$. It is hence the time consumed that best characterizes the difficulty of a separation. If we calculate the quotient

$$I = \frac{\text{theoretical plate number} \times \text{amount of reflux}}{\text{operating hold-up of the column}} \tag{128}$$

for two columns I and II from the operating data, the times t_{I} and t_{II} required for effecting the same separation are related as $I_{\mathrm{I}}:I_{\mathrm{II}}$, as long as the distillation conditions are otherwise identical. The characteristic value I is termed the *intensity* of countercurrent exchange [68]:

$$I = \frac{n_{\mathrm{th}} R}{H} \ \mathrm{sec}^{-1}. \tag{129}$$

Its physical dimension is a reciprocal time, which is that of a frequency or — if the distillation is regarded from the aspect of labour economy — that of an investment return. I is independent of the scale and can be formulated for a volume element of arbitrary size in a column, having an arbitrary height and diameter.

In the total time required we must include the period of equilibration t_{A} during which the lowest-boiling component in the vapour is concentrating at the column head and distillate should not be taken off. According to von Weber [170] this time t_{A} can be calculated by the formula

$$t_{\mathrm{A}} \simeq \frac{(n_{\mathrm{th}} + 1)^2}{2I}. \tag{130}$$

The time for running-in is therefore roughly proportional to the square of the number of theoretical plates or to the column length [152], [169]. The equilibration time will be discussed more fully in connection with the separation of stable isotopes (section

5.1.4) as it requires special attention when the number of theoretical separating stages exceeds 100.

Von Weber [170], taking as basis Kuhn's model of a countercurrent system [3] — which consists of two vertical, parallel, plane surfaces — calculated intensity values for the test mixture n-heptane-methylcyclohexane, starting with the maximum number of separating stages (3.54 per cm) and the optimum vapour velocity (0.1525 cm/sec). The figures so obtained are collected in Table 20.

Table 20

Intensity values for the test mixture n-heptane-methylcyclohexane in Kuhn's model of a countercurrent system, as a function of the number of separating stages and the vapour velocity

w = vapour velocity (cm/sec)	0.1525	0.305	0.4575	0.610	1.525	7.62
n_{th} = number of theoretical stages per cm	3.54	2.83	2.12	1.66	0.70	0.14
I = intensity value (10^3/sec)	260	367	381	375	322	217

Table 21

Distillation conditions of columns packed with gauze discs at an optimum load of 2/3 times the maximum load

Internal diameter mm	R Amount of reflux g/sec	n_{th} Number of theoretical stages cm^{-1}	H Operating hold-up g/cm	$I \cdot 10^3$ Intensity sec^{-1}
17.0	0.139	0.460	0.239	268
25.4	0.333	0.370	0.228	537
50.8	1.530	0.144	0.328	670

It will be seen from Table 20 that the maximum number of theoretical stages, 3.54 per cm, does not correspond to the optimum intensity, which is 381 with a stage number of 2.12 per cm and a vapour velocity of 0.4575 cm/sec. Further it appears that the intensity falls again after its maximum of 381, but much more slowly than one would expect from the greatly diminished number of separating stages. If a high intensity is the object it does not therefore pay to work with very low vapour velocities. At high vapour velocities the flow of vapour becomes turbulent, a factor having a favourable effect, similar to that of an increase in the diffusion coefficient. If the throughput is raised above the optimum value, the amount of reflux will increase to such an extent that its return will be obstructed by the ascending vapour; the operating hold-up H then increases more than twofold and the intensity is consequently lowered.

If, following von Weber's [170] experiments, we compare the separating effect of columns of various diameters packed with gauze discs, the columns all being loaded to 2/3 of their maximum throughput, we find the figures given in Table 21.

If these figures are converted to those for a constant number of theoretical stages and a constant ratio of the operating hold-up H to the charge, the following values are obtained (Table 22).

The last and largest column operates the most intensively, though all three distil at about the same rate per unit cross-sectional area.

In order to demonstrate the order of magnitude of the intensity, three more figures, determined by von Weber [170], will be quoted (Table 23).

The intensity is consequently a characteristic that is easily calculated and can be employed for comparing the most diverse types of columns; it is of value because it is a factor compounded of several parameters.

A similar conclusion was reached by Kolling [171], who compared various forms of packing as regards efficiency and defined the separating power as the amount of a certain purity collected in unit time. Fig. 81 shows the relationship between the

Table 22

Distillation conditions for a separation with a constant number of theoretical stages and a constant ratio of H to the charge

Charge kg	Column diameter mm	Length of column m	Duration of the distillation h
1.0	17.0	1.0	100
1.18	25.4	1.24	49
4.40	50.8	3.20	40

Table 23

Maximum intensities of various columns

Type of column	Max. intensity at 2/3 of the max. load
Column packed with glass helices, diam. 0.3 cm	165×10^{-3}
Column packed with Raschig rings, 2.4 × 2.4 mm, matt	370×10^{-3}
Bruun plate column	140×10^{-3}

Table 24

Distillation conditions for a distillate with 90 mol% of n-heptane

Reflux ratio v	Number of theoretical stages per metre n_{th}	Column load ml/cm² · h	Distillate take-off rate ml/h
25:1	61	50	14
50:1	36	230	30

degree of purity, the number of theoretical stages and the reflux ratio for a mixture of 50 mol% of n-heptane and 50 mol% of methylcyclohexane. Thus to obtain a distillate containing, say, 90 mol% of n-heptane, either of the following conditions may be chosen (Table 24).

One can therefore take off double the amount of distillate of the same purity by increasing the load by a factor of 4.6 and doubling the reflux ratio.

Collecting the distillate at a constant rate, the following values (as shown in Fig. 82) are found (Table 25).

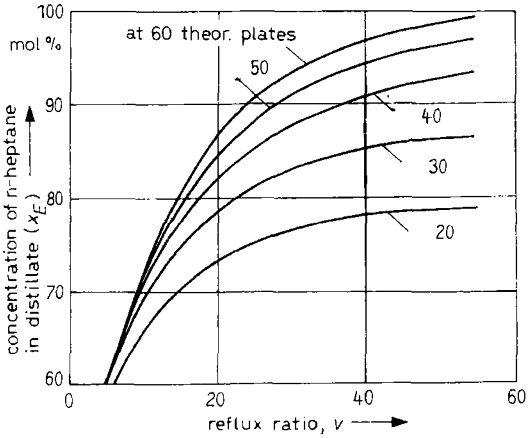


Fig. 81
Dependence of the purity of the distillate on the number of theoretical stages and the reflux ratio

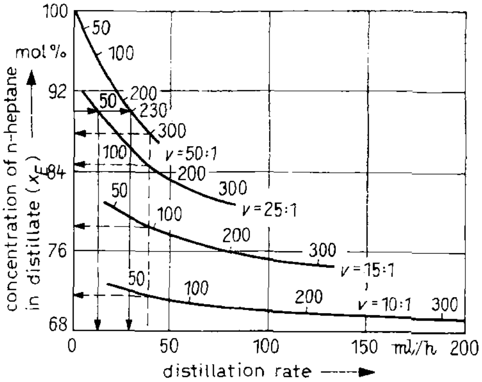


Fig. 82
Dependence of the degree of purity of the distillate (with various reflux ratios v) on the rate of distillate removal

x_B = 50 mol% n-heptane, 50 mol% methylcyclohexane; figures against the curves are the load in ml/cm^2 · h

Table 25
Distillation conditions for a constant rate of distillate take-off (40 ml/h)

Reflux ratio v	Column load ml/cm² · h	Concentration of distillate mol%	Distillate take-off rate ml/h
10:1	70	71.5	40
15:1	100	78.5	40
25:1	160	84.5	40
50:1	300	88.0	40

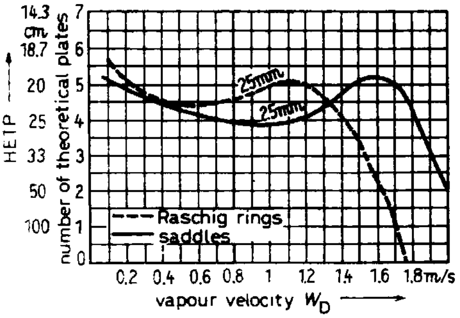


Fig. 83
Dependence of the HETP of 25 mm Raschig rings and saddle packing on the vapour velocity

The view, often held in the past, that the vapour velocity (and consequently the load on the column) should be kept as low as possible in order to obtain the greatest separating effect must therefore be revised, as already shown by the intensity figures. The higher the column load, the better are the results obtained at a particular rate of distillate take-off; in this connection it may be remembered that large quantities of liquid are, relatively speaking, distributed better over the packing, so that the wetting becomes more complete. This statement is, of course, only true up to a certain limit, above which the separating efficiency again drops. The relationship is clearly seen if the HETP of a packed column is plotted as a function of the vapour velocity [103]. In the case of 25 mm (1 inch) Raschig rings, for instance, the same HETP is found with loads of 0.2 and 1.0 m/sec (see Fig. 83), *i.e.* under conditions corresponding to a throughput ratio of 1:5. 25 mm saddle packing gives values of the HETP of 19 cm at 0.08 and 1.6 m/sec. As can be seen from the curves it is not advisable to work with vapour velocities between these figures, as the separating effect will then be lower.

4.9 Determination of the number of plates and transfer units in the batch and continuous separation of multicomponent mixtures

The term *multicomponent mixture* will be used to denote liquid mixtures containing more than two components. We shall further make a distinction between mixtures comprising a few definite constituents and complex mixtures containing a very large number of components, whose boiling points may lie very close together. Examples of the latter type are crude mineral oils and gasolines; in general these mixtures are characterized only by their distillation curves. This is determined, according to circumstances, either with an Engler apparatus (see section 7.2) or with an efficient column capable of yielding narrow fractions.

If the mixture is a ternary one, the conditions of distillation may be determined with the aid of a graph on triangular coordinates [72—74, 78]. The minimum reflux ratio in the continuous distillation of ternary and quaternary ideal and azeotropic mixtures can be calculated with a method evolved by Kohrt [172].

Hausen succeeded in solving the differential equation for ideal ternary mixtures [173] and van Wijk and Thijssen [174] developed a graphical procedure based on the approximation of considering multicomponent mixtures as binary systems. This procedure had already been suggested by Lvov [175], in whose fundamental study the process of the countercurrent distillation of an arbitrary multicomponent mixture is regarded as consisting of the sum of numerous separations of binary mixtures proceeding in parallel. The problem then reduces to that of finding the binary mixture containing the "key components" which are the most difficult to separate (*i.e.* having the lowest value of α) and of basing the calculation on the equilibrium curve for this mixture.

In the usual practice of laboratory distillation the "key component method" is the most suitable, particularly as the approximations involved may be checked by relatively simple trial distillations.

Mostafa [175a] divides a multicomponent mixture into equivalent binary mixtures of different volatilities and determines the plate number by using the McCabe-Thiele diagram. For each group of several components a key component is selected the α-value of which corresponds to the average of the component α's. Wagner and Blaß [175d] have reviewed approximate calculations pertaining to multicomponent separations. Their paper includes also methods of determining relative volatilities, key components and the distribution of the components in the product flows.

A method for the exact calculation of the minimum plate number in a multicomponent distillation is reported by Chien [175b]. An approximate method was developed by Serov et al. [175a].

Continuous operation is simpler to calculate because the conditions of distillation remain constant. Furthermore it is possible to obtain single components or several components together as top and bottom products. If we wish to produce m fractions, $m - 1$ columns are necessary. Let us take as an example a mixture of the lower normal fatty acids C_4—C_8, the distillation curve for which [176] is shown in Fig. 84. To separate it continuously into individual components we need four columns. Experience proves that it is best to collect the fractions as far as possible as distillates if clear and colourless products are required. We shall then perform the operation according to the diagram given in Fig. 85. It is, however, also possible to work according to a scheme such as that shown in Fig. 86.

Let us first consider column IV of Fig. 85. A binary mixture of C_7 and C_8 is separated here, and the calculation of the conditions of distillation is therefore simple. In column III the feed is a ternary mixture; the distillate is a single compound and the bottom product is a mixture of two components. In this case we compare the equilibrium curves of the mixtures C_6/C_7 and C_7/C_8, and for the calculation use the equilibrium curve corresponding to the lower α-value of the two curves. The feed to column II is a mixture of four components. We again determine α for the individual binary mixtures, C_5/C_6, C_6/C_7, C_7/C_8, and base the calculation on the equilibrium curve for the lowest value of α. We must, however, consider the fact that the compounds C_7 and C_8 are almost completely absent from the vapour; they should rather be looked upon as a diluent. It is therefore necessary to correct the value of α, taking into account the expected bottom temperatures, the volatility of the bottom compo-

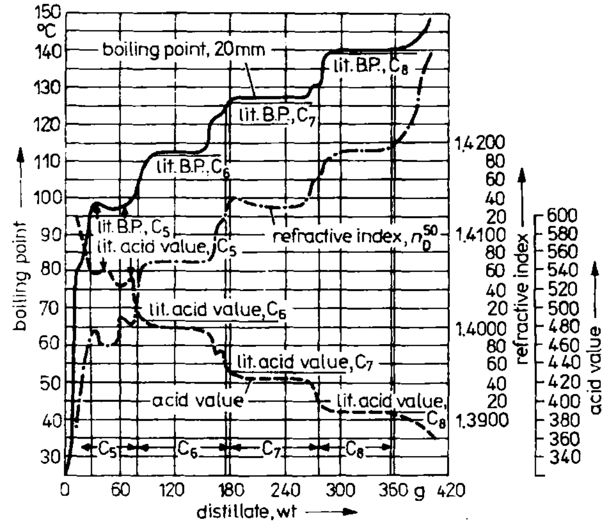


Fig. 84
Fractionation of a mixture of the normal C_4-C_8 n-fatty acids at 20 mm Hg pressure

nents and their respective amounts. If the bottom temperature is relatively high, so that an appreciable proportion of each component is vaporized, the lowest α of the three mixtures should be chosen. If this temperature is lower, it is sufficient to choose the lowest α-value of the first two mixtures. If we take account of the hold-up and of the fact that the C_5 acid is present in a relatively small amount (Fig. 84) it may even be necessary to base the calculation on the C_6/C_7 mixture and to regard the remainder as diluent. Matters are similar in column I. The bottom temperature will be high with respect to the top temperature and we can hence choose the lowest α of the mixtures C_4/C_5 and C_5/C_6.

In *homologous series*, as occur in the present instance, the values of α diminish with rising C-number, and the separation consequently becomes more difficult as the molecular weight increases (Table 26).

We may, however have to deal with a case in which the top and bottom products to be taken off are mixtures of various components. An example is seen in column I of Fig. 86. The top product is here C_4/C_6 and the bottoms are C_7/C_8; the cut must therefore be made between C_6 and C_7. We may follow the procedure of first using the equilibrium curves for the two extreme pairs of components, *i.e.* C_4/C_5 and C_7/C_8, to calculate the number of stages and distillation conditions required to enrich the mixture to 95 mol% ($= x_E$). The average of the two figures so obtained is taken. Alternatively we may base the calculation on the equilibrium curve for C_6/C_7 since C_4/C_6 will preponderate in amount and C_8 scarcely takes part in the exchange between vapour and liquid.

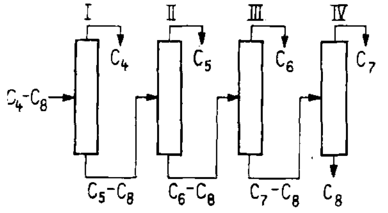


Fig. 85
Scheme for the continuous distillation of the C_4-C_8 n-fatty acids
C_4 to C_7 collected as distillates, C_8 as bottom product

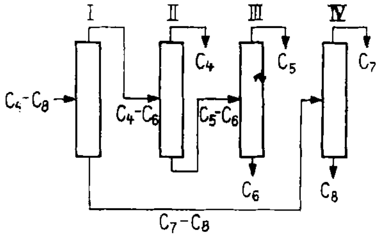


Fig. 86
Scheme for the continuous distillation of the C_4-C_8 n-fatty acids
C_4, C_5 and C_7 collected as distillates, C_6 and C_8 as bottom products

Table 26

Average values of α for mixtures of the normal C_4 to C_8 fatty acids at 20 mm pressure

Mixture	α
C_4/C_5	2.66
C_5/C_6	2.50
C_6/C_7	2.10
C_7/C_8	2.13

Studies of heat economy made by Faldix and Stage [176a] have resulted in optimum column connexions in two-column systems. Flow diagram variants for the multicomponent separation in columns with intermediate take-off were developed by Müller [176b].

Billet [176c] shows that deviations from optimum column lay-out may lead to a drastic increase in cost. The connexion of main and side columns and the use of partial condensation in direct and countercurrent operation, where appropriate are also discussed. These principles should be considered in laboratory and semitechnical work. Comparative studies of the applicability of heuristic rules and approximate methods in the selection of appropriate column connexions for multicomponent countercurrent distillation were made by Jobst et al. [176d].

For *ideal multicomponent mixtures* there have been developed numerous methods of calculation, which have been reviewed by Thormann [177] and Ellis and Freshwater [178]. Special attention may be drawn to the method of approximation evolved by Colburn [179] and the exact procedure of Underwood [180] for determining the minimum reflux ratio. A simple approximate method for finding the minimum number of stages with $v = \infty$ is due to Fenske [181], who also adopts the simplification of considering a multicomponent mixture as a binary system. The method involves the restrictions that, in the series of boiling points in the mixture, the successive key components must predominate, and that the differences in the boiling points of the successive components shall be not too widely different. If x_N denotes the content of the lowest-boiling key component, the amount of which in the bottom product is to be limited, and x_O the content of the higher-boiling key component, the amount of which is to be limited in the top product, and if the compositions of overhead and bottoms are denoted by E and W, the Underwood-Fenske formula for the minimum number of stages is

$$n_{\min} = \frac{\log \{(x_{NE}/x_{OE})\,(x_{OW}/x_{NW})\}}{\log \alpha_{NO}} \tag{131}$$

in which α_{NO} is the vapour pressure ratio of the two key components.

An exact method for calculating the minimum number of separating stages has been developed by Harbert [182], who refers the volatilities of the individual components to the vapour pressure of the most volatile constituent. An excellent article by Bruijn [183] deals with the theory of multicomponent distillation at a minimum reflux ratio. The thermodynamic foundation of multicomponent rectifications has been treated systematically by Wagner in a series of publications [183a]. Starting from the physical properties of mixtures the various steps in distillation practice are described in an exemplary manner. The description is supplemented by a great number of references.

The exact calculation of column and operating parameters for the separation of multicomponent mixtures requires electronic computers. Problems of modelling and optimization can then be solved comparatively quickly. Applications of digital and analog computers in the calculation of separations will be discussed in chap. 4.15.

4.10 Testing plate columns and packed columns

So far we have considered only the methods available for determining the number of separating stages or transfer units necessary to effect a given separation. The procedure of testing, or calibrating, a column with a known mixture has the object of establishing the number of stages or transfer units that the column provides. Such tests are essential because there is no satisfactory method for finding the efficiency of a laboratory column by calculation. A test mixture of known composition is put into the still and brought to the boil. In general the test is carried out at an infinite reflux ratio, that is to say without withdrawing distillate, as the conditions are then easy to reproduce. Samples, of such small size that they do not affect the stationary condition, are taken at the column head and from the still pot during the distillation. By analyzing these samples one can find the enrichment obtained. The theory and practice of column testing were discussed in detail by Underwood [184] some time ago.

The number of theoretical stages present in a plate column is in general lower than the number of actual plates that it contains. An actual plate thus does not function ideally, a fact which we express by reporting the ratio of the number of theoretical stages to the number of plates present (Kirschbaum's average stage efficiency) [103]:

$$s_m = \frac{n_{th}}{n}, \tag{132}$$

in which s_m = the average stage efficiency, n_{th} = the number of theoretical plates and n = the number of actual plates.

In the case of a packed column, the height of a theoretical stage or plate is used:

$$h = \frac{\text{column length}}{n_{th}} \text{ cm}. \tag{133}$$

Investigations of Hübner and Schlünder [103a] show that the Murphree efficiency can be calculated sufficiently exactly with the turbulent diffusion model if the material transfer and the intensity of turbulent mixing in the vapour and liquid phases are known. The efficiencies in the countercurrent distillation of ternary mixtures are discussed by Vogelpohl and Ceretto [103b].

If the height of a separating stage is identical with the height of an actual plate the plate operates ideally. In a packed column the height of a separating stage corresponds to the HETP.

The number of separating stages found with a test mixture depends on its equilibrium curve and the conditions of distillation maintained, and it is obviously also dependent on the dimensions of the column. If the manufacturer of a column merely quotes a number of theoretical stages, without further information, the statement is of little value. Only if the data in Table 27 are available can the separating efficiency of a column be fully assessed and the reported figure be reproduced.

4.10.1 Column diameter

According to experiments performed by Murch [185] the height of a separating stage increases with the column diameter if the size of the packing units remains unchanged. This influence is, however, less pronounced for the wire mesh type of packing (such as that of Stedman and McMahon) than for Raschig rings or saddle packing, for instance. It is shown by Mullin's systematic experiments on wall flow [186] that it is advisable to keep the ratio between the diameter of the column and the size of the packing units within the range of 10:1 to 12:1. Otherwise, as many points of flow redistribution as possible should be provided for (see chap. 4.2, 4.8.1). Groenhof and Stemerding [186a] examined the influence of column diameter on material transfer, remixing and liquid distribution. They employed columns of 14, 29 and 44 cm diameter packed with Raschig rings of 8.4 mm diameter to a height of 2.07 m. The experimental conditions were the same for the three columns. The most important conclusion is that the distribution is not influenced by the variation of the column diameter provided that the liquid introduced into the column does not change in distribution uniformity with increasing column diameter.

Table 27

Data required for judging the number of separating stages

Section	(a) Packed columns	(b) Plate columns	(c) Columns with various elements
1. 4.10.1	Column diameter	1 and 3–7 as for packed columns	1 and 3–7 as for packed columns
2. 4.10.2	Length of packing	Active column length	Active column length
3. 4.10.3	Test mixture (composition, mol %)		
4. 4.10.4	Reflux ratio and amount of reflux referred to the free cross-section (ml/cm^2 · h)		
5. 4.10.5	Operating hold-up		
6. 4.10.6	Operating pressure		
7. 4.10.7	Load (ml/h) or vapour velocity (m/sec)		
8. 7.8	Shape, material (nature of surface), dimensions (height, diameter, wall thickness), active surface area of packing	Plate distance	Description of operation with essential data (*e.g.* speed of rotation of revolving parts)
9.		Dimensions of an actual plate	

4.10.2 Effective separating length; the introduction of column packing

By effective separation length we denote the effective height of any type of column. In packed columns the effective length is that of the packing. Owing to channelling and wall flow, it is desirable to subdivide this length into sections, since the countercurrent exchange in the lower part of the column will otherwise be deficient (Refs. chap. 1: [39]). Thus it has been shown by Kirschbaum [187] that in industrial columns the number of theoretical stages does not increase in proportion to the length. For laboratory columns, Kazanskii [188] demonstrated that a column of 149 cm length, not subdivided, corresponded in certain conditions to 18 theoretical plates, and that this number increased to 24 by subdivision into three sections. More recent work by Bushmakin and Lyslova [189] has confirmed these results. As column packing they employed constantan helices of 1.8 mm diameter. They found that subdivision at every 25 cm of the length produced an optimum efficiency of the column. On increasing the number of subdivisions from zero to the optimum every subdivision resulted in an increase of efficiency corresponding to 1.5 theoretical plates. The question of the sectioning of columns for the better distribution of reflux has also been investigated by the writer, who used 4 × 4 mm saddle packing and an infinite reflux ratio.

The data are summarized in Table 28.

Table 28

Influence of the effective length and of subdivisions on the HETP

	Effective length 45 cm	Effective length 90 cm	
		1 section	2 sections
HETP (cm) at a load of 200 ml/h	4.73	6.93	6.93
HETP (cm) at a load of 600 ml/h	6.00	11.25	7.83

Test mixture: benzene-carbon tetrachloride; charge 300 ml; 40 mol% carbon tetrachloride

Pressure: atmospheric

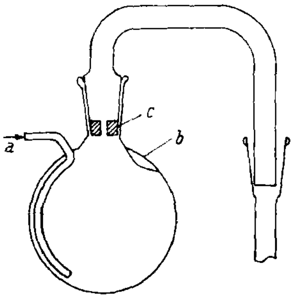


Fig. 87
Device for the random introduction of small packing units (Allenby and L'Heureux)

These results demonstrate the following facts, which so far have been given little attention in laboratory work.

1. The HETP, at a constant load, is dependent on the effective column length.
2. Subdivision of the column has no influence at a low load, but improves the efficiency at a high load.

The total surface of the packing in a length of column depends on the *way in which the packing is introduced*; this also affects the thickness of the liquid film [190], the pressure drop and the separating efficiency [191]. In order to obtain a random distribution of the packing Myles et al. [192] filled the column with mineral oil and dropped in the packing units one by one. It is simpler to fill the column by putting in three or four packing units at a time and tapping the column repeatedly with a length of wood. By the use of a device described by Allenby and l'Heureux [193] (Fig. 87), small packing elements may be rapidly introduced singly into the column, so that a random arrangement of the packing is assured. The packing is put into the flask in a layer about 1 cm thick. Air is blown in through the tube a; the packing is whirled

Table 29

Properties of test mixtures

ϑ_A, ϑ_B = boiling points of substances A and B at 760 torr (°C),
$\Delta\vartheta = \vartheta_B - \vartheta_A$ = boiling point difference

I. Normal pressure	Binary mixture	Boiling point			n_D^{20}		Δ	α	For test of n_{th}
		ϑ_A (°C)	ϑ_B (°C)	$\Delta\vartheta$ (°C)	A	B	n_D^{20}		
760 torr	benzene-toluene	80.1	110.6	30.5	1.50122	1.49647	0.0048$^{1)}$	2.36/2.61	2–7
	benzene-n-heptane	80.1	98.4	18.3	1.5011	1.3876	0.1135	2.12/1.11	5–20
	methylcyclohexane-toluene	100.98	110.6	9.62	1.4232	1.4968	0.0736	1.306/1.328	5–25
	benzene-1.2-dichloroethane	80.1	83.5	3.4	1.5011	1.4448	0.0563	1.162/1.107	15–20
	n-heptane-methylcyclohexane	98.4	100.85	2.45	1.3878	1.4232	0.0354	1.076/1.074	20–80
	p-xylene-m-xylene	139.10	138.35	0.75	1.4960	1.4973	0.0013$^{2)}$	1.0203/1.0204	50–250

II. Vacuum		α 5 torr	α 10 torr	α 100 torr	n_D^{20}		Δ	Application	For test of n_{th}
					A	B	n_D^{20}		
to 1 torr	2-methylnaphthalene-1-methylnaphthalene	1.1400/ 1.1417	1.1312/ 1.1328	1.1035/ 1.1047		$^{1)}$	$\Delta n_D^{40} = 0.0050$	max. pressure 100 torr	15–45
to 5 torr	trans-decalin-cis-decalin	1.483/ 1.460	1.440/ 1.420	1.314/ 1.300	1.46932	1.48098	0.01166$^{1)}$	min. pressure 5 torr	4–20
		α 50 torr	α 300 torr	α 760 torr					
to 20 torr	benzene-ethylbenzene	1.188/ 1.194	1.140/ 1.143	1.130/ 1.130	1.5246	1.4958	0.0288	min. pressure 20–30 torr	10–30

III. Pressure		α 8 atm.	α 12 atm.	α 16 atm.		Δ n_D^{20}	Application	For test of n_{th}
to 8 atm.	isobutane-n-butane	1.308/ 1.241	1.261/ 1.217	1.220/ 1.195		[1]	min. pressure 8 atm.	6–25
		α 1 atm.	α 3 atm.	α 5 atm.	α 10 atm.			
to 1 atm.	methanol-ethanol	1.644/ 1.866	1.474/ 1.559	1.395/ 1.447	1.289/ 1.319	[1]		4–20

[1] Analysis preferably by gas chromatography

[2] Analysis preferably by infrared spectroscopy or gas chromatography

round in the flask. The projection b acts as a deflector; the hole in the cork c allows only one packing unit to pass at a time through the connecting tube into the column.

In plate columns and columns provided with other elements the separating length is equal to the effective column height, *i.e.* to the distance between the lower edge of the lowest plate and the lower edge of the topmost plate plus 1 plate distance in the case of plate columns. For columns carrying certain elements the separating length is defined as the total height of the effective element; in the case of rotating elements this will be the height of the rotor.

4.10.3 Test mixtures and the composition of the charge

Strictly speaking, every column should be tested with the mixture that is to be separated in it. However, for purposes of comparison, and because the pure components of the mixture in question may not be available, it is usual to employ certain *test mixtures* having particularly suitable properties. They should primarily be so chosen that the separability of the components is suited to the expected efficiency of the column. A test mixture with a low value of α may possibly be used both for columns with a large and a small number of separating stages; mixtures with a high value of α can be used only for columns having a small number of stages. According to Haldenwanger [194] the properties of a test mixture may be summarized as follows:

1. The properties of the mixture must approximate to those of an ideal system, *i.e.* it must conform closely to Raoult's law and have a separation factor that is nearly constant at all concentrations.
2. The vapour-liquid equilibria must be known or be obtainable by calculation.
3. The mixture shall consist of two components only, so as not to complicate the measurements and calculation.
4. The separation factor must have such a value that an adequate, but not too thorough separation is attained in the apparatus to be tested.
5. The boiling points should lie in such a range that no difficulties are experienced with the thermal insulation of the column.
6. The substances must be stable under the conditions of the distillation.
7. The substances and their mixtures must not attack the materials of construction.
8. The substances must be readily obtainable.
9. The substances must be free from contaminants; it should be possible to test their purity by analysis.
10. A simple analysis for determining the composition of the mixtures should be available.

On the basis of extensive experimental work international co-operation within the European Federation of Chemical Engineering has resulted in the standardization of test mixtures. The booklet published by Zuiderweg [195] contains the equilibrium data as well as all important physical properties and data concerning the chemical stability of the components for 11 systems. It is suggested to use mainly the test mixtures listed in Table 29 so that it should be possible to compare the efficiency of packings and columns.

It has become international practice to employ the mixtures n-heptane-methylcyclohexane, 1.2-dichloroethane-benzene, benzene-carbon tetrachloride und benzene-ethylene dichloride (for plate numbers up to 50 or 60) and benzene-carbon tetrachloride (for plate numbers up to 30) for tests at atmospheric pressure. Brandt and Röck [196] examined the system n-heptane-methylcyclohexane as regards its ideality of behaviour. It was found that the mixture must be classed as a separate type, termed "pseudo-ideal", because the heats of mixing are not negligible in spite of the constancy of the relative volatility. The system is also very suitable for testing under reduced pressure. A further advantage is that the molar heats of evaporation of the components are almost the same (7.575 kcal/mole). For plate numbers from 100 to 500 heavy water is suitable as a test substance [214]. The system $H_2{}^{16}O-H_2{}^{18}O$ allows tests to be performed up to a few thousand theoretical plates although the equilibration times are of the order of months (chap. 5.1.4). Exact column tests may also be performed using substances labelled with the radionuclides ^{14}C, ^{35}S and ^{36}Cl.

Table 30

Constants k_1, k_2 and k_3 in Murch's formula [185]

Type of packing	Size (mm)	k_1	k_2	k_3
Raschig rings	9.5	13.58	−0.37	1.24
	12.7	44.95	−0.24	1.24
Saddle packing	12.7	25.61	−0.45	1.11
McMahon packing	6.35	0.0114	0.5	1.0
	9.5	0.199	0.25	1.0
	12.7	0.356	0.20	1.0

In the pressure range from 20 to 400 mm the mixture cyclopentylcyclohexane-n-dodecane has been found to be nearly ideal, whilst dicyclohexyl-n-tridecane proved to be approximately ideal only in the concentration range of 30 to 90% dicyclohexyl [197].

Murch [185] succeeded in establishing the ***influence of certain physical properties of the mixture*** on the separating effect. He found that the height of a separating stage is directly proportional to the expression $\alpha \cdot \eta/\varrho$, in which α is the relative volatility, η the dynamic viscosity in centipoises and ϱ the density in g/ml. By an evaluation of experimental data Murch arrived at the following empirical formula:

Height of a separating stage (HETP)

$$= k_1 M^{k_2} \cdot d^{k_3} \cdot h^{\frac{1}{3}} \cdot \alpha\eta/\varrho \tag{134}$$

in which M = mass velocity of the vapour in kg/m²h, d = column diameter in m, h = height of the packed part of the column in m.

The constants, k_1, k_2 and k_3 are dependent on the nature and size of the packing units and are listed in Table 30.

The validity of Murch's formula is subject to the following restrictions:

1. The distillation must be at atmospheric pressure.
2. The value of M must lie between 25 and 80% of the limiting load.
3. The ratio of the column diameter to that of the packing units must be larger than 8—10.
4. The HETP is that valid for an infinite or very high reflux ratio.

The accuracy of the formula is said to be ±10%. Its originator, however, suggested that 20% should be added to the calculated figure as a safety factor. Formula (134) hence gives a rough approximation to the true value and its results should be checked by experiment.

The HETP is dependent on the *concentration of the still pot liquid* [92, 199] and experience shows that this concentration is best kept above a value of 40 mol%, whilst the amount of the charge should preferably be about 8 times the operating hold-up of the column. The test mixture should be so chosen that the distillate does not contain more than 90% of low-boiling component. We can consequently divide the test mixtures, according to the differences in boiling points of the components, into three groups:

	Test mixture with Δ *Kp*.
for a large number of separating stages (> 40)	0.5 to 3.0
for a medium number of separating stages (10—40)	3.0 to 10.0
for a small number of separating stages (< 10)	> 10

For the most important test mixtures tables have been drawn up [92, 146, 147 195] from which it is possible to construct a diagram corresponding to Fig. 71, showing the number of separating stages against the refractive index of the mixture. The refractive indices of the top and bottom products are marked along the abscissa and the corresponding difference in the number of separating stages is read off; the latter figure is then the number of stages for the column tested (section 4.7.4).

4.10.4 Reflux ratio and quantity of reflux

As a rule the number of separating stages is determined at total reflux. In practice, however, it may be necessary to measure how the *number of stages changes with finite reflux ratios*, or what factor must be taken into account for a finite reflux ratio if the test has been performed at $v = \infty$. This may be done by carrying out an experiment at a given load and a finite reflux ratio, the distillate not being actually removed, however, but returned to the still pot (Fig. 88). Periodically, simultaneous samples are taken of the top distillate and the still pot contents and their composition is determined [164]. After the samples have been taken, distillate should be removed for a time in the normal manner, whereupon the determination is again carried out at the new composition of the boiler contents. Experiments performed in this way by the author, with a column of 30 mm diameter and 1.15 m packed length containing 2 × 2 × 0.2 mm helices, resulted in the factors F shown in Fig. 89. Investigations by Neumann and Leibnitz [201] confirmed the results.

F is the factor by which the number of separating stages, determined at $v = \infty$, should be multiplied in order that the actual number of stages at a certain finite reflux ratio may be obtained:

$$n_{v_\infty} \times F = n_{v_\text{finite}}. \tag{135}$$

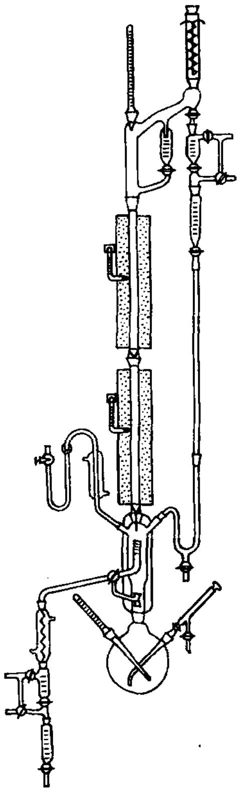


Fig. 88
Arrangement for testing *a column with a finite* reflux ratio

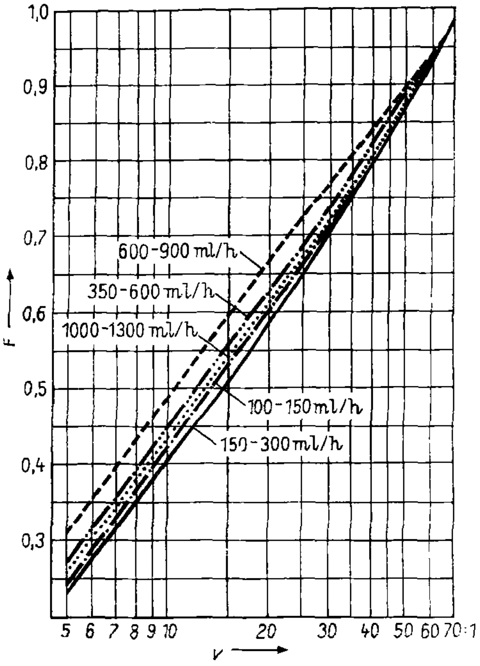


Fig. 89
Factor *F* for 2 × 2 mm helices and reflux *ratios of 5:1 to 70:1*

From Fig. 89 it will be seen that with a column such as that tested, containing 60–70 theoretical plates, there is little point in increasing the reflux ratio above, say 70:1. This agrees with formula (110) developed by Rose, which implies that there is no advantage in laboratory distillation in using a reflux ratio greater than the theoretical plate number of the column.

Another experimental approach is to carry out a batch countercurrent distillation with the test mixture at the selected load and reflux ratio; small samples of the distillate (about 1% of the still charge) are regularly taken and also — together with every second sample — a few drops of the liquid from the still pot; the compositions are then determined. By plotting the concentrations of the distillate and still pot contents against the amount of distillate removed, two curves are obtained, as illustrated in Fig. 90 for the system chlorobenzene-ethylbenzene at 760 and 20 mm pressure and $x = 8:1$ [92]. These results are compared with tests at infinite reflux to obtain the plate equivalent and the useful efficiency.

The plate equivalent is the minimum number of plates required at infinite reflux ratio to attain the same enrichment ($x_B \rightarrow x_E$) as in a countercurrent distillation with a finite reflux ratio. All distillation conditions except the reflux ratio remain the same. Thus, in the McCabe-Thiele diagram the separating stages are drawn between the diagonal and the equilibrium curve ($v = \infty$).

As an example (Fig. 90), after the removal of 30 vol% of distillate (at 20 mm pressure and $v = 8:1$), the composition of the still pot contents, 17 mol%, (x_B) corresponds to a distillate concentration (x_E) of 60 mol % chlorobenzene. If these two values, 17 and 60 mol%, are now entered into a McCabe-Thiele construction or the Fenske formula (114), it is found that this enrichment, with $v = \infty$, corresponds to 17.5 theoretical stages. This procedure can be repeated for a number of points and then yields a curve as shown in Fig. 91. It is seen from this figure that the plate equivalent — as would be expected — becomes higher at a larger reflux ratio, and that with a low reflux ratio its value drops appreciably in the early stages of distillation after equilibration at total reflux. Further it will be observed that pressure has no appreciable influence on the plate equivalent. The relation between the number of theoretical stages at $v = \infty$ and $v = 27:1$ and the plate equivalent is demonstrated by Fig. 92, constructed from values determined by Collins and Lantz [200]. The column employed, containing 30 actual plates, gave the following results when tested with the mixture n-heptane-methylcyclohexane at a load of 3000 ml/h:

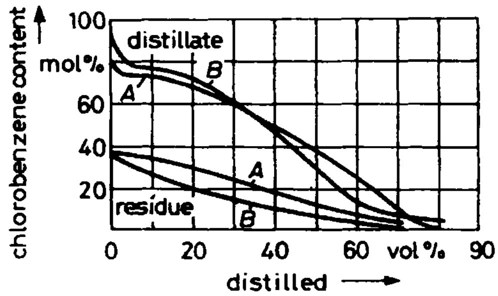


Fig. 90
Composition of the distillate and boiler contents as a function of the distillate taken off (chlorobenzene-ethylbenzene)
(Offtake: 44 ml/h, $v = 8:1$)
x_B at start of distillation: 37 mol%
A — 760 torr pressure; B — 20 torr pressure

with $v = \infty$, 19 theoretical stages;
with $v = 27:1$, 17.5 theoretical stages;
with $v = 27:1$, 12.5 plate equivalents.

This result signifies that the separation effected at $v = 27:1$ could also have been attained at $v = \infty$ with 12.5 theoretical stages. Conversely, one would have to choose a column that, at a load of 3000 ml/h, produces an enrichment equivalent to 19.0 stages at $v = \infty$.

Relating the plate equivalent $n_{\text{äqu}}$ to the plate number n_∞ at $v = \infty$ for the same load we obtain, according to Obolonzev and Frost [202], the useful efficiency of a column:

$$N = \frac{n_{\text{äqu}}}{n_\infty} \quad \text{(at the same load).} \tag{136}$$

This value may at most be unity and approaches unity as the selected reflux ratio increases.

The method involving plate equivalents and the useful efficiency has the distinct

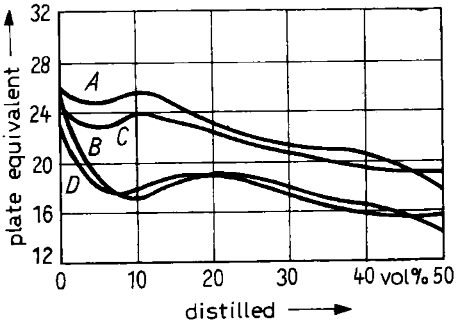


Fig. 91
Plate equivalent as a function of the amount of distillate taken off, from 0–50 vol% (chlorobenzene-ethylbenzene)
A: $v = 24:1$ (20 torr), B: $v = 8:1$ (20 torr), C: $v = 24:1$ (760 torr), D: $v = 8:1$ (760 torr)

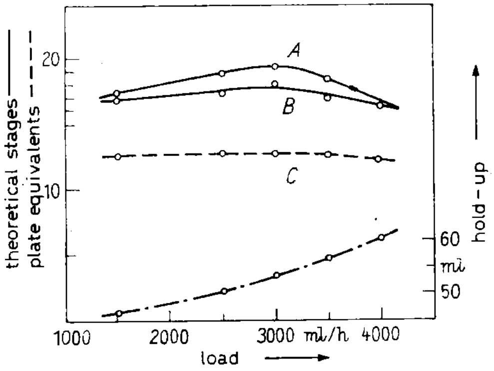


Fig. 92
Theoretical stages (———) and plate equivalents (— — —) as a function of load
A = Number of theoretical stages, $v = \infty$, B = Number of theoretical stages, $v = 27:1$, C = Plate equivalents , $v = 27:1$

advantage of allowing columns to be compared under varied conditions, as all plate numbers are referred to $v = \infty$.

The determination of the amount of reflux is in principle performed at the column head. If the column were to operate adiabatically, that is to say without gain or loss of heat, and the molar heats of evaporation of the components were identical, the amount of reflux measured just above the still pot would be equal to that measured at the top. In practice, however, the quantity of "bottom" reflux is generally

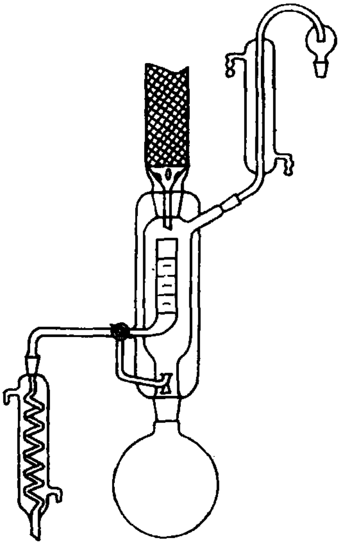


Fig. 93
Destinorm unit for measuring the amount of bottom reflux and the hold-up

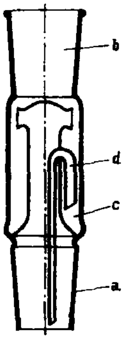


Fig. 94
Reflux measuring device with syphon (Sigwart and Stage)
a = connection to still pot,
b = connection to column,
c = reflux collecting vessel,
d = syphon

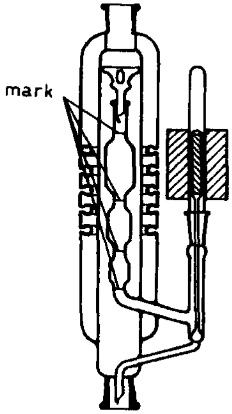


Fig. 95
Labodest reflux meter with magnetic valve (Stage)

higher than that of top reflux, owing to loss of heat. In order to find out whether the column is operating adiabatically it is hence useful also to determine the amount of bottom reflux. This can be done by employing the apparatus shown in Fig. 93. During a measurement the tap is so regulated that the reflux does not flow into the flask, but is collected in the graduated funnel. The amount flowing into it in unit time is observed with the aid of a stop watch. The form of apparatus illustrated has the advantage that the quantity measured can be varied in accordance with the conditions of the distillation, but a disadvantage is that tap grease may be dissolved. This is avoided in modifications developed by Sigwart. Fig. 94 shows a model with a syphon and Fig. 95 the preferred form with a magnetic valve. An excellent review of reflux measuring devices including numerous constructional details is given by Gemmeker and Stage [245].

4.10.5 Total, static and operating hold-up

The term *total hold-up* is used to denote the amount of substance that is present in operating a distillation apparatus, as liquid and vapour, between the surface of the liquid in the still pot and the condenser. The total hold-up is the sum of the *static hold-up*, remaining when the column is at rest, and the dynamic column content or *operating hold-up*. A knowledge of the total hold-up is of importance, since — as we have already seen in section 4.7.1 — its influence increases with the number of separating stages and is unfavourable for separation at a high reflux ratio, but favourable at a low reflux ratio, whilst with a very high hold-up the reflux ratio loses almost all its influence on the separation. For Raschig ring packings the theoretical calculation of the liquid operating hold-up after Yilmaz and Brauer [116] is possible (see chap. 4.2.2). Blaß and Kurtz [268] express the liquid static hold-up of Raschig ring packings as a function of the Bond number:

$$B_{OL} \equiv \varrho_L \times g/\varrho_L \times a^2. \tag{137}$$

At small widths, $B_{OL} < 1$, the static hold-up assumes an almost constant value.

For the total hold-up of liquid, V_{LO}, below the flooding point an empirical correlation is given.

The rise of liquid hold-up with increasing vapour velocity W_G is proportional to $(W_G/W_{GF})^{10}$, where W_{GF} is the vapour velocity at the flooding point.

Hold-up profiles in various packings were determined by Achwal and Stepanek [269] in a column with a diameter of 5 cm and a packing of 6 mm ceramic cylinders.

The quantity of liquid remaining in a column after flooding or after terminating a distillation and cooling is known as the *static hold-up*. To determine it, an amount of liquid equal to about five times the expected value is put into the still pot and distillation is allowed to proceed for an hour. After the column has cooled the liquid that has collected in the pot is measured. The difference with respect to the charge is the static hold-up. In packed columns this quantity is made up of liquid clinging to the packing, to the walls of the columns, the still head and the condenser. In plate columns the major part consists of that remaining on the individual plates. A simplified procedure that can be adopted is to pour a measured amount of the liquid to be distilled through the upper end of the condenser and subsequently to determine how much is retained by the column. This measurement (which does not refer to the distillation temperature) should be repeated several times, so as to ensure that wetting is complete and that a good average is obtained.

If we add to the static hold-up the amount of liquid temporarily present during a distillation between the still pot and the condenser (which we call the *operating hold-up*), we get the total hold-up. The operating hold-up is found by rapidly removing the still pot heater during distillation (and if possible also disconnecting the still pot), and collecting the downflowing liquid in the piece of apparatus shown in Fig. 95.

For an indirect determination of the total hold-up, both with packed and plate columns, a small quantity of a high-boiling substance, such as stearic acid, or α-bromonaphthalene ($n_D^{20} = 1.6580$) is added to the test substance (say n-heptane). During distillation some of the low-boiling substance passes into the column, so that the concentration of the additive in the liquid remaining in the still pot increases. Samples of the still pot contents are periodically taken during distillation and are analyzed for their additive content. If stearic acid is used, analysis may be performed by titration or by evaporating off the test liquid. The content of α-bromonaphthalene is determined refractometrically. The total hold-up H is then calculated by the formula:

$$H = V_B\left(1 - \frac{x_1}{x_2}\right), \tag{138}$$

in which V_B = the volume of the still pot charge; x_1 = the concentration of additive before distillation; x_2 = the concentration of additive in the still pot during distillation.

For purposes of comparison it is convenient to calculate the static hold-up, operating hold-up and total hold-up per theoretical or practical plate. The total hold-up varies with the load, but the literature gives little definite information on this relationship. For an Oldershaw sieve-plate column with a diameter of 28 mm, containing 30 actual plates, Collins and Lantz [200] published the values shown in Fig. 92. The total hold-up lies between 43 and 60 ml, depending on the load, so that it can be taken to be 1.4—2.00 ml for each actual plate and 2.5—3.5 ml for each theoretical plate. According to measurements of the author's, the total hold-up of packed columns is about the same, as will also be seen from Fig. 96, which indicates

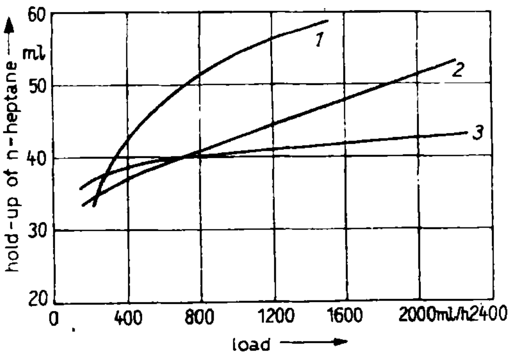


Fig. 96
Dependence of the total hold-up on the load with various types of packing at 730 torr

1 = Perforated half cylinders of metal sheet,
2 = Gauze saddles,
3 = Raschig rings

the dependence of the total hold-up in ml of n-heptane at 97 °C on the load at 730 mm pressure [203]. The column diameter was 19 mm, its effective length 812 mm.

In the calculation of the plate number for batch distillation Zuiderweg [158] takes into account the influence of the total hold-up and the magnitude of the transition fraction. Mixtures having α-values from 1.07 to 2.42 were used to study the dependence of "separation sharpness" on relative total hold-up, reflux ratio and plate number. By means of the pole height S the optimum reflux ratio can be determined. The method corresponds to the determination after McCabe-Thiele with a final state $x_B = 5$ mol%.

4.10.6 Operating pressure

The operating pressure is understood to be that observed at the head of a column during distillation, measured in the gas space just beyond the condenser. Strictly speaking the pressure should be measured in the vapour at the point of condensation, *i.e.* at the same place as the temperature measurement. As this would be difficult, the tubes of the condenser should be wide enough for the difference in the pressure between the vapour space before the zone of condensation and the gas space beyond it to be negligible. The difference is more important when high vacuum is employed, in which case it is advisable to make comparative measurements before and beyond the condenser. The pressure in the still pot is equal to the sum of the pressure in the vapour space at the point of condensation and the pressure drop occurring in the column. In a vacuum distillation there is a greater volume of vapour to be handled; it is then often the practice to use packing larger than 1/10 th of the column diameter, at least in the upper part of the column, where the lowest pressure prevails and flooding is most likely to take place.

The question of how far a *reduction in pressure* affects the number of separating stages has so far not been definitely answered. Von Weber [204] found that the number of theoretical stages changes little; the throughput is lower owing to the larger volume of vapour, but the relative volatility generally becomes more favourable (see section 4.6.2). Myles et al. [192] observed with various forms of packing that the HETP has a minimum at about 200 mm pressure, whilst Struck and Kinney [203] concluded that the HETP passes through a minimum between 50 and 100 mm, the value at about 100 mm being equal to that at atmospheric pressure (see also sections 4.8 and 4.10.4).

On the basis of extensive experimental data — some of them collected by Myles [192] — David [191] and Zuiderweg [205] showed conclusively that the number of stages becomes smaller the lower the pressure. If the specific number of stages n_s (theoretical stages per metre) is plotted against the pressure drop, a good comparison of the efficiency of separation is obtained. Fig. 97 shows such curves for the mixture benzene-ethylenedichloride, as determined by David [206]. A similar conclusion was reached by Kirschbaum et al. [191], who drew attention to the fact that, owing to the pressure dependence of the relative volatility, the change in the specific stage number will not follow the alteration in the distillate composition.

Zelvenskij et al. [209] studied the influence of pressure on material transfer in a packed column using the radionuclides ^{14}C, ^{35}S and ^{36}Cl. They found that reducing the operating pressure decreases the efficiency of the column.

Szapiro [207] derived an equation which can be used to calculate the composition of the liquid in the flask and of the reflux at the n-th plate as a function of pressure for ideal binary systems at full reflux.

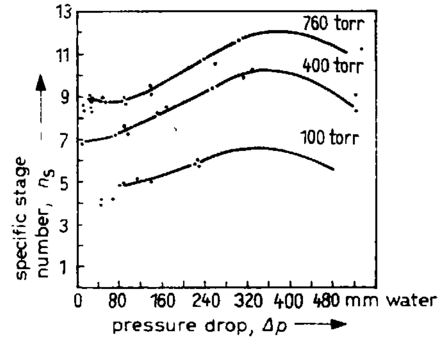


Fig. 97
Specific stage number n_s in relation to the pressure drop (David). Test mixture: benzene-ethylenedichloride, $x_B \sim 14$ mol%

4.10.7 Load and vapour velocity

The term "load" is used to denote the amount of substance which reaches the column head as condensate in unit time, and is composed of the quantity of reflux plus the amount of distillate removed. In industrial usage it is customary to express the load on a column in terms of the vapour velocity, referred to the free column cross-section. In laboratory practice this figure is calculated only if a comparison with a semi-technical or industrial installation is required. It may be usefully expressed as ml/cm^2 h.

The separating efficiency of a column is dependent on the load and this influence is greater, the higher the reflux ratio (Fig. 98). In reporting tests it is therefore necessary to state the load. According to a proposal of von Weber tests should be performed at 2/3 of the maximum load, in order that results may be comparable. The maximum load is understood to be just below the load at which the ascending vapour prevents the reflux from flowing down. In this case the column "floods" and countercurrent exchange becomes impossible.

Further important observations are that the efficiency of small packing units (2—4 mm diameter) is more dependent on the load than that of larger packing (5—10 mm), as shown in Fig. 98, and — as has already been stated — that the *optimum load* with respect to intensity does not lie at a low figure, but rather just below the point of flooding (Fig. 83) [214]. The highest *efficiency* of laboratory columns, however, is not situated at the upper limiting velocity, as indicated by David [191] for industrial columns, but at a very low load, approaching the minimum load.

If it is desired to compare laboratory columns with semi-technical or industrial columns, account should be taken of the fact that the *vapour velocities* in the former are generally very much lower, and lie in the range of 0.02 to 0.5 m/sec, whilst in

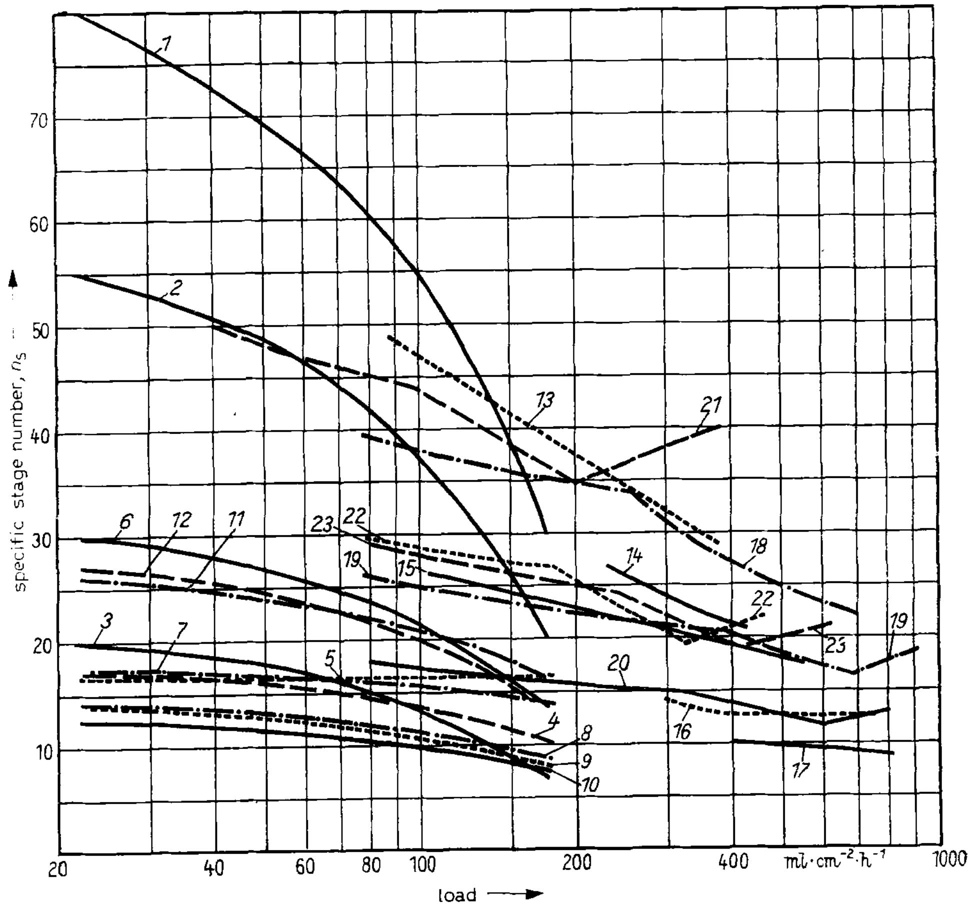


Fig. 98
Specific stage number n_s (n_{th} per m) as a function of the load for various packings according to Stage (Refs. chap. 1: [39])

Curves *1—12:* Test mixture benzene-1.2-dichloroethane
Curves *13—23:* Test mixture n-heptane-methylcyclohexane

Measurements of Schultze and Stage

1 = V2A helices, 2 × 2 × 0.2 mm ∅
2 = V2A helices, 4 × 4 × 0.4 mm ∅
3 = glass Raschig rings, 6.5 × 6.5 mm ∅
4 = glass Raschig rings, 4.5 × 4.5 mm ∅
5 = small glass spheres, 3 mm ∅
6 = large glass spheres, 7.5 mm ∅, matt
7 = small glass spheres, 4 mm ∅, matt
8 = porcelain Raschig rings, 8 × 8 mm ∅
9 = earthenware Raschig rings, 10 × 10 mm ∅
10 = glass spirals, 3 mm ∅, 1—5 mm long
11 = iron single-turn helices, 1—3 mm ∅, ca. 2 mm thick
12 = porcelain Raschig rings, 5.5 × 5.5 mm ∅

Measurements of H. Kolling

13 = V2A helices, 2 mm ∅
14 = V2A helices, 3 mm ∅
15 = V2A helices, 4 mm ∅
16 = V2A helices, 6 mm ∅
17 = V2A helices, 8 mm ∅

Measurements of H. Brauer

18 = V2A spaced helices, 3 × 3 × 0.4 mm ∅
19 = V2A spaced helices, 4 × 4 × 0.45 mm ∅
20 = V2A spaced helices, 3 × 3 × 0.45 mm ∅
21 = V2A helices, 2 × 2 × 0.2 mm ∅
22 = V2A helices, 3 × 3 × 0.45 mm ∅
23 = V2A helices, 4 × 4 × 0.4 mm ∅

industrial installations they attain values of 0.1 to 2.0 m/sec and more [184]. With packed columns it is important to keep this velocity constant; in the case of plate columns the efficiency is not so greatly affected by variations in the vapour velocity.

Other factors dependent on the load are the total and operating hold-up, the pressure drop and the limiting velocity. The latter varies with the shape and size of the packing (or the size and arrangement of the plates) and with the properties of the substances to be separated. These aspects will be dealt with in detail in chap. 4.11. An exhaustive treatment of the loading conditions in packed columns was given by Stage and Bose (Refs. chap. 1, [39]).

4.10.8 Method of column calibration

Preparation of the column

In calibration it is necessary to work with painstaking care. The whole apparatus must be rigorously clean and dry, and so it is desirable to leave the jacket heating switched on overnight before the test. Column packing must also be thoroughly cleaned before use. A good method is to carry out a preliminary cleaning with carbon tetrachloride and trichloroethylene, then to wash with hot benzene and finally to rinse again with trichloroethylene. When filling the column care should be taken not to touch the packing with the fingers.

The method employed for filling a packed column is important. The best procedure is to put in 3 or 4 packing units at a time, the column being constantly tapped with a piece of wood. With small-sized packing a rapid method of obtaining a random arrangement is to use the apparatus shown in Fig. 87. It is also useful to remove the packing after a test, to re-introduce it after cleaning and drying and then to repeat the test. This will show whether the method of filling exerts an influence on the result.

The cleaning of plate columns is more difficult because traces of liquid tend to remain on the plates. The most satisfactory procedure is to distil a volatile solvent through the column and then to dry it with a current of hot air, the column being surrounded meanwhile by a heated jacket.

The *amount of test mixture* should be 8 times the total column hold-up, and this figure should previously be determined, as described in section 4.10.5. The size of the still pot should be such that it is initially about two-thirds full. The composition of the test mixture should be adjusted to 30–40 mol% of low-boiling component. The influence of the composition on the separating effect has as yet not been fully established [208].

The *purity of the components* used for the test mixture requires close attention. It is not safe to employ substances sold as "pure" or "analytical grade" without a previous examination. A measurement of the refractive index alone is not enough. Unambiguous analyses can be carried out only with infrared spectroscopic and, above all, gas-chromatographic measurements [195]. If the properties agree with published figures and if the distillation range (measured with a thermometer graduated in tenths of a degree C and with correction for barometric pressure) shows variations of less than 0.1 deg C, a further purification is not necessary. Most substances, however, require purification by chemical means [210, 211, 212] and a subsequent sharp fractionation at a high reflux ratio. If insufficiently pure components are used two dangers exist: firstly that the refractive index calibration curve will be displaced, secondly that the impurities will be concentrated during the test at the top or in the still pot and will vitiate the results.

With the carefully purified components mixtures are prepared in the range of 5 to 95% (wt), their refractive indices are measured and a *calibration curve* (n_D^{20}-% wt) is plotted. If desired, the number of stages required with $v = \infty$ for a series of enrichments may be calculated by means of the Fenske equation (114), and a chart for these values (Fig. 71) against the refractive index constructed. From this chart the number of stages may be read off directly after taking samples and determining the refractive indexes.

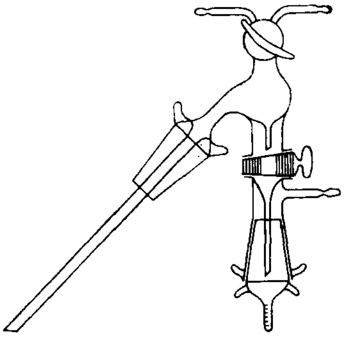


Fig. 99
Destinorm sampling device for normal and reduced pressures

It is necessary to ensure that the small samples (0.1—0.2 ml) taken from the column head or the still pot are not contaminated by tap grease. The large errors that can result have generally been overlooked. For the removal of samples from the still the arrangement illustrated in Fig. 99 has proved satisfactory. The still head employed must be so designed that it not only has a small dead space but also allows single-drop samples to be taken without contact with a tap. An example is illustrated in Fig. 100. During the equilibration period the small funnel a is turned downwards. When a sample is to be taken it is turned up and liquid is drawn off by connecting b to vacuum via a rubber tube and pinchcock and opening the latter carefully. The liquid falls through the wide passage of tap d; when 0.1—0.2 ml has been collected, tap d and the pinchcock are closed and air is admitted for an instant through valve c, forcing the liquid in the tube back into the column. Atmospheric pressure is restored in the receiver space i through b. If normal pressure is used air is blown in at the vacuum connection, in order to empty the funnel tube completely. Further examples will be given in chap. 7.5.3 (see also Refs. chap. 1, [39]).

If reliable data are to be obtained it is necessary to operate the column adiabatically. The still pot and all components up to the condenser should therefore be carefully insulated, for example with asbestos cord and glass wool, so as to minimize loss of heat (*cf.* section 7.7). Since, even at temperatures below 80 °C, a certain amount of "false reflux" is formed, it is essential to compensate for the loss of heat from the column by providing a heating element inside the jacket. Automatic control of this heating element may be effected by means of gas thermometers (*cf.* section 8.2.2). Heating jackets that can be opened on hinges (section 7.7.3) may be used with advantage, since they can be fitted after building up the glassware and can be removed at any time during a distillation in the event of trouble. The sections between the still pot and the column jacket, between the latter and the still head and the section up to the condenser are first encased in a layer of about 20 mm of asbestos cord and this is again surrounded by a winding of glass tape. The total thickness of the insulation should be about 60 mm. The safest course is to apply heating tapes to the insulation.

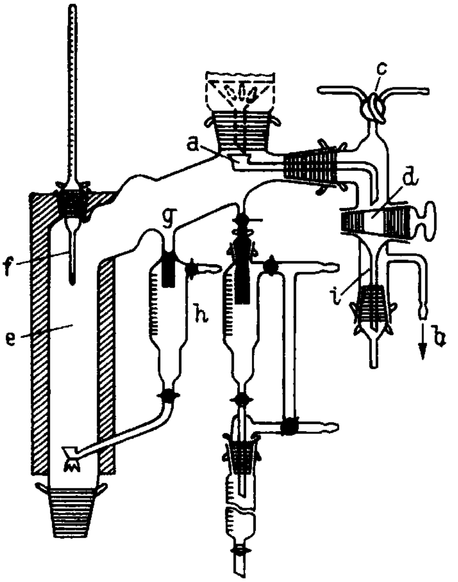


Fig. 100
Destinorm column head with device, having almost no dead space, for taking single-drop samples
(see accompany text)

Particular care must be taken that the point at which the vapour temperature is measured in the column head is not wetted by undercooled liquid reflux. Furthermore, when working at reduced pressures, there should be no loss in pressure between the points where the temperature and the pressure are measured. These conditions are satisfied in the Destinorm column head (Fig. 100). The temperature is measured in the insulated vapour tube e by means of a thermometer f or a thermocouple. Since the reflux is returned to the column through g and the reflux measuring pipette h at a level below the thermometer, the latter cannot be wetted. The pressure is measured directly beyond the wide cold trap, so that no appreciable reduction in cross section occurs between the thermometer and manometer.

Adjustment of test conditions

The separating effect of the column is dependent in the first place on the load and this must therefore be kept constant during a test run. A satisfactory method is to control the rate of evaporation by the pressure drop, using a contact manometer (section 8.4.2), and observing the heat input on an ammeter. Before the load is adjusted, however, the column (if of the packed type) should be flooded, so that the packing is thoroughly wetted. To do this, the heating current to the still pot is increased, while watching the contact manometer, until flooding starts at the foot of the column and advances up to the column head. The column is flooded in this way for about 15 minutes, whereupon the heat is reduced, so that the reflux can return. This operation may be repeated several times, after which the desired load is adjusted by means of the contact manometer (see also Refs. chap. 1: [39]).

A somewhat less effective procedure consists of "cold-flooding" the column by filling it with the mixture to be distilled, drawing off the liquid and then carrying out the distillation.

How strongly "warm flooding" influences the efficiency is clearly seen in Fig. 101. The tests were done in a Podbielniak column of 25 mm diameter with Heli-grid packing (Fig. 275) at a load of 1000 ml/h. It is seen that the stationary state was reached only after 8 to 10 hours and that the flooding increased the plate number up to 50% [213].

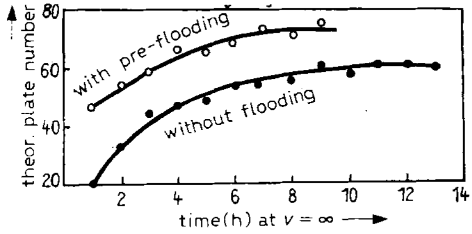


Fig. 101
Dependence of the separating efficiency on flooding (after Brandt et al.)

This flooding is particularly recommendable for wire packings of sizes between 1.6 and 4.0 mm whereas for Raschig rings of 4.5 × 6.0 mm the initial degree of wetting does not influence the efficiency. For flooding under reduced pressure, see chap. 5.4.1. Flooding points and points of optimum efficiency of a column packed with Raschig rings (5.5 × 4.0 mm) and wire gauze units (V4A steel, 2 mm) were determined by Lentz [214]. The test substances were H_2O-D_2O (27% D_2O) and n-heptane-methylcyclohexane, the column diameter was 37.5 mm. n_s and the pressure drop Δp were determined via the vapour velocity. The point of optimum efficiency lies in the flooding point for the Raschig rings and between 81 and 88% of the maximum load for the wire gauze packing. Operating a packed column in the state of "flooding onset" may increase the transfer of matter by a factor of 6 together with an inreased throughput [214a]. Kafarov et al. [214b] call this state phase inversion, in which the liquid fills the spaces in the packing almost completely and the vapour in the form of threads and vortices disperses ("emulsifies") the liquid. The liquid hold-up as well as the pressure drop and the plate number rise drastically. Relations and diagrams for estimating the particular parameters are given.

After the column has been adjusted and has run at total reflux for about 2 hours a quantity of 1—2 ml of liquid is removed at the top and is rejected. After a further hour the first samples of 0.1—0.2 ml are taken from the top and the still pot for examination. The same precautions are observed as in sampling for phase equilibrium measurements (section 4.6.3). The compositions of the samples are determined;

samples are taken every hour until the compositions of the overhead distillate and the still pot contents remain constant. The samples should be as small as possible, so as not to upset the stationary condition of the column. Equilibrium re-establishes itself more rapidly in a short column than in a long, multi-stage column; in the latter case it may be necessary to make the intervals between the taking of samples much greater than an hour. With the usual test mixtures the time required for reaching a stationary state is approximately 10 to 20 hours. It is advisable to carry out the tests in the order both of decreasing and increasing loads [208].

To find the separating efficiency of a column under operating conditions, the procedure described in section 4.10.4 for determining stage equivalents should be followed.

Calculation of the number of separating stages

When 3 to 5 values of the top and bottom concentrations remain constant the test is stopped; it should, however, preferably be repeated another day under the same conditions for corroboration.

The number of separating stages is now determined. In order to do this by calculation the figures for x_E (distillate) and x_B (still pot composition) are introduced into the Fenske equation (114). For a graphical determination the method of McCabe-Thiele is followed (section 4.7.1). If the run was carried out under operating conditions, that is to say with a finite reflux ratio, the stage equivalent may be calculated as described in section 4.10.4. The number of stages to which the separating efficiency of the column corresponds under operating conditions may also be computed by means of a formula due to Obolentsev and Frost [202]:

$$\log \frac{x_F}{x_F - a x_E} = a^{n}_{\text{äqu}} \cdot \log \frac{1 - x_F}{(1 - x_F) - a(1 - x_E)} \tag{139}$$

in which a = mol. fraction of distillate removed from charge; x_E = content of low-boiling component in the distillate (mole fraction); x_F = content of low-boiling component in the initial mixture (mole fraction).

Obolentsev and Frost proposed that the procedure for determining the number of separating stages in the column should be as follows. After equilibrium has been established a sample of the distillate is taken at a finite reflux ratio and at a point where the fraction distilled corresponds approximately to the weight or mole fraction x_F in the original charge. In this way one obtains the number of plate equivalents, $n_{\text{äqu}}/v$ (*cf.* section 4.10.4). According to this method the column is first allowed to run for 3 hours with $v = \infty$ at the selected load, and then at a finite reflux ratio. As the formula is inconvenient to use, a corresponding nomogram has been developed [84, 202].

4.10.9 Data for packed and plate columns

It is practically impossible to obtain reliable comparative values for the HETP's of packed columns and for the plate efficiencies (or average enrichment ratios) of plate columns from data published in the literature, since these data refer to various test mixtures and were obtained under different conditions. Only in rare cases are all the necessary data, mentioned in section 4.10, given. Some agreement on a standardized testing procedure should be reached, so that published results may be comparable. Other sources of uncertainty are that the purity of the substances used in testing is not always certain, and that errors due to dissolved grease from sampling taps may have arisen. With our present knowledge of such matters it is desirable to test the more important types of packed and plate columns again, using accurate modern analytical methods, such as infra-red spectroscopy, gas chromatography and mass spectrometry.

However, with the object of providing a rough idea, the present data for the most important types of packed and plate columns [215] have been collected in Table 31. The various forms of packing and plate columns will be described further in sections 7.8 and 7.3.3.

4.11 Pressure drop, limiting velocity and calculation of column dimensions

In the laboratory it is usual to employ columns having diameters of 10—30 mm for distillations at normal pressures and of 20—50 mm for distillations at reduced pressures. For very large throughputs, even at normal pressure, a diameter greater than 50 mm is necessary. The recent view that a column should be loaded to just below the point of flooding makes it necessary to settle on its diameter beforehand, so that the desired throughput may be realized.

The load on a column is the amount of substance that passes through it and condenses at the column head in unit time, *i.e.* the sum of distillate and reflux. As the packing, or other obstructions present, offer a resistance both to the ascending vapour and the descending liquid, the load cannot be increased beyond a certain limit. If we measure the pressures at the top and bottom of the column we observe that their difference (the loss in pressure or *pressure differential* over the column) rises with increasing speed of evaporation or column load. This pressure loss is dependent on the nature and dimensions of the column, on the packing or plates present, on the distillation pressure and the properties of the mixture distilled. The pressure drop in annular columns may be calculated by formula (195) (section 7.3.1). Pressure drop figures for columns with rotating elements have been collected in Tables 62 and 64.

Plate columns have the advantage that they can be used at very low loads and that the separating effect may then be a maximum, whilst packed columns require a minimum load to ensure a proper countercurrent exchange. In large-scale operation columns are often controlled by the pressure differential, so that flooding may be avoided and an optimum separating effect maintained. The same method can be used with advantage for laboratory columns (*cf.* section 8.4.2).

The term *lower limiting velocity* is used to denote the vapour velocity (referred to unit cross section of the empty column) below which the effectiveness of the column begins to fall off, the term *upper limiting velocity* for the vapour velocity at which flooding is so intense that, in plate columns, the layer of liquid on a plate is entrained upwards, and in packed columns a quantity of spraying liquid rises from the foot of the column to the top. Since the fundamental publications by Mach [219],

Table 31

I. Test data for packed columns

Packing						Column
Type of packing	Material	Diameter (mm)	Height (mm)	Wall thickness (mm)	Surface area of one litre (m^2)	Column diameter (mm)
Raschig rings	Glass, smooth	3.0	3.0	0.7	1.320	
	Glass, smooth	4.0	4.0	0.6	1.109	
	Glass, smooth	4.5	4.5	0.5	1.382	24
	Glass, smooth	5.0	5.0			35
	Glass, smooth	6.0	6.0			20
	Glass, smooth	6.5	6.5	0.5	1.109	24
	Glass, smooth	10.0	10.0			50
	Porcelain	5.5	5.5	1.1		24
	Porcelain	8.0	8.0	1.1		24
	Earthenware	10.0	10.0	1.7		24
Dixon rings	Wire mesh	3.0	3.0			25
	Wire mesh	5.0	5.0			20
	Wire mesh	6.0				50
Prym rings	Metal	2.2	2.5			
Wilson spirals	Glass	3.0	1.5—3.0	0.4		24
	Glass	5.0	5.0	0.65	1.66	
	Glass	6.3				25
Fenske helices	Glass	2.1				10
	Glass	3.1				13
	Glass	3.1				20
	Glass	6.3				25
Helices	Stainless steel	1.6	1.6	0.2		40
	Stainless steel	2.0	2.0	0.2	4.55	24
	Stainless steel	4.0	4.0	0.4	1.49	24
Beads	Glass, smooth	3				24
	Glass, smooth	4			0.9	
	Glass, matt	4				24
	Glass, matt	7.5				24
Saddles	Porcelain		4		1.5	30
	Porcelain		6		1.15	30
	Porcelain		8			30
	Porcelain		10		0.72	30

Sigwart: No further data supplied.
Thormann: The lower HETP's are for smaller loads and conversely.

		Height equivalent to a theoretical plate, cm					
Cross-sectional area (cm^2)	Packed height (cm)	Schultze and Stage chap. 4. [216]	Sigwart chap. 4. [217]	Thormann chap. 4. [218]	Myles et al. chap. 4. [192]	Other	References
				5–7			
				6–9			
4.5	60	5.82–9.52					
9.6	90		11.1	7–12			
3.1	125		15.5	8–14			
4.5	60	5.0–14.3					
19.6	95		18.2				
4.5	60	3.69–7.5					
4.5	60	7.07–11.3					
4.5	60	7.23–12.8					
4.9	100					1.4–2.8	Ch. 7.8
3.1	60		4.35				
19.6	100					1.4–3.5	
				3–5			
4.5	60	8.0–13.35					
				7–12			
4.9	107				7–9.2		
0.8	80		4.8				
1.3	126		7.4	4–6			
3.1	125		9.5				
4.9	107				3.6–4.2		
12.5	100					1.4–2.0	Author's measurements
4.5	60	1.25–3.32					
4.5	60	1.82–5.0		2–5			
4.5	60	6.00–6.06		5–6			
				6–7			
4.5	60	5.82–7.22					
4.5	60	3.31–7.50					
7.0	45					4.7–6.3	Author's measurements
7.0	45					6.0–9.0	Author's measurements
7.0	45					7.5–11.4	Author's measurements
7.0	45					9.0–12.8	Author's measurements

Myles et al.: Test mixtures are n-heptane-methylcyclohexane and n-dodecane-cyclopentylcyclohexane; the HETP's are for various pressures and a medium reflux flow.

Table 31 (continued)

II. Plate columns [215]

Column type (due to)	Distance between plates (mm)	Column diameter (mm)	Plate capacity (ml)	Plate efficiency (%)[1]
Keesom	23–25	≈ 33	1.0	50
Groll-Oldershaw	25	25	ca. 1–2	80–90
Sigwart	65	50	ca. 7.5	100–110
Bruun	20 and 40	5	0.7 and 1.4	70–100
Greiner and Friedrichs	40	45	ca. 2–2.5	64–66
Stage (vapour-collision plates)		60		70–90
Stage (bubble-cap plates with shielded downcomers)		50		80–95
Stage (vapour-collision bubble-cap plates)	35–150	30–120	3–75	75–95
Schmückler and Fritz				80–90
Brand				40–90
Normschliffgeräte				40–95

[1] Caution should be used in comparing these figures since they represent only rough estimates of the plate efficiencies (cf. chap. 7.3.3)

Barth [220] and Leva [221] appeared, a large number of contributions have been written with the aim of elucidating the principles of pressure drop in packed columns. In an extensive investigation on the relation between pressure drop and the fractionating effect in packed columns Brauer [208] determined the pressure drop with 13 types of packing (Table 32) as a function of the flow. The experiments were performed in a column of 37 mm I. D. and 1 m length with the test mixture n-heptane-methylcyclohexane. The results of these measurements are represented in Fig. 102 and bring out the following facts:

1. All curves have the same characteristic form. The limiting breaks in the curves lie on straight lines $a - a$, $b - b$, $c - c$.
2. In all the ranges of load limited by the breaks in the curves the course of the pressure drop lines can be represented by a formula of the form

$$\Delta p/h = c f^n. \tag{140}$$

	Type of vapour flow
$n = 1.0$ in the range below $a - a$	Laminar
$n = 1.78$ between $a - a$ and $b - b$	Turbulent
$n = 2.7$ between $b - b$ and $c - c$	Turbulent
$n = 3.3$ in the range above $c - c$	Flooding, formation of a layer of spray

3. The value of c in formula (140) is a function of the properties of the vapour and the liquid and of the characteristics of the packing.

Fig. 103 shows the relation between pressure drop and the fractionating effect. The number of theoretical plates per metre of the spiral packing listed in Table 32 was plotted against the pressure drop in the turbulent region. The linear form of the curve shows that the same relationship exists between the flow and exchange of heat and material in the whole of the turbulent region, in other words that the mechanism of exchange is constant. Above the break line c—c the vapour passes as bubbles through the accumulated liquid and the process of exchange follows other laws [203, 206, 208].

In his investigations Kast [222] considers the actual path of the two-phase flow

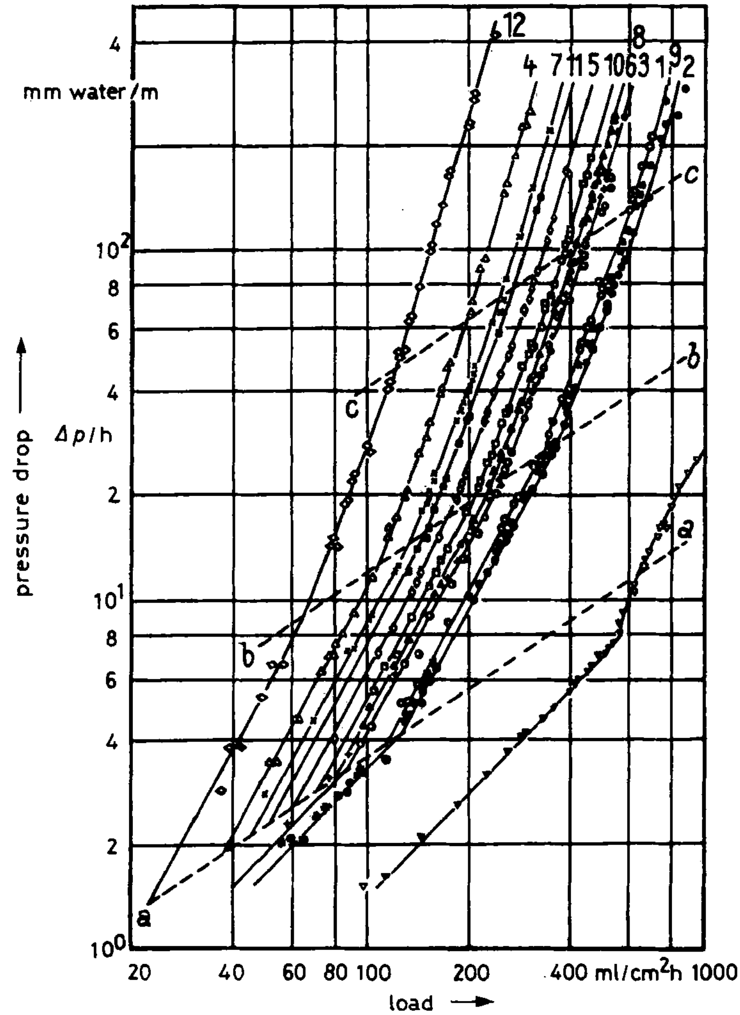


Fig. 102
Pressure drop caused by the packings listed in Table 32 as a function of the liquid load (Brauer)

Table 32

Packings used by Brauer for pressure drop measurements [208]

No.	Dimensions mm	Type	Material	Diameter ratio, packing unit: column $d_{Fk}d_K$	Relative free volume I ε_0	Specific surface of packing o (m^2/m^3)	Unwound length l_r (mm)
1.	3 × 3 × 0.45	spaced spiral	18—8 stainless steel	1:12.3	0.777	1802	43
2.	4 × 4 × 0.5	spaced spiral	18—8 stainless steel	1:9.25	0.822	1480	61
3.	3 × 3 × 0.40	spaced spiral	18—8 stainless steel	1:12.3	0.771	1815	44
4.	2 × 2 × 0.3	close spiral	18—8 stainless steel	1:18.5	0.661	2680	32
5	3 × 3 × 0.45	close spiral	18—8 stainless steel	1:12.3	0.704	1717	60
6.	4 × 4 × 0.4	close spiral	18—8—3 stainless steel	1:9.25	0.760	1543	100
7.	2 × 2 × 0.25	Sheet-metal rings with cross piece	18—8 stainless steel	1:18.5	0.716	1965	10.5
8.	4 × 4 × 0.3	Sheet-metal rings with cross piece	18—8 stainless steel	1:9.25	0.824	1176	18.7
9.	6 × 6 × 0.4	Sheet-metal rings with cross piece	18—8 stainless steel	1:6.16	0.811	946	24.1
10.	5 × 5	Raschig rings	Porcelain	1:7.4	0.475	977	
11.	3.7 × 7.4	Ellipsoids	Aluminium		0.306		
12.	2	Balls	Glass	1:18.5	0.339	1786	
13.	16 × 16	Raschig rings	Porcelain	1:2.3			

and replaces the length of packing H_K with an effective length μH_K, where μ is a physically justified path factor. In the region of transition from laminar to turbulent flow in packed columns Kast reports good agreement of measurements by himself and others with the pressure drop formula for packing units up to a size of 50 mm. Teutsch [223] derived a semi-empirical equation which allows a straightforward calculation of pressure drop in terms of a dimensionless pressure loss. The range of validity is mentioned, there being the limitation that Teutsch's work covered only packing units $\geqq$ 25 mm. Gelbe [224] examined spaced helices of size 4 × 4 × 0.5 mm with the mixture n-decane-trans-decane in the range from 10 to 740 torr. On the basis of Gelbe's measuring results Glaser [225] developed the following relation for a coefficient ε_1:

$$\varepsilon_1 = \frac{\varrho_D \mathrm{HTU}/H_K}{\Delta p/X_K}, \tag{141}$$

where ϱ_D = vapour density (kg/m³), K_K = length of packing (m), HTU = height of a transfer unit (m), Δp = pressure drop (kp/m²).

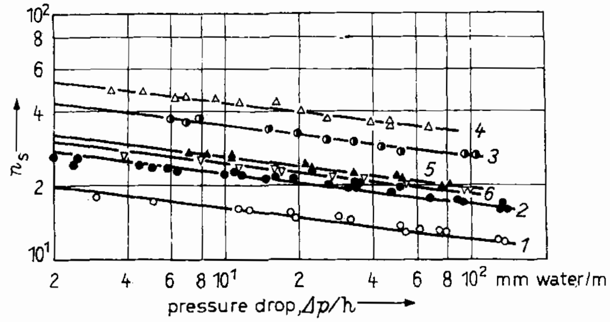


Fig. 103
Relation between pressure drop and fractionating effect (Brauer) (cf. also Table 32)

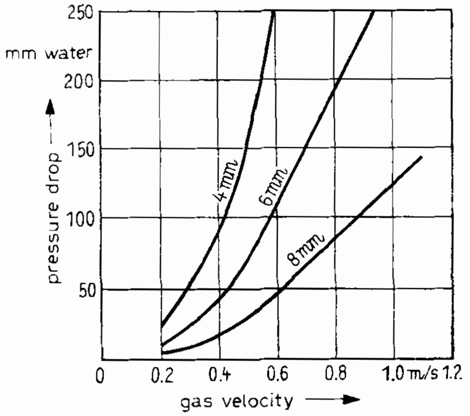


Fig. 104
Pressure drop with porcelain saddle packing (4—8 mm) as a function of the rate of gas flow (air); liquid (water):
40 ml/cm² × h

The coefficient ε_1 as a function of the relevant parameters can also be given as a dimensionless value. It varies with the load in a way which clearly indicates the close connexion between flow and material transfer and the influence of pressure.

Reichelt and Reichelt and Blass used their own measuring data and those of others to investigate the flow through packings consisting of Raschig rings and spheres. They found equations for the calculation of the pressure drops in sphere and cylinder packings with one-phase flow.

Heckmann and Krell [226] carried out measurements of the pressure drop across porcelain saddle packing (4, 6 and 8 mm), with air as gas and water as liquid. The effective column length was 1 m, the column diameter 22 mm. Fig. 104 gives the results.

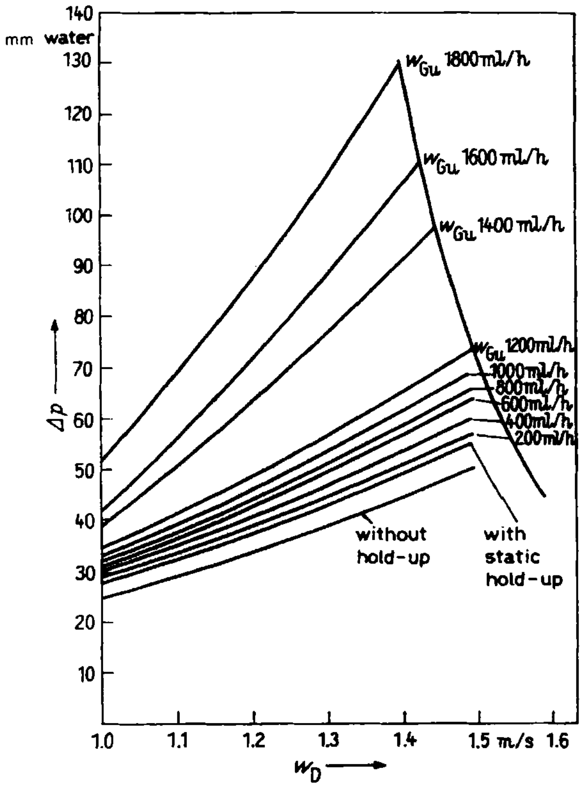


Fig. 105
Pressure drop across Wilson spirals (3 mm) with an increasing flow of water, as a function of the gas velocity (air)

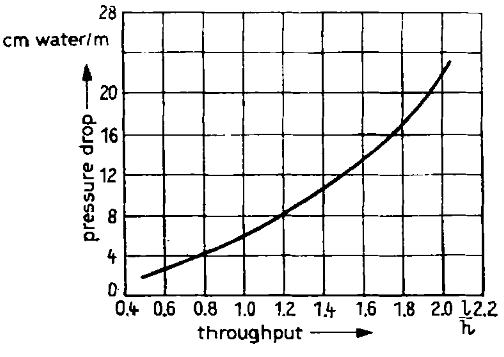


Fig. 106
Pressure drop found with wire gauze rings (3 × 3 mm) as a function of the throughput at atmospheric pressure. Column diameter: 25 mm; average height of packing: 1 m (measurements by Thürkauf)

The effect of an increasing flow of liquid with 3 mm Wilson spirals is shown in Fig. 105. A very favourable pressure drop relationship is found with wire gauze (*e.g.* Dixon) rings, as can be seen from Fig. 106 and 107. The figures plotted are average values obtained with a number of different test mixtures.

The "comparable" air velocity as a measure of the vapour or gas load was derived by Neumann [227] from empirical results.

Reed and Fenske [228] have evolved a formula for calculating the pressure drop in packed columns which is given by Brauer [208] in this form:

$$\Delta p = \frac{1.67(D \times \varrho/\eta \times O)^{1.59}}{p \times M \times (\varepsilon_0 - V_F/V_K)^3} \times \boldsymbol{R} \times T \times H_K \times \boldsymbol{g} \times \eta^2 \times O^3 \qquad (142)$$

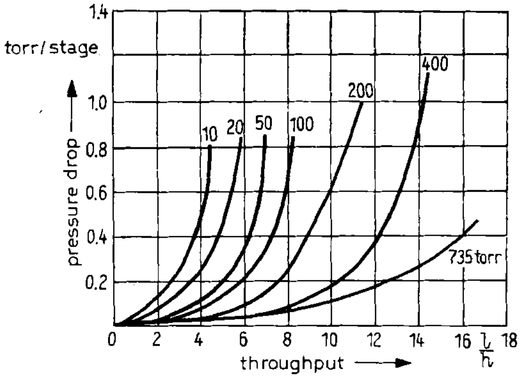


Fig. 107
Pressure drop per separating stage found with wire gauze rings, as a function of the throughput at various operating pressures. Column diameter: 50 mm (2 inches); average height of packing: 1 m (measurements by Thürkauf)

in which p = the absolute pressure (kg/m^2); Δp = the pressure differential (kg/m^2); M = the molecular weight; $\varepsilon_0 = (V_K - V_{FK})/V_K$ = the relative free volume of the dry packing; V_K = the volume of the effective length of column (m^3); V_{FK} = the volume of the packing (m^3) (measured by displacement of liquid); V_F = the volume of the liquid present in the column (m^3); $\boldsymbol{R}$ = the gas constant (kg · m/K); T = the absolute temperature (K); H_K = the effective length of the packing (m); $\boldsymbol{g}$ = acceleration due to gravity (m/sec^2); η = dynamic viscosity of the vapour (kg · sec/m^2); ϱ = density of the vapour (kg · sec^2/m^4); O = surface area of packing, relative to column volume (m^2/m^3); D = vapour rate (m^3/m^2 sec).

The agreement with experimental data is very good if the packing has been charged in the optimum manner.

The fact that the properties of the substance undergoing distillation have an appreciable influence on the pressure drop is apparent from the curves shown in Fig. 108 [229] and from Table 33 [200]. The data listed in the latter table were determined in an Oldershaw sieve-plate column (28 mm diameter) with 30 actual plates.

It should be noted that the substances mentioned in Table 33 were so chosen that they differed in density and surface tension at their boiling points.

Umholtz and van Winkle [230] also determined the pressure drop as a function of load for sieve-plate columns, which had a diameter of 25 mm (1 inch), a plate spacing of 50 mm (2 inches), a free area of 16.2% and contained a varying number of holes of different diameters.

Data showing the dependence of the pressure drop and the limits of load on the

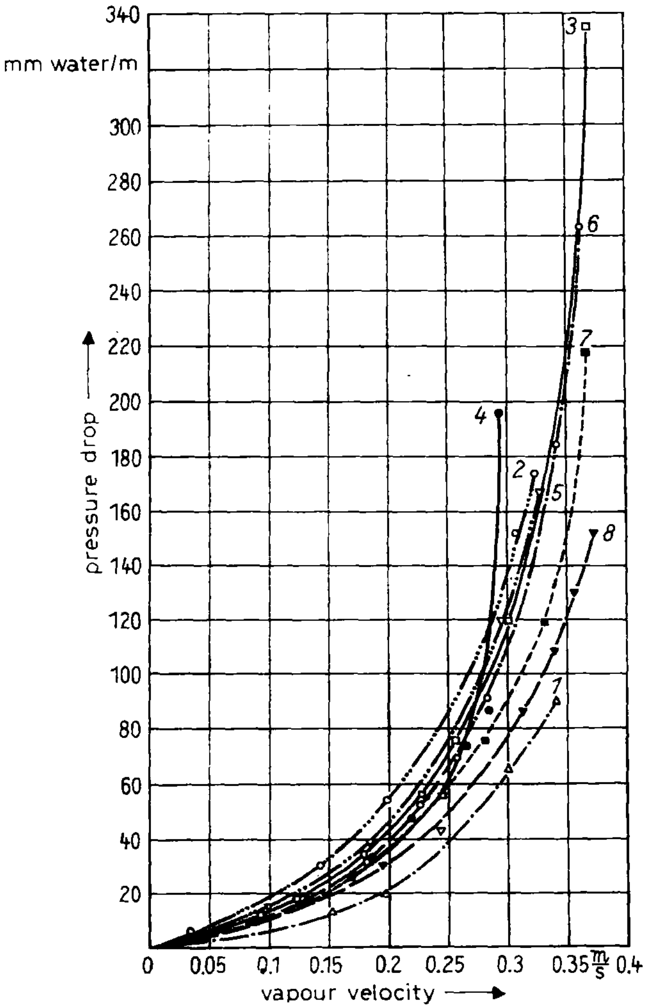


Fig. 108
Pressure drop as a function of the vapour velocity for various substances, according to Stage

1 = Ethanol, 2 = Chloroform, 3 = Benzene, 4 = Heptane, 5 = Di-isopropyl ether, 6 = Amyl alcohol, 7 = Toluene, 8 = Ethyl acetate

distillation pressure, for various types of packing, have been collected in Table 34 [192]. From these figures it can be seen that spheres have a relatively narrow load range and cause a large pressure drop on account of their small free volume (26%). On the other hand Heli-grid packing (section 7.3.4) gives a wide load range and a high upper load limit (see also Refs. chap. 1: [39]).

For a calculation of the *required column diameter* it is necessary to know the upper limiting velocity. Schumacher [231], on the basis of theoretical considerations, has calculated velocity constants b_G for various types of packing by means of the following formula:

$$k_G = \varrho_R \times \frac{w_G^2}{d \times g}, \qquad w_G = \sqrt{\frac{k_G \times d \times g}{\varrho_R}} \text{ m/s}, \tag{143}$$

where $\varrho_R = \varrho_D/\varrho_F$ (= density of vapour/density of liquid, in the same units at the operating pressure), and further w_G = the limiting velocity, m/sec; k_G = the limiting velocity constant; d = the diameter of the packing units in m; g = the acceleration due to gravity (9.81 m/sec^2).

Table 33

Pressure drop in an Oldershaw sieve-plate column during the distillation of substances having various densities and surface tensions [200]

n-Heptane		Methylcyclohexane		Benzene		Formic acid	
Load (ml/h)	Pressure drop per actual plate (torr)	Load (ml/h)	Pressure drop per actual plate (torr)	Load (ml/h)	Pressure drop per actual plate (torr)	Load (ml/h)	Pressure drop per actual plate (torr)
1000		1000		1000	0.76	200	0.88
1500	0.50	1500	0.62	1500	0.82	400	0.95
2000	0.53	2000	0.63	2000	0.84	600	1.02
2500	0.55	2500	0.65	2500	0.87	800	1.09
3000	0.57	3000	0.67	3000	0.91	1000	1.18
3500	0.60	3500	0.71	3500	1.00	1125	1.23
4000	0.64	4000	0.77	4000	1.11		
4500	0.70	4500	0.85	4280	1.17		
5000	0.77	5000	0.93				
5230	0.80	5230	0.97				

Column diameter: 28 mm; number of actual plates: 30.

Substance	$Kp._{760}$	ϱ_{20}
Benzene	80.09	0.87895
n-Heptane	98.424	0.68368
Formic acid	100.75	1.2206
Methylcyclohexane	101.10	0.76944

The surface tension of these substances in contact with air lies in the range of 20—40 dynes/cm at 20 °C.

Table 34

Pressure drop and load limits for various types of packing at a number of pressures [192]

Packing	Size (mm)	Column diameter: 25 mm	20 torr		50 torr		100 torr		150 torr		760 torr	
		length: 1.07 m	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
Heli-grid	—	Pressure loss (torr),	—	—	5	28	5	28	6	27	1	27
		Load limits (g/h)	—	—	1200	1650	650	1600	550	1100	500	5500
Spheres, loose packing	3.6	Pressure loss (torr)	6	26	5	32	6	35	5	32	3	27
		Load limits (g/h)	450	700	500	900	700	1150	1000	1400	125	2500
Spheres, close packing	3.6	Pressure loss (torr)	3.5	31	3.5	30	4	30	4	35	5	25
		Load limits (g/h)	380	720	620	900	800	1170	1000	1300	—	—
Saddle packing	6.3	Pressure loss (torr)	2	8	1	8	—	—	2	8	2	8
		Load limits (g/h)	450	800	600	1100	—	—	900	2200	2600	4800
Triple glass helices	6.3	Pressure loss (torr)	1	5	1	5	—	—	1	5	1	—
		Load limits (g/h)	450	900	800	1400	—	—	1000	2200	1200	1600
Single glass helices	6.3	Pressure loss (torr)	2	14	3	14	—	—	3	18	2	—
		Load limits (g/h)	450	900	970	1200	—	—	1450	2000	2400	—

This formula deals with the influence on the limiting velocity of the size and type of the packing and the density of the vapour and the liquid, but does not take into account the viscosity of the vapour and liquid and the surface tension of the liquid.

The values found for the constant k_G were as follows:

for Raschig rings	0.01
for Prym rings	0.021
for Berl saddles	0.019
for solid packings	0.004
for helices	0.0126 (the author's measurements)

As an aid in determining the limiting velocity a nomogram was developed (Fig. 109), the use of which can be illustrated by the following example.

The limiting velocity is to be determined for the countercurrent distillation of a C_7 fatty acid at 20 mm Hg (boiling point 125.0 °C at 20 mm), using 4 mm saddle packing.

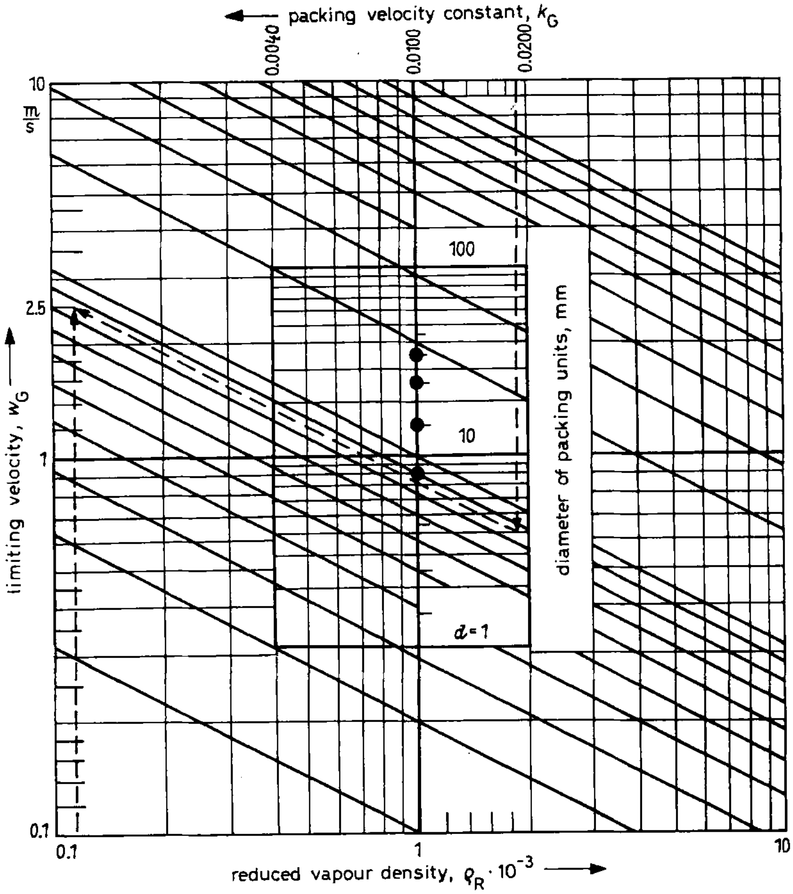


Fig. 109
Nomogram for the determination of limiting velocities for packings (Schumacher)

Determination of the necessary data

$$k_G = 0.019;\ \varrho_D = \frac{20}{398} \times 130 \times 0.01605 = 0.105 \text{ (formula (37))};$$

$$\varrho_R = \varrho_D/\varrho_F = 0.105/900 \text{ (g/l at 200 mm)} = 0.1165 \times 10^{-3}.$$

Use of the nomogram

The example has been indicated by dashed lines in Fig. 109. Through the point of intersection of the vertical line for the constant $k_G = 0.019$ and the horizontal line for the diameter of the packing used, $d_p = 4$ mm, we draw a line parallel to the inclined network. From the point where this parallel intersects the vertical line from $\varrho_R = 0.12$ we then proceed horizontally to the vertical scale for the limiting velocity, where the required figure, 2.5 m/sec, is read off.

Obviously the column cannot be loaded to this limit in practice. A load of 50 to 70% of the calculated limiting velocity, say 60% = 1.5 m/sec, may be taken as suitable.

If we modify the previous example by adding the requirement that the C_7 fatty acid shall be distilled at 20 mm pressure with a load of 440 g/h, we can calculate the necessary column cross section from the limiting velocity just determined, by using the formula

$$f = \frac{\mathbf{D} \cdot 22400 \cdot (273 + \vartheta) \cdot 760}{\mathrm{w_D} \cdot 3600 \cdot 273 \cdot p}, \tag{144}$$

in which f = the column cross sectional area in cm²; $\mathbf{D}$ = the amount of vapour in g moles/h; ϑ = the distillation temperature in °C; $\mathrm{w_D}$ = the selected vapour velocity in cm/sec; p = the distillation pressure, mm Hg.

This formula reduces to

$$f = \frac{17.3 \times \mathbf{D} \times \mathbf{T}}{\mathrm{w_D} \times \mathbf{p}} \text{ cm}^2. \tag{145}$$

At a throughput of $\mathbf{D} = 440$ g/h = 3.4 g moles/h and $\mathrm{w_D} = 150$ cm/sec we find

$$\mathbf{f} = \frac{17.3 \times 3.4 \times 399}{150 \times 20} = 7.9 \text{ cm}^2 \tag{146}$$

from which the radius works out at

$$r = \sqrt{7.9/\pi} = 1.6 \text{ cm}. \tag{147}$$

When the distillation is carried out at normal pressure, formula (145) becomes

$$\mathbf{f} = \frac{0.0228 \cdot \mathbf{D} \cdot \mathbf{T}}{\mathrm{w_D}} \text{ cm}^2. \tag{148}$$

For comparison we shall calculate the limiting load for a column of 30 mm diameter, in which n-heptane is distilled at normal pressure; 4 mm saddle packing is employed. The limiting velocity for this packing is 0.38 m/sec. Then, by formula (148),

$$\begin{aligned} D &= \frac{f \cdot w_D}{0.0228 \cdot T} = \frac{7.9 \times 38}{0.0228 \times 371} = 35.5 \text{ g mole/h} \\ &= 3550 \text{ g/h} = 5200 \text{ ml/h}. \end{aligned} \tag{149}$$

That such high loads can actually be realized with a column of 30 mm diameter is confirmed by measurements carried out by Kolling [171]. The second calculation above was included to show to what extent the use of reduced pressure increases the vapour velocity and thereby reduces the possible load.

Schumacher [231a] has introduced an equation for the determination of the wet pressure drop and divided it into two dimensionless coefficients for pressure drop and gas flow. This allows the points of flooding onset, spraying and flooding to be characterized consistently for all packings wetted by falling films. A more recent dimensionless irrigation coefficient makes it possible to calculate the admissible gas velocities not only for the regions of intense gas load but also for those of intense irrigation.

Methods for calculating the limiting velocity for plate columns of laboratory size have, as far as the author is aware, not been published. The formulae valid for industrial columns prove to be inapplicable to small-scale apparatus. Experience shows that plate columns can be submitted to only about one third of the load that can be applied to packed columns of the same diameter; this is due to the resistance resulting from (a) the liquid present on the plates and (b) the restrictions in the vapour passages.

The aerodynamic aspect of vapour flow in packed columns has been dealt with by Barth [220], who demonstrated that packing having sharp angles gives rise to two or three times the pressure drop caused by rounded bodies.

By considering flow, David [191] derived a method for calculating the theoretical plate number of a packed column.

He assumed that since the pressure drop, velocity and density of the vapour greatly influence the efficiency of a packed column the calculation should be based on these parameters. By analogy with a well-known equation for the pressure drop in pipes, he formulated a flow factor ξ as follows:

$$\xi = \frac{\Delta p \cdot 2g}{w_D^2 \cdot \varrho_D} \cdot \frac{d}{l} \tag{150}$$

in which Δp = the pressure drop (mm water column), g = the acceleration due to gravity (m/sec^2), d = the diameter of the packing units (m), w_D = the vapour velocity, relative to the empty column cross section (m/sec), ϱ_D = the density of the vapour (kg/m^3), l = the height of the packing (m).

The quotient of the specific stage number and the flow factor was regarded as a fundamental value, independent of the Reynolds number Re. This quotient proved to be 0.13 for all mixtures evaluated by David, at any pressure. As he assumed that the greatest separating effect is obtained at the upper limiting velocity, the expression

$$n_{\text{opt}} = 0.13\xi \tag{151}$$

would give the optimum efficiency of a laboratory column with a packed height of 1 m.

All experimental data taken together yield an empirical formula for the height of packing:

$$H_K = 1 + (n_{th} - 0.13 \times \xi) \times \frac{10 + d}{120} \text{ (m)}. \tag{152}$$

The formula refers to a reflux ratio $v = \infty$, *i.e.*, for a liquid-vapour ratio $F/D = 1$. Beck [244] evaluated 115 experiments on the system water-air and derived new equations for packing sizes from 8 to 80 mm and column diameters from 150 to 1200 mm. Savkovič-Stevanovič, Simonovič and Popovič [244a] examined the efficiency of a laboratory column (diameter, 25 mm; separating length, 1.2 m) by determining the HETP values for various pressure drops and vapour velocities. The packing units were of 0.35 mm steel wire with a diameter of 4 mm. The system benzene/carbon tetrachloride (30 mol% carbon tetrachloride) was used as test mixture.

Eq. (152a) yields HETP values as a function of the reflux rate. The mean deviation from experimental data is as small as 1.7%:

$$\ln \mathrm{HETP} = 29.0028 + 11.0310 \ln \mathrm{M} - 0.9774 \ln^2 \mathrm{M}, \tag{152a}$$

M = reflux rate (g/cm² h),

HETP = height equivalent to a theoretical plate (cm).

The dependence of the HETP values on the vapour velocity was determined using eq. (152b):

$$\mathrm{HETP} = 0.0689 + 0.1310 w_D - 0.3823 w_D^2, \tag{152b}$$

w_D = vapour velocity (m/s).

A comparison of experimental and calculated data for the HETP shows that the equation of Murch [185] and eq. (152a) give good results. In contrast, the equation of Hands-Whitt [J. Appl. Chem. (London) 1 (1951) pp. 135—140] gives large deviations.

4.12 Heat calculations

Heat calculations are seldom carried out in connection with laboratory distillation, since the amounts of energy consumed are relatively small, and heat economy is usually of minor importance. With electricity a higher voltage than necessary is generally used and the current is regulated with resistances or auto-transformers. Gas is still utilized in the laboratory for certain forms of distillation, such as the ASTM and Engler procedures, and for heating oil, sand or metal baths. As a rule, however, gas flames are avoided because of the dangers of breakage and superheating, and of explosion in the distillation of inflammable substances. Heating by means of electric resistances in the form of embedded wires or hot plates is at present the preferred method. Recently, infrared heaters with bright or dark elements have also become popular, particularly for low temperatures; they have the advantage of giving radiation in a concentrated form [232]. The use of high-frequency heating in the laboratory is still in the experimental stage.

In *batch operation* the initial mixture is first heated in the still pot to its boiling point. A further supply of heat, corresponding to the heat of evaporation, converts the liquid into vapour. The rate of evaporation depends on the amount of heat supplied in unit time. In *continuous distillation* part of the heat is usually introduced by the preheater. An additional quantity of heat is supplied in the still pot, since an exchange of heat takes place in the column in countercurrent distillation.

If the total heat required is Q, the heat balance for the various types of distillation (disregarding the heat necessary for bringing the charge to its boiling point) can be formulated as follows.

I. *Simple distillation*

$$Q = Q_K = Q_D + Q_V = Q_{Ko} + Q_V. \tag{153}$$

II. *Countercurrent distillation*

a) batch

$$Q = Q_K = Q_D + Q_R + Q_V = Q_{Ko} + Q_V \tag{154}$$

b) continuous

$$Q = Q_K + Q_Z = Q_D + Q_R + Q_V = Q_{Ko} + Q_V \tag{155}$$

where Q = the heat supplied to the still pot; Q_K = the heat supplied to the preheater in continuous distillation; Q_D = the heat content of the distillate as vapour; Q_R = the heat content of the reflux as vapour; Q_V = the heat loss; Q_{Ko} = the heat removed by the condenser for condensation and cooling.

These equations are valid only if the distillate and reflux are cooled to the same temperature as the liquid present in the still pot. Fig. 110 shows these quantities diagrammatically.

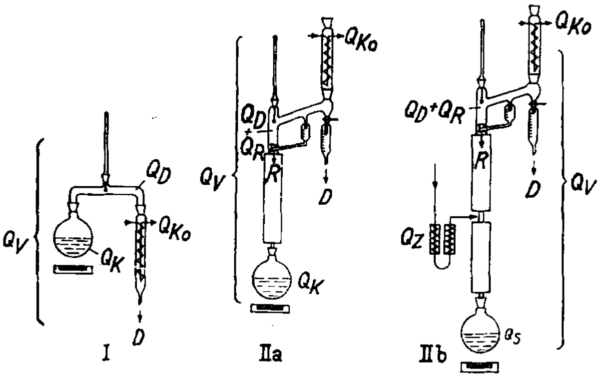


Fig. 110
Heat supplied or withdrawn in I. Simple distillation, IIa) batch countercurrent distillation, IIb) continuous countercurrent distillation

As an illustration of the quantities of heat required in a laboratory distillation the following example is given.

A mixture of benzene and toluene (50—50% wt.) is to be separated at normal pressure with a reflux ratio of 2:1 at a load of 0.5 kg/h, the charge being 2 kg (temp. 20°C; Table 35).

In the calculation it will be assumed that only benzene evaporates, though actually, of course, a certain amount of toluene will also vaporize. As the heat of evaporation of toluene is lower than that of benzene, however, the small error so made is on the safe side. The heat loss is difficult to estimate and can be largely avoided by proper insulation (see chap. 7.7). The question of how heat losses may be avoided will be discussed below.

Table 35

Data for the components

Component	$Kp._{760}$	Spec. heat, c_p (kcal/kg)	Heat of vaporization, $\Delta_V H$ (kcal/kg)
Benzene	80.1	0.43 (50°C)	93.8 (B.p. 760 mm)
Toluene	110.6	0.43 (50°C)	86.5 (109.7°C)

Heat required to bring the mixture to 80°C

$$Q_K = B(\vartheta_2 - \vartheta_1)\,c_p + Q_V; \tag{156}$$

$$\begin{aligned} Q_K &= 2(80 - 20)\cdot 0.43 = 51.6\ \text{kcal} \\ \text{Heat loss (say 10\%)} &= \underline{5.2\ \text{kcal}} \\ &\ 56.8\ \text{kcal} \end{aligned} \tag{157}$$

(B = charge, kg; ϑ_1 and ϑ_2 = initial and final temperatures)

Heat required to evaporate the distillate and reflux

$$Q_K = (E + R)\cdot \Delta_V H + Q_V; \tag{158}$$

$$\begin{aligned} Q_K &= (0.5 + 1.0)\cdot 93.8 = 140.7\ \text{kcal/h} \\ \text{Heat loss (say 10\%)} &= \underline{14.0\ \text{kcal/h}} \\ &\ 154.7\ \text{kcal/h} \end{aligned} \tag{159}$$

The heat equivalent is taken to be:

$$1\ \text{kWh} = 860\ \text{kcal}; \tag{160}$$

the heating source must therefore supply

$$154.7/860 = 0.18\ \text{kW} \tag{161}$$

for the intended operation.

The method of calculating the necessary condenser surface area will be described in section 7.4. The formula in question (191), can also be used to estimate the heating surface of the heater required in continuous distillation, Q then being the amount of heat supplied to the liquid, F the surface area and $\Delta\vartheta_m$ the difference in temperature between the heating agent and the liquid. The mean temperature difference is calculated after (199). In the laboratory, glassware is generally employed. With glass the heat transfer coefficient is only 2.5×10^{-2} kcal/cm^2 h deg. C, but if round-bottomed flasks are used, as will normally be the case, a sufficient area for heat transfer is available at the customary speeds of evaporation. The same applies to condensers, which will become overloaded only at extremely high distillation rates.

Table 36

Heat loss from a column insulated with magnesia (85%)

Temperature differential		Thickness of insulation					
		1 inch			2 inches		
$\Delta\vartheta$	Substance	Heat loss		Condensate	Heat loss		Condensate
(°C)		cal/h	cal/cm^2·h	ml/h	cal/h	cal/cm^2·h	ml/h
55	Benzene	4800	20.0	54	3450	14.3	42
85	Toluene	7600	31.6	101	5400	22.4	73
151	p-Cymene	13800	57.2	238	9800	40.7	170

For insulating the column against heat loss, substances of low heat conductivity are chosen (section 7.7), for instance magnesia, asbestos, mineral wool and glass wool, or vacuum jackets [153]. They are, of course, never completely effective, as exemplified by the data in Table 36. These data were obtained with a column of one inch diameter and a length of one foot. The insulation consisted of magnesia, in layers one and two inches thick. The temperature differential was the boiling point at 760 mm minus 25 °C (average room temperature). The fourth and seventh columns show the heat loss per unit area of the glass columns.

Junge [233] has carried out similar measurements on a column provided with a vacuum jacket and on a column insulated with glass wool 50 mm (2 inches) thick. The heat losses found, in calories per cm^2 per hour, are shown in Fig. 111 against the inner column temperature. This figure also includes the data of Rose [153] already listed in Table 36. The heat lost by an insulated distillation column is by no means negligible. It gives rise to a "false reflux" that can be avoided only by incorporating a heating element in the insulating jacket. It is necessary for the column to operate adiabatically if reliable and reproducible results are to be obtained.

The heat losses Q of an insulated column can also be calculated by means of the following formula:

$$Q = \frac{\lambda \cdot 2\pi \cdot H_K \cdot \Delta\vartheta}{2.3 \log d_a/d_i} \text{ (kcal/h)}, \tag{162}$$

in which λ = the thermal conductivity of the insulation in kcal/m · h · °C; H_K = the column length in m; $\Delta\vartheta$ = the difference in temperature (column interior ambient); d_a = the external diameter of the insulation (m); d_i = the column diameter (m) = inner diameter of insulation.

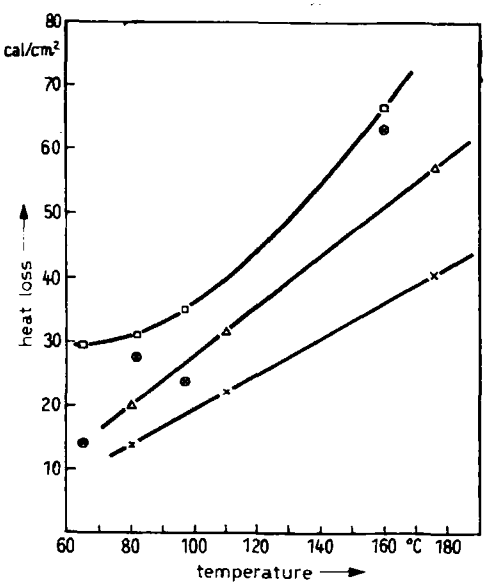


Fig. 111
Heat loss of insulated columns in cal/cm² h as a function of the inside column temperature

(△) = Column insulated with magnesia (85%), thickness one inch (25.4 mm)*;
(×) = Column insulated with magnesia (85%), thickness two inches*;
(⊗) = Column insulated with glass fibre, thickness two inches**;
(□) = Column insulated with a vacuum jacket**

* Rose [153]; ** Junge [233]

Example. A column 25 mm in diameter and 5 m long has been covered with channel shaped sections of glass wool insulation (λ = 0.055 kcal/m · h · °C) with a wall thickness of 62.5 mm. The internal temperature is 76.6 °C, room temperature 18 °C. Required: the heat loss. By formula (162):

$$Q = \frac{0.055 \times 6.28 \times 5 \times 58.6}{2.3 \times \log 6} = 56.5 \text{ kcal/h}. \tag{163}$$

Thus, despite insulation a heat loss of 56.5 kcal/h arises which has to be offset by an additional heater in order to avoid wall flow.

4.13 Distillate properties and distillation diagrams

In the practice of laboratory distillation it is customary to report not only the boiling point curve, but also subsidiary data for the distillate, such as the density, the refractive index, the solidification or melting point and occasionally also values such as the molecular weight and the iodine value (Fig. 112). Of late, infrared spectroscopy, mass spectrometry and gas chromatography have been used to an increasing extent for identifying the fractions. The present trend is towards determinations with continuous flow apparatus, so as to obtain continuous readings. The collection of comprehensive data is particularly desirable in the case of an analytical distillation, where the characterisation of the distillate by boiling point alone is usually not sufficient [234].

Constants for chemical compounds are to be found in the usual books of reference, *e.g.* [235], but the published figures should be considered critically. Considerable

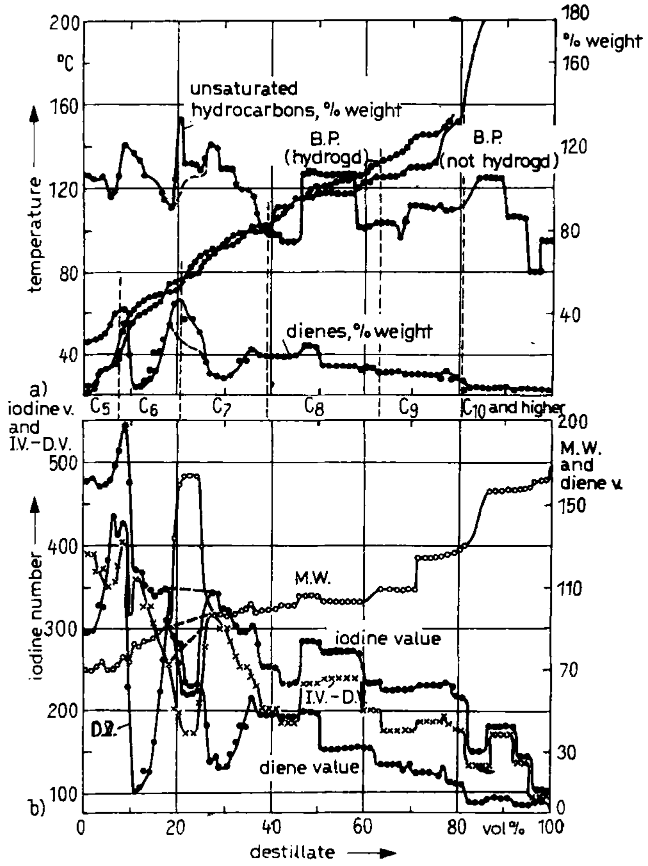


Fig. 112
Distillation curve of a gasoline with curves for distillate properties

differences often occur between the values reported by various authors, even in the case of well-known substances such as benzene and 1.2-dichloroethane. In general, preference should be given to recent data, which are more likely to have been determined with sufficient accuracy. By plotting the constants for pure compounds in a distillation diagram (Fig. 84), identification is greatly facilitated.

Unfortunately it will frequently occur that the desired constants are not to be found in the literature in the required form, and that they will need conversion to other conditions or recalculation. The fundamental work by Reid and Sherwood [235] deals with the properties of gases and liquids and their calculation. Another excellent reference book has been written by Hecht et al. [236]. It contains a systematic survey of the methods for calculating thermodynamic data of gases and liquids.

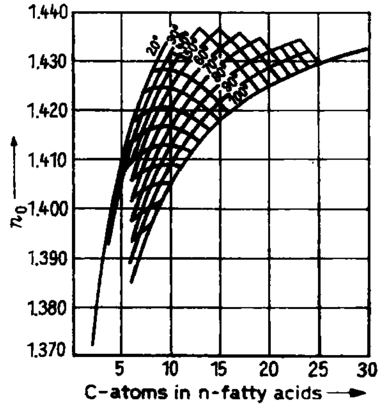


Fig. 113
Relation between the refractive indices at various temperatures of the normal fatty acids and the number of carbon atoms

The refractive index is generally given for various temperatures in books of reference, so that interpolation is possible If the refractive indices of a homologous series of compounds, at a series of temperatures, are plotted as a function of the number of carbon atoms, one obtains, according to Stage [237], a family of hyperbolae. This property may be used for extrapolation (Fig. 113). It should be noted that, on an average, a change in temperature of 1 deg. C causes a change in the refractive index of about 5 units in the 4th decimal place, and it is therefore necessary to measure the temperature of observation accurately (if possible to within 0.1 deg. C). Convenient nomograms for deriving various properties of materials are to be found in publications of Kharbanda [238] and Orlicek and Pöll [239].

When a distillation is performed at atmospheric pressure it is necessary to take several readings of the barometric pressure. Variations of 20 mm in the reading can, for instance in the case of benzene, give rise to differences in the boiling point of 1 deg. C. The barometer should be checked against a precision instrument and a correction should be applied for the influence of temperature on the mercury column and the scale. This can be done without calculation by means of a nomogram due to Häussler [240] (Fig. 114). It is based on the formula

$$b_{\text{korr}} = b \cdot [1 - (\alpha - \beta) \cdot \vartheta] \text{ torr} \qquad (164)$$

in which b_{korr} = the corrected barometric pressure, mm Hg; b = the barometer reading, mm Hg; α = the coefficient of expansion of mercury (0.000182/deg. C); β = the coefficient of expansion of the scale material (brass: 0.000019; glass: 0.000008/deg. C); ϑ = the air temperature in °C.

Glass thermometers (*cf.* section 8.2.1) are as a rule, but not always, calibrated with the stem immersed in the constant temperature bath up to the top of the mercury thread. In this case a correction must be applied if part of the thread is not at the required temperature. For this purpose a second thermometer is suspended alongside the projecting stem of the first, so as to indicate the average temperature of the emerging mercury thread. The observed temperature is then corrected by means of the formula

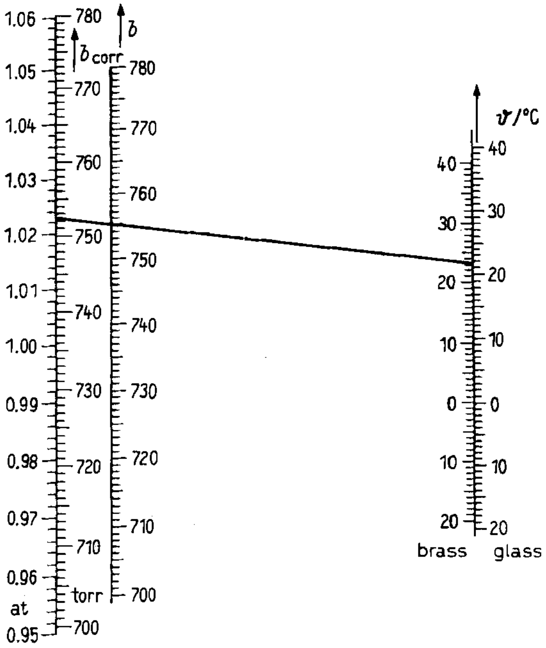


Fig. 114
Nomogram for barometer correction (Häussler)

$$\vartheta_{\mathrm{korr}} = \vartheta + k \cdot a(\vartheta - \vartheta_{\mathrm{m}}), \tag{165}$$

in which $\vartheta_{\mathrm{korr}}$ = the corrected temperature; ϑ = the observed temperature; k = the apparent coefficient of expansion of mercury in the glass of which the thermometer is made (generally about 0.00016); a = the length of the emerging mercury thread, expressed in deg. C; ϑ_{m} = the average temperature of the emergent thread.

A nomogram due to Cole [241] for performing this correction is based on formula (165) with k = 0.000156. It further enables the boiling point, in distillations at atmospheric pressure, to be converted to a pressure of exactly 760 mm, whereby the data reported become strictly comparable. The correction K_1, of the boiling point, for pressure is based on the formula

$$K_1 = (b - 760) \cdot \mathrm{d}\vartheta/\mathrm{d}p \qquad (166)$$

where $\mathrm{d}\vartheta/\mathrm{d}p$ is the pressure variation of the boiling point of the substance being distilled. By a combination of formulae (165) and (166) the total correction, K, to 760 mm pressure becomes

$$K = [k \times a(\vartheta - \vartheta_0)] - [b - 760] \times \mathrm{d}\vartheta/\mathrm{d}p. \qquad (167)$$

Nomogram 9 (Fig. 115) is used as follows. The temperature difference $\vartheta - \vartheta_0$ is marked on scale A and this point is joined to the scale reading for a. The point of intersection of this line with scale C is then connected by a straight line to the barometric pressure on scale D. The point where this straight line intersects the line corresponding to $\mathrm{d}\vartheta/\mathrm{d}p$ for the substance in question gives the final correction in the boiling point for 760 mm pressure and a completely immersed thermometer stem.

Example. In an atmospheric distillation, the top temperature suggests the presence of phenol. The observed temperature ϑ is 179.8 °C. The emergent mercury thread of the thermometer is 40 centigrade degrees long (a), and its average temperature, ϑ_m, is 30 °C. The barometric pressure read off is 750 mm Hg; the value of $\mathrm{d}\vartheta/\mathrm{d}p$ for phenol is 0.045. Point 150 ($= \vartheta - \vartheta_m$) on scale A is joined to point 40 on scale a;

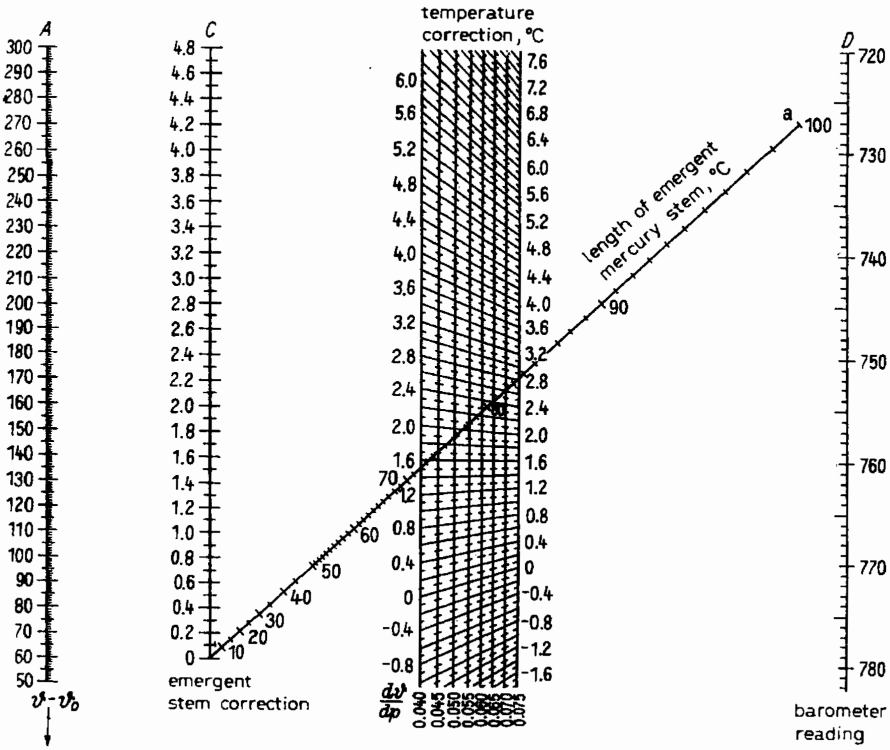


Fig. 115
Nomogram for thermometer correction (Cole)

this line intersects scale C at 0.95. This is the correction for the emergent thread only. If we now connect this point to 750 on scale D, we find that the line for $d\vartheta/dp = 0.045$ is intersected at a point corresponding to +1.4 deg. C. The boiling point, fully corrected to 760 mm pressure and for emergent stem is then $179.8 + 1.4 = 181.2\,^\circ C$.

A similar procedure for determining boiling points at 760 torr was evolved by Reckhard [57]. He obtained group data for 400 organic substances. The procedure is also applicable to multicomponent mixtures.

It is useful to employ printed forms for entering the results of distillations. Such forms make the subsequent graphical representation much easier.

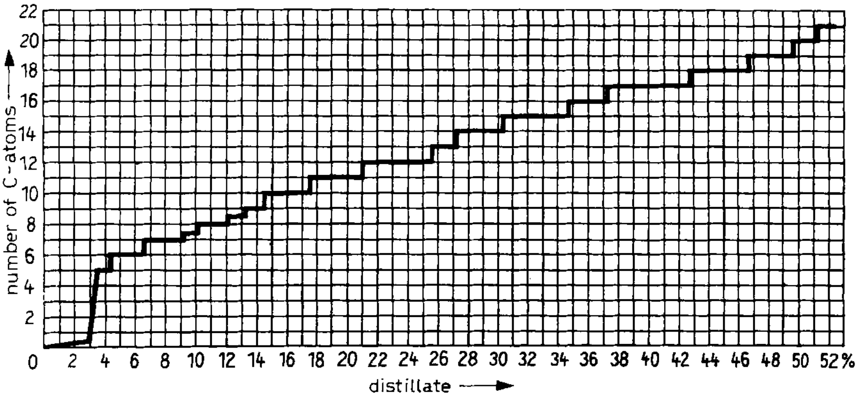


Fig. 116
Step diagram of the distillation of a crude fatty acid mixture

A distillation curve is obtained by plotting the amount of the distillate against the vapour temperature, with the temperature either as the horizontal scale (Fig. 118) or the vertical scale (Figs. 84, 112). Whilst the first type is still employed to some extent in industry, the second type is generally used. It is advisable to draw the diagrams to standard dimensions. The temperature scale may with advantage be made larger than the quantity scale, in order that small differences in temperature may show up. If there is no danger of loss of clarity, all observed values should be included in the diagram, for instance the still pot temperature and the distillation pressure. If certain components have been identified from the results, the fractions in question should be marked off by heavy vertical lines. An example is shown in Fig. 84, which illustrates the fractional distillation of normal fatty acids at 20 mm pressure. For binary mixtures a satisfactory form of diagram is also obtained by plotting the composition of the distillate on one axis against the amount distilled on the other (Fig. 90).

For evaluating the results of a distillation performed on a mixture of homologous compounds it is useful to construct an idealized step diagram (Fig. 116) [242]. From the latter, a diagram of the distribution of the individual compounds may be derived (Fig. 117). A somewhat similar type of figure is that constructed according to the method of Meier-Grolman and Wesolofsky [243], which provides a

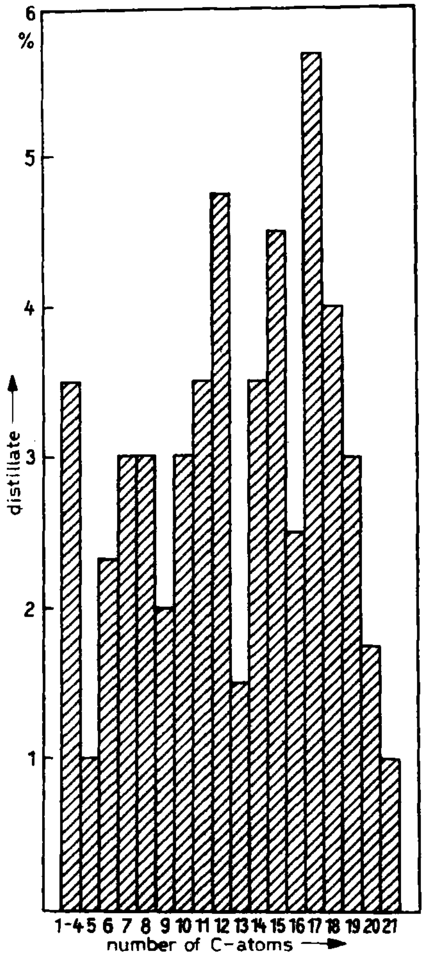


Fig. 117
Distribution diagram showing amount of constant-boiling fractions against the number of C-atoms, for a crude fatty acid mixture

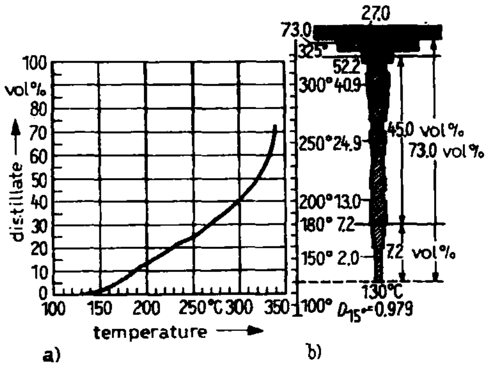


Fig. 118
Boiling point diagram (a) and surface diagram (b) for a shale oil

means of visualizing distillations (particularly those carried out by the ASTM, Engler and other standard procedures) on multicomponent mixtures, such as fuels, tars or shale oils. In this method the diagram is drawn by plotting the temperature along the y-axis, and the percentages that have passed over between intervals of 10 deg. C are plotted in both directions along the x-axis. In this way there result "root" or "onion-shaped" figures, having very characteristic and distinctive forms. On the left-hand side of such a diagram a column of figures is included, indicating the total percentages passing over up to various temperatures, on the righthand side a similar column showing the percentages obtained between certain temperature limits. In the case of crude oils, for instance, 180 °C can be taken as the limit of the gasoline and 300 °C for kerosine. Fig. 118 gives a comparison between this type of diagram and the boiling point curve of a shale oil.

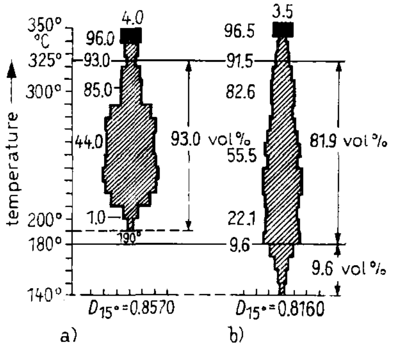


Fig. 119
Surface diagram for (a) diesel fuel and (b) special diesel fuel

The advantages of such surface diagrams are:

1. the amount of residue is seen at a glance;
2. the onset of decomposition is shown by a swelling out of the surface at high temperatures (320 °C or more);
3. various distillations may be compared rapidly by superimposing corresponding (transparent) diagrams.

As a further illustration of this form of graphical representation Fig. 119 gives the diagrams for a diesel fuel (a) and a special diesel fuel (b).

4.14 Instructions for the calculation of distillation conditions

The plan of work indicated in Table 4 will be illustrated by means of an example showing the methods of calculation employed.

4.14.1 Batch distillation at atmospheric pressure

In a certain laboratory a considerable quantity (about 10 litres per week) of a benzene-n-heptane mixture is obtained as waste product, and this is to be separated into its components. The distillate is to contain 99 mol% of benzene, the residue not more than 2 mol%.

Data for components

Component	Amount in mixture (mol%)	Mol. wt.	$Kp._{760}$ °C	Density ϱ at 20°C	Separation factor α
Benzene	60	78.11	80.2	0.87895	
n-Heptane	40	100.20	98.42	0.68368	1.77

1. *Estimation of the number of theoretical stages required*

At atmospheric pressure the difference in boiling point is 18.3 deg. C. A rough estimate, assuming ideal behaviour of the mixture, indicates that there will be required

(by the diagram in Fig. 72)	9 theoretical stages,
(by formula (100))	16 theoretical stages.

However, as will appear in paragraph 3, the mixture is not ideal and the number of theoretical stages needed will therefore be higher. The following example shows that only a strict calculation yields reliable values and that the difference in boiling point provides no more than a rough approximation.

2. *Vapour pressure curves*

As it has been decided, for convenience, to carry out the separation at atmospheric pressure, the optimum pressure for distillation need not be gone into.

It should be noted, however, that the boiling point should be corrected to 760 mm (see Figs. 114, 115) and that temperatures should be corrected for emergent stem.

3. *Calculation of the number of separating stages and the reflux ratio*

The equilibrium curve of the system has been published (see Table 29, chap. 4.10.3) and shows an asymptotic approach to the diagonal in the neighbourhood of 100 mol%.

Taking the values of chapter 4.10.3 as basis, we now draw the equilibrium curve to a size of 50 × 50 cm on a mole fraction basis.

As described in section 4.7.1 we then proceed to determine the conditions for distillation graphically. The operating line ($x_B = 60$ mol% and $x_E = 99$ mol%) cuts the vertical axis at $y = 32$. From formula (82) we find that

$$v_{\min} = \frac{99}{32} - 1 = 2.09.$$

We decide on a reflux ratio of $v = 9$, which by (79) gives us

$$y = \frac{99}{10} = 9.9.$$

The operating line connecting $y = 9.9$ and $x_E = 99.0$ for $v = 9$ is employed for drawing in the steps between this line and the equilibrium curve. We find that 25 theoretical stages are needed in the initial conditions.

The final conditions required are a distillate of $x_E = 99$ mol% and a residue concentration of 2 mol%. The operating line corresponding to these conditions cuts the ordinate at $y = 3$, so that now

$$v_{\min} = \frac{99}{3} - 1 = 32.$$

We estimate that the reflux ratio selected again requires 25 theoretical stages and choose a value of $v = 50$, which gives us

$$y = \frac{99}{51} = 1.94.$$

The points $y = 1.94$ and $x_E = 99.0$ are connected. Between this new operating line and the equilibrium curve the steps are again drawn in. As expected, they indicate $n = 25$ theoretical stages.

The conditions for distillation so determined are thus:

Required number of theoretical stages	$n_{\text{th}} = 25$
Reflux ratio, initial	$v = 9$
Reflux, ratio, final	$v = 50$

4. *Load, distillate take-off and running-in time*

First we must convert molecular percentages into percentages by volume, (see section 3.4, formula (15)):

$$\text{benzene, vol\%} = \frac{\dfrac{78.11 \times 0.6}{0.879}}{\dfrac{78.11 \times 0.6}{0.879} + \dfrac{100.2 \times 0.4}{0.684}} = 48 \text{ vol\%}.$$

About half the still pot contents will therefore remain as residue. The operating hold-up, estimated at 100 ml, will be taken off as intermediate fraction and added to the charge in the next distillation, since such a small quantity cannot be separated adequately in the same still.

If we require an hourly distillate take-off of 200 ml, the column must be loaded to the extent of 2000 ml/h, with a reflux ratio of 9 in the initial conditions. The flow of reflux is then 1800 ml/h.

At a constant column load of 2 litres/h, the distillate take-off at the end, where the reflux ratio is to be 50, would amount to only $\frac{2000}{51}$ = *approx.* 40 ml/h. Were we to keep the the take-off rate at 200 ml/h, the column load would finally have to be $200 \times 51 = 10{,}200$ ml/h. This would clearly be impossible in practice, since the column, with a fivefold increase in load, would no longer provide the 25 theoretical stages needed for the separation. We therefore need to maintain the load constant and to increase the reflux ratio from 9 to 50 in accordance with the reduction in the amount of volatile component in the still pot.

The complete calculation can be performed using an equation derived by Billet [135]. Since this requires extensive preliminary calculations the reader is referred to the original paper.

We will now estimate the equilibration time, *i.e.* the time that must elapse before the distillate has attained a concentration of 99 mol%. (See section 4.8.3). For this purpose we have to know the operating hold-up. If this is not to be determined exactly (section 4.10.5), it may be taken to be about 3 ml per theoretical stage of a packed column. We shall assume the figure to be 75 ml.

By formula (129) the intensity of countercurrent exchange ($R = \frac{2000}{3600} = 0.55$ml/sec) can be calculated:

$$I = \frac{25 \times 0.55}{75} = 0.18\ \mathrm{sec}^{-1}.$$

If we introduce this figure into equation (130), we find the approximate equilibration time to be

$$t_A = \frac{26^2}{0.18 \times 2} = 1877\ \mathrm{sec} = ca.\ 30\ \mathrm{min}.$$

The summary of rates and times is: Column load 2 litres/h; distillate take-off at outset, with $v = 9.200$ ml/h; equilibration time 30 min, assuming adequate flask heating.

5. *Calculation of column dimensions*

In order to calculate the column diameter needed at a load of 2 litres/h we must first know the limiting velocity for the packing employed. We have decided to use 4 mm porcelain saddles. The method of calculation is fully described in section 4.11.

The reduced vapour density is

$$\varrho_R = \frac{\varrho_D}{\varrho_F} = \frac{27}{878.95}\ 3.07 \times 10^{-3},$$

in which, by formula (37)

$$\varrho_D = \frac{78.11 \times 760}{353.35} \times 0.01605 = 2.7\ \mathrm{kg/m^3}.$$

With the aid of the nomogram of Fig. 109, using a value of $k_G = 0.019$ for saddle packing, we find that the limiting velocity in the conditions concerned is 0.49 m/sec. This value may also be obtained by means of formula (143):

$$w_G = \sqrt{\frac{0.019 \times 0.004 \times 9.81}{0.00307}} = 0.49\ \mathrm{m/sec}.$$

Taking the limiting velocity at 60% of this figure, *i.e.* 30 cm/sec, we find the required cross-sectional area of the column, by formula (148) to be

$$f = \frac{0.0228 \times 22.5 \times 353.35}{30} = 6.0\ \mathrm{cm}^2 \text{ at a value}$$

of $\mathrm{D} = 2000$ ml/h $= 1758$ g/h $= 22.5$ mol/h.

We decide on a column diameter of 30 mm ($f = 7.06$ cm^2) so that we obtain a specific load of 285 ml/cm^2 h. At this load the HETP with 4 mm saddle packing can be taken to be about 8 cm (see Table 31).

Hence we require a column having the following dimensions:

Inside diameter 30 mm; effective length 2000 mm.

Total length, including ground joints, 2150 mm.

For the heat calculations the reader is referred to section 4.12, where examples have been given. The amount of heat necessary to bring the charge to the boiling point is found by formula (156), that for evaporation of the distillate and reflux by formula (158). The required condenser surface area may be calculated by means of formula (198).

The heat that must be supplied to compensate for losses may be calculated with the aid of formula (162). An example in chap. 4.12 illustrates its use.

6. *Testing the column*

The column cannot be tested (section 4.10.8) with the mixture in question. Even if a charge having a concentration of only 2 mol% were employed, only 18 theoretical stages would be needed to enrich the distillate to 99 mol% with $v = \infty$. The test might be performed with the mixture n-heptane-methylcyclohexane at a load of 2 l/h. If, under these conditions, 25 theoretical stages were not attained, the column would have to be lengthened. An HETP of 8 cm, as quoted above for 4 mm saddles at a specific load of 285 ml/cm^2 h, was only an extrapolation.

7. *Arrangement of the apparatus*

The apparatus must be adequately insulated and the column jacket provided with the requisite heat compensation (section 7.7.3). The use of an automatic column head (section 7.5.3) allows the distillation to be performed with a minimum of attention. In the present case it would be useful to place a contact thermometer, connected to a bell via a relay (section 8.2.2), in the column head. The thermometer would be set to the boiling point of benzene, and when a signal was heard, the initial reflux ratio of 9 would be increased, say, to 20. In the same way it would be progressively raised to the final value of 50. The load may conveniently be regulated by means of a contact manometer actuated by the pressure differential (section 8.4.2). In accordance with the amount of the charge the still pot may be a pilot-plant flask (section 7.6.1) or a round-bottomed flask of 4 to 10 litres capacity, heated by a flask heater (section 7.7.1).

For further automation the reader is referred to chapter 8, for the construction of the apparatus to chapter 9.

4.14.2 Continuous distillation

The special methods of calculation used for continuous distillation are dealt with in:

Section 4.7.2 Example: Separation of a C_6-C_7 fatty acid mixture containing 81 mol% of C_6, at a pressure of 20 mm Hg, $x_E = 96$ mol%, $x_A = 0.5$ mol%.

Section 4.9 Example: Separation of a multicomponent mixture of normal fatty acids, C_4—C_8, at 20 mm pressure.

The apparatus for continuous distillation and its execution are described in section 5.2.2.

4.14.3 Vacuum distillation

The calculations necessary for vacuum distillation are carried out along lines corresponding to those for distillations at atmospheric pressure. The following additional points should be observed.

1. Choice of the optimum distillation pressure (section 4.6.2; 4.10.6).
2. Calculation of the equilibrium curve for ideal and non-ideal mixtures at a given pressure (section 4.6.1, Table 10).
3. Dependence of the volume of vapour on the pressure (section 4.11).
4. Basic principles, calculation of tube diameters and testing for vacuum tightness (section 5.4.1).
5. Measurement and control of pressure (section 8.3).

4.15 Distillation calculations by computer

If the use of electronic computers is advantageous on the laboratory and pilot-plant scale it is a must in industrial distillation with its complex control problems. Nowadays the whole separating process in a multistage plant is controlled by a process computer. A comparison of the essential criteria of the various process computers used for laboratory automation is given by Blatt and Fleissner [259].

We distinguish between digital [246] and analog computers [247] and the combination of the two in hybrid computational systems [248]. The digital computer supplies the data in tables of figures whereas the analog machine represents the results as time-dependent voltages which may be recorded in various forms. It would lead us too far to go into details here: the reader is referred to books on the subject [248, 249].

All calculations occurring in distillation practice may be carried out on electronic computers. The determination of vapour pressure and phase equilibrium data as well as the calculation of optimum conditions for the plate number and the reflux ratio may in certain cases be done even with desk calculators. To save time in the investigation of the dynamic behaviour of packed columns, for example, the mole fractions were derived from density and refractive index values using an IBM 7040 computer [162]. Numerous programmes have been elaborated for the thermodynamics of the phases [109]. An extensive Fortran programme serves to calculate the phase equilibrium of multicomponent mixtures [89]. According to Roth [250] differential evaporation (Engler and ASTM methods, see chap. 7.2), which is mostly used to control industrial processes, involves complex thermodynamic conditions. On the basis of a model recalculations can be done with a ZRA 1 computer. A programme for an

IBM 705 machine based on the McCabe-Thiele method was worked out by Schubring [251] for binary mixtures. It may be used to calculate plate numbers for ideal, non-ideal and non-ideal azeotropic binary mixtures on the assumptions (which are frequently sufficient in practice) that the molar heat of vaporization is independent of concentration and that no heat of solution occurs. The equilibrium data and the concentrations of feed, top and bottom are fed into the programme through punched cards. The computing times range from 15 seconds to 5 minutes for one problem. For each problem the machine prints a series of possible plate numbers as a function of reflux ratio or re-evaporation ratio. The block diagram of Fig. 120 illustrates the computing process and Fig. 121 shows the diagram for the continuous separation of a binary system in terms of plate number vs. reflux or re-evaporation ratio. The representation of the relation between v_R and v_D in a nomogram enables the corresponding values for the upper and the lower section of the column to be plotted in one diagram [251]. Chien [251a] presents a method for calculating the minimum reflux ratio on a digital computer, with an exact description of the requirements for the calculation.

The calculation of batch distillations of multicomponent mixtures is particularly difficult. Rose [251b] developed a computer programme which simulates the dynamic behaviour of discontinuous distillation processes.

Sealey [252] used an English Electric KDF 7 computer to optimize the total efficiency of an Oldershaw laboratory plate column (cf. Fig. 268) with a diameter of 31.8 mm and 12 and 10 actual plates in the lower and upper sections, respectively. He analyzed 280 cases using methyl cyclohexane-toluene as test mixture. The optimum plate number was defined as the one which minimizes the errors. These sources of error were investigated:

- measurements of mixture composition
- position of operating lines
- slope of operating lines
- equilibrium data.

Fig. 122 shows the dependence of the total deviation in per cent on the plate number over a range of interior reflux ratios from 1.0 to 1.3 in the lower column section. The curves for the upper column section have similar shapes. The minima of the curves increasing with rising v decrease from 1.0 to 0.7.

The mathematical model of a semitechnical rectification column with stationary operation was elaborated and experimentally tested by Großhennig [267]. The tests were made in an NW 310 bubble-cap column with 35 plates using the system chloroform-carbon tetrachloride. A comparison showed that even the simplified version of the model gave satisfactory agreement.

The use of computers is imperative for the exact calculation of distillation columns run for the separation of multicomponent mixtures [264]. Possibilities of modelling a primary distillation of crude oil were discussed by Kirbach, Frenzel and Strankmüller [265]. The computing programme as prepared for a ZRA 1 computer for ideal multicomponent mixtures was published by Leibnitz and Schuhler [253]. The calculating procedure for non-ideal multicomponent mixtures was dealt with by Nagel et al. [254]. Morozova and Platonov [266] developed a method for examin-

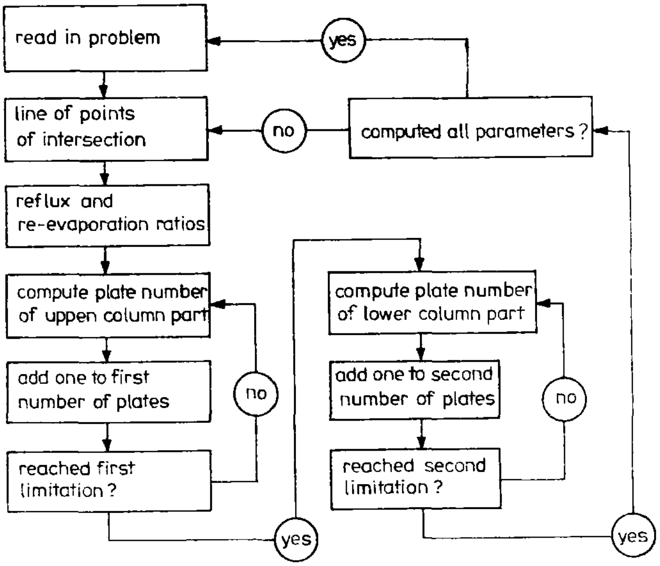


Fig. 120
Block diagram after Schubring [251]
Process of determining the number of theoretical plates on an electronic computer of the IBM 705 type

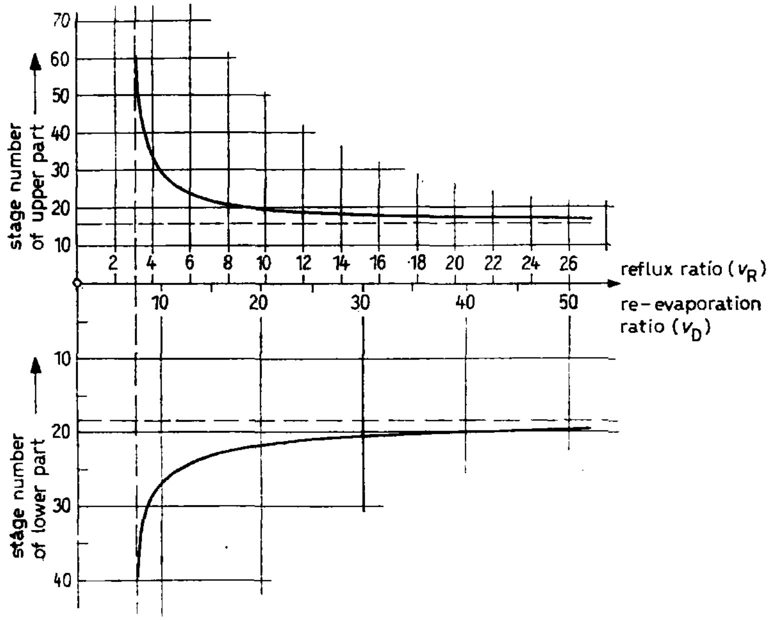


Fig. 121
Data for a continuous distillation [251] with
$\alpha = 1.5$; $x_Z = 65$ mol%; $x_E = 99.9$ mol%; $x_A = 0.1$ mol%

ing the various possibilities of separating multicomponent mixtures with azeotropes. The method allows the influence of pressure changes and additives to be determined. A programme for plate-to-plate calculations with columns for complex mixtures (crude oil and petrol mixtures) without circulation and with the addition of stripping steam was elaborated by Gohrke and Kleemann [273].

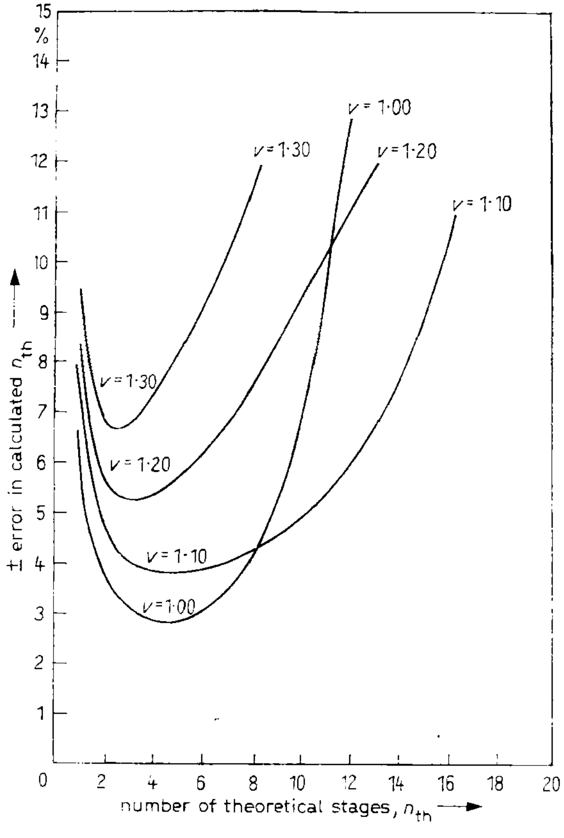


Fig. 122
Total error for calculated number of stages in the lower part at various inner reflux ratios v (methylcyclohexane-toluene)

The progress made in modelling the distillation of complex mixtures with pseudo-components has been reviewed by Weiß and Kirbach [274] who in their turn have presented more advanced methods of calculation.

Analog computers may be employed in many ways in process engineering for the calculation of material and heat transfer processes [255]. In the last 10 years chiefly those methods have been further developed which can only be used by means of electronic computers [6]. These are, above all, the so-called matrix methods as evolved by Wang and Henke [256], Sargent and Murtagh [257] and Stainthorp et al. [258].

Together with studies of flow resistance and material and heat transfer in packing layers at rest Brauer and Mewes [260] worked out Fortran programmes for the calculation of pressure drop and packing layer height, taking into account the structure of the packing.

Using the system dichloroethane-toluene as an example Wagner and Blass [262] describe a procedure for a hybrid analog computer which simulates stepwise rectification. This allows the determination of the still head or still pot concentration in the separation of binary mixtures for given operating parameters and equilibrium curves as a function of time.

The theory and practice of column dynamics for large-scale plants are discussed by Köhler and Schober [264].

5. Separating processes

When the preliminary calculations for a separation have been carried out, the next step is to consider the actual procedure by which the separation is to be performed. The method chosen will need to be adapted to the quantity of substance, to the desired throughput and to the properties required of the distillate. Besides, the properties of the mixtures to be separated as well as the apparatus and the energy sources available have to be taken into account.

5.1 The scale of operation

The dimensions of the apparatus to be used for the distillation must obviously be suited to the amount of the charge. It would, of course, be possible in an emergency to distil large quantities in a small apparatus with a great expenditure of time, but on the other hand too large an apparatus would lead to excessive losses and erroneous results.

In the laboratory cases may occur in which the distillation of a few milligrams of material is necessary and a *micro-technique* has to be adopted, whilst at the other extreme it may be essential to work with a throughput of 5—10 kg/h, so that the operation falls into the *semi-technical* range. Pilot plant distillations involving scaling problems have increasingly been carried out in recent years.

5.1.1 Micro- and semi-micro-distillation

In the first place a definition of the quantities involved will be given. In preparative micro-operations the amounts of substance handled often lie below 0.1 g. Since, however, the physical properties of liquids give rise to considerable difficulties in the distillation of such small quantities, a distillation with a charge up to 5 ml can be considered as a microprocedure, and one with a charge between 5 and 50 ml as a semi-micro process. Furthermore, we must distinguish between simple unfractionated evaporation or distillation on the one hand and countercurrent distillation on the other. Stage and Gemmeker [1] point out that micro-distillation procedures have by no means been replaced by gas chromatography, in particular by preparative gas chromatography. On the contrary, it has been found that in most cases a preliminary distillation of the mixtures is necessary in order to make full use of a gas-chromatographic technique. An excellent survey of the appropriate types of column is given and constructional details and devices used are described. A detailed description of modern distillation equipment has been given by Stage [1a].

For the simple distillation of a liquid in an amount of a few milligrams up to 1 ml distillation capillaries, bulb tubes and small flasks are employed. Columns with a very small hold-up — empty columns, columns with concentric tubes (annular columns) and spinning band columns — are utilized for quantities of 1.0—25 ml, whilst charges of 25—50 ml can be distilled with semi-microapparatus provided with packed columns.

Bodenheimer [2] has described apparatus with which milligram quantities of material can be distilled and boiling points can be determined with an accuracy of 1—2 deg. C (Fig. 123). The end of tube a, which has been drawn out to an internal diameter of 1 mm, is inserted in a heating block d. Two thermometers are provided for temperature measurement. The sample of liquid is placed in the capillary at b and the remaining volume of the capillary within the block is filled with glass powder. The portion of tube a emerging from the block has been etched internally so as to give it a matt surface. The temperature of the heating block is raised at a steady rate of 4—6 deg. C per minute. When the boiling point is approached a film of liquid is seen to form on the cold part of tube a, and at the boiling point the glass becomes transparent. From the length of the transparent section an estimate can be made of the amount of distillate, on the strength of preliminary experiments. In order to obtain further fractions, one can again warm up the first deposit, so that another region of condensation is formed further along tube a, which is cooled with wet filter paper.

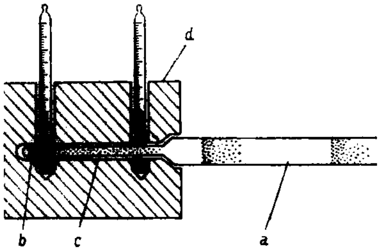


Fig. 123
Bodenheimer's micro-distillation apparatus
a = Condensation tube, b = Capillary containing sample, c = Glass powder, d = Heating block with two thermometers

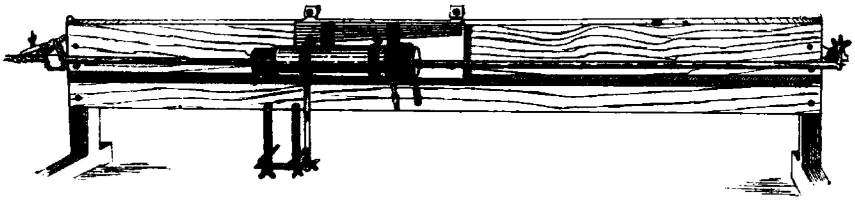


Fig. 124
Horizontal micro-distilling device (Jantzen)

By means of the horizontal distillation device of Jantzen (Fig. 124) it is possible to carry out a countercurrent distillation with 1—100 mg of substance in a tube of 120 cm length and 5.5—5.7 mm I.D. [3]. In the heating cylinder a temperature gradient of about 30 deg. C is produced; a current of hydrogen assists the transport of material in the sense of this gradient. As a result, the low-boiling components migrate further than those with a high-boiling point. The device is intended for substances of low volatility. Fig. 125 shows the separation that it gave with a mixture of dodecanoic and tetradecanoic acids. The most recent, automatic version of the device is described by Fischer [3a].

Quantities of 0.05—0.5 ml are frequently distilled in a small bulb blown at the end of a tube. The method of filling is to heat the bulb (similar to Fig. 126) gently and allow it to suck up the liquid during cooling, or to employ a capillary pipette. The use of bulb tubes has been extensively treated by Bertele and Humbel [3b]. Even vacuum distillations may be performed on a micro-scale. Fig. 126 shows an apparatus developed by Babcock [4], that gives three fractions at *a*, *b* and *c*. To collect several fractions without interrupting the distillation, micro-equipment is provided with rotating vacuum receivers (Fig. 127). Any number of fractions can be taken with the apparatus of Krell (Fig. 128). This small device may be employed both for atmospheric and reduced pressures and can be adapted to the size of the charge. If the latter is only 1—2 ml it is best to work with an empty riser tube. If necessary, one or two gauze cones may be placed as spray traps above the flask, and these also give a certain rectifying effect (see Fig. 273). For distilling a charge of 3—5 ml, glass Raschig rings or 4×4 mm helices may be placed on a glass grid in the riser; if the charge is 5— 10 ml, 2×2 mm helices, supported by a gauze cone, can be used. Distillation is started with the fine-control valve closed until a constant temperature

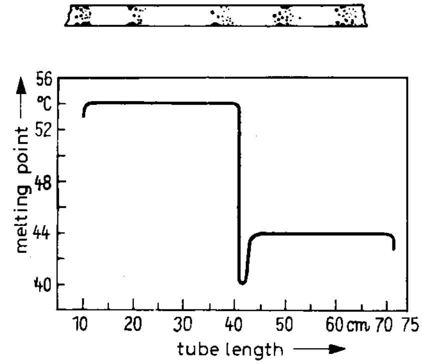


Fig. 125
Separation of a mixture of dodecanoic and tetradecanoic acids in Jantzen's horizontal distillation apparatus

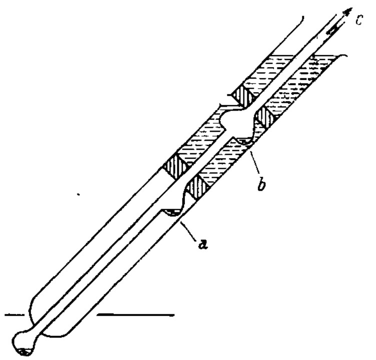


Fig. 126
Babcock's micro-distillation apparatus for use at reduced pressures

is established, after which arbitrary, measurable loads and reflux ratios can be applied with the aid of the dropping capillaries *a*. These provisions make it possible to carry out reproducible distillations with small amounts of material.

In contrast to an empty column (chap. 7.3.1), the Vigreux column has a considerable surface area and leads the reflux to the centre by means of the indentations in the walls. Shrader and Ritzer [5] equipped their micro-distillation apparatus with such a column (Fig. 129). Other special features of this equipment are the flat-bottomed flask *a*, which ensures a constant surface area for evaporation, and the receiver *b* containing tubes *c* of 0.1 ml capacity. The distillate is led to the tube in question by the glass thread *d*. The apparatus can, however, be employed only for high-boiling

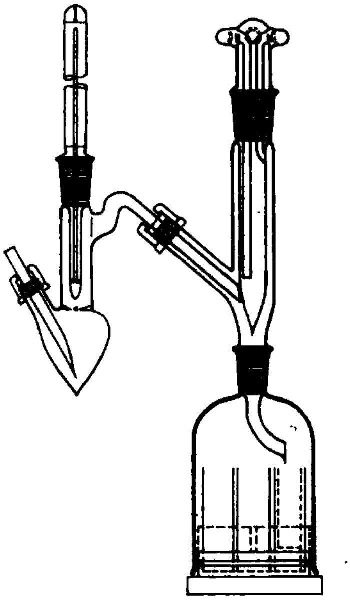


Fig. 127
Micro-distillation apparatus,
model 00100
distilling flask: 5 ml, fraction collectors: 6 × 6 ml or 9 × 2 ml

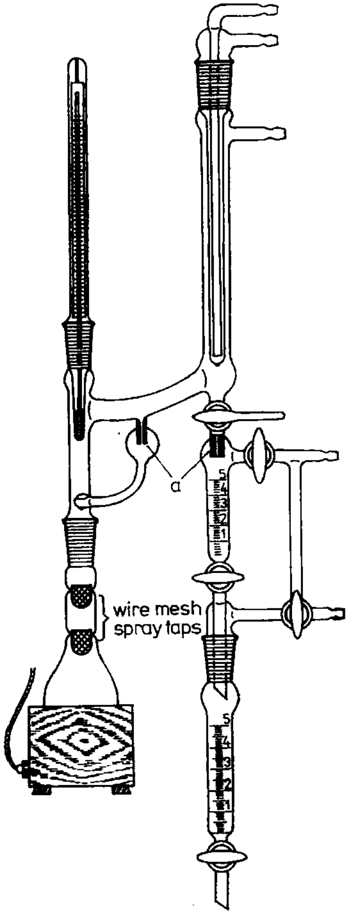


Fig. 128
Micro-distillation apparatus of Krell for atmospheric and reduced pressures; charge 1—10 ml

materials, as there is no condenser. The larger apparatus due to Klenk [6] is also equipped for condensation by air cooling only. Its column, 8.5 or 13 cm long, which contains a spiral of metal tape and is surrounded by a vacuum jacket, appears capable of effecting sharp separations with a low hold-up (Fig. 130).

Both packed and plate columns can only partly be used for semi-micro-distillations since their hold-ups are too large (see chap. 4.10.5). The point is to keep the column dimensions as small as possible for a given amount of material. Only helices of 1.6 to 2 mm size can then be used as packing (chap. 7.3.2, 7.3.3 and 7.8). Concentric tube (chap. 7.3.1) and spinning band columns (chap. 7.3.5), however, are particularly suitable for sharp separations of very small amounts. Both types are also of great importance in analytical and micro-scale distillations of high-boiling substances in vacuum [7].

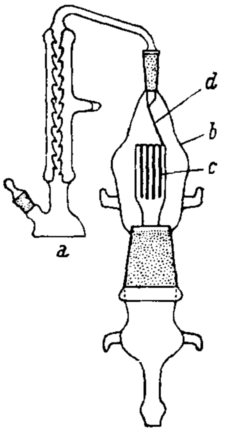


Fig. 129
Micro-distillation apparatus of Shrader and Ritzer with Vigreux column

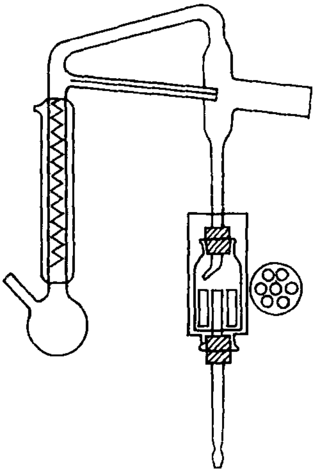


Fig. 130
Klenk's apparatus for micro-distillation, with spiral column, for charges of 4 ml or more

Winters and Dinerstein [8] have described an assembly of 8 semi-micro columns, which are used for analytical distillations and are provided with a central measuring point. The assembly contains spinning band columns, Hyper-Cal columns by Podbielniak and concentric tube columns with characteristics as shown in Table 37. The separation of essential oils with spinning band columns at 4 to 13 torr has been reported by Spiegelberg [9]. Examples of separations of high-molecular organic compounds with a concentric tube column are given by Jantzen and Witgert [3] and Fischer [7].

Molecular distillation (section 5.4.4) on a micro-scale may be performed by both the cold-finger method and that of the falling film or thin layer. A practical example of a cold-finger apparatus is illustrated in Fig. 131 [10]. The mixture to be separated is heated in A, and condenses on the cold finger B; the distillate builds up at C, from

Table 37
Data of semi-micro columns used in analytical work [8]

		Spinning band column	Hyper-Cal column	Concentric tube column
inner diameter	mm	5	8	8
length	cm	90	60—90	60
capacity	ml	10—50	20—100	10—50
size of fractions	ml	0.5	0.5—1.0	0.5
throughput	ml/h	10—30	20—30	20—30
amount of take-off	ml/h	0.5—1.5	0.5—1.5	0.2—0.5
reflux ratio		40:1	40:1	100:1
HETP	cm	1.1.	0.7	0.9
hold-up per 90 cm	ml	1.9	4.8	3.2

which it drips into the rotatable receiver *D* containing the tubes *E*. For quantities smaller than 4 g Breger [11] has described a useful arrangement (Fig. 132). The evaporating surface is on the outside, the condensing surface on the inside of the cylindrical space. The apparatus, which has a length of only 18.5 cm, can be rotated about its centre, so that the mixture may first be degassed, and the original charge or the distillate may if desired be repeatedly distilled as a falling film at increasing temperatures. With the apparatus of Paschke et al. [12] a molecular distillation of about 0.5 g can be performed. Fig. 133 shows the method of operation. The substance to be distilled is dripped onto a ball of glass wool *a*, which is suspended on a spring balance in the tube. After high vacuum has been established the heating jacket *b* is put into operation; the quantity of distillate is read off on scale *c*.

The heating of small flasks presents difficulties in micro-distillations, and flooding of the column often occurs. If possible the diameter of the latter should therefore be not less than 6—8 mm. A micro-heating device, equipped with a dark infra-red lamp,

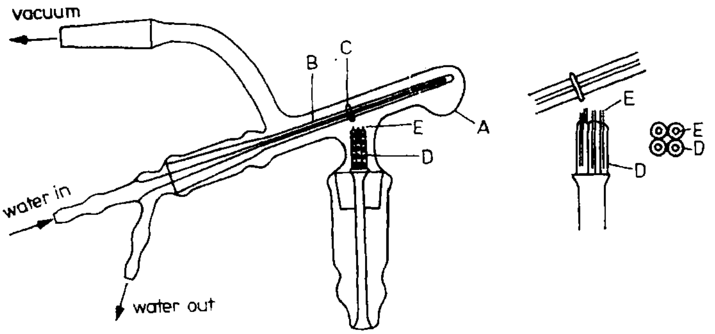


Fig. 131
Micro-form of molecular distillation apparatus according to Gould et al. (cold-finger method)
(see accompany text)

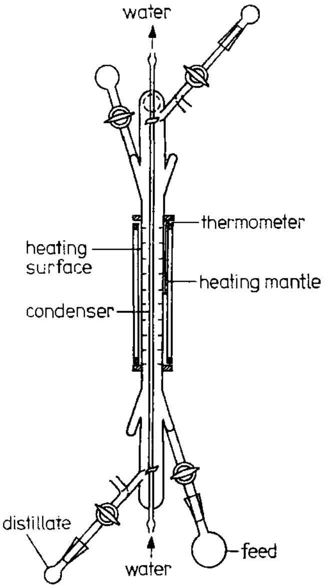


Fig. 132
Micro-form of molecular distillation apparatus after Breger (falling film principle) for less than 4 g charge

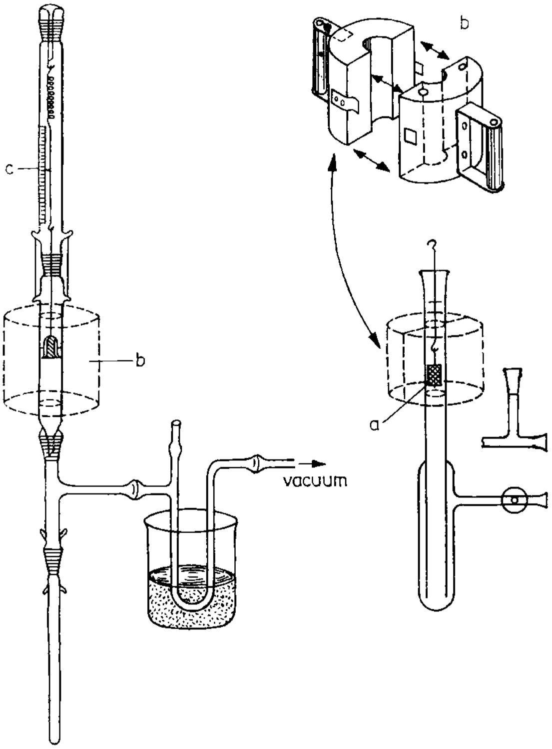


Fig. 133
Apparatus for molecular distillation on a micro-scale for 0.5 g charge (Paschke et al.)

has given excellent results in practice. It also allows micro-distillations to be carried out under reduced pressure, as bumping is avoided.

Preparative microprocedures including distillation apparatus have been surveyed by Pfeil [13]. In this connexion mention should be made of Eigenberger's micro-density balance which allows densities of very small amounts of material to be determined relatively quickly. A simplified version has been built by Clasen [15].

5.1.2 Analytical distillation

The object of carrying out an analytical distillation is to obtain the components of a binary or multicomponent mixture in as pure a form as possible. Their purity is determined by the measurement of suitable physical properties, such as the refractive index, the density, the solidification or melting point and the molecular weight. As it is frequently not known what constituents the mixture contains, or in what proportions they are present, the distillation is usually carried out batchwise. A column with an adequate number of separating stages, calculated as described in sections 4.7 to 4.12, is employed and it is provided with a column head that allows the reflux ratio to be regulated precisely. For an accurate determination of the amounts of the components it is necessary to keep the transition fractions as small as possible. A transition fraction is the distillate passing over between two pure components and consisting of a mixture of the two in changing proportion (Fig. 56). The size of the charge must be chosen according to the smallest fraction that is to be isolated; for the transition fractions to be small, the ratio of the hold-up to this smallest fraction must be sufficiently low. The use of a high hold-up to improve the separation (*cf.* section 4.7.1) need not be considered, since an analytical distillation is always performed with a high reflux ratio. The book of Bock [15a] gives a good introduction into analytical distillation. The author points out that column distillation allows larger amounts of material to be employed and thus appears to be especially suited for the enrichment of trace impurities.

As a considerable number of separating stages will be required for an analysis and as the hold-up increases with the number of stages, a narrow column should be chosen for the purpose. According to Stage [16] the smallest fraction to be isolated must be at least ten times as large as the hold-up. This means that if the hold-up is say, 120 ml, and the smallest fraction to be obtained pure is present to the extent of 10%, a charge of 12 l would be necessary. This probably applies only to very narrow-boiling mixtures, requiring a high reflux ratio, and where the purity to be attained is nearly 100%. Thus, besides packed columns especially the efficient concentric tube and spinning band columns as well as columns with stationary inserts will be used for analytical purposes on account of their very low hold-ups (chap. 7.3.1, 7.3.4, 7.3.5).

For *multicomponent mixtures,* if a sufficient amount is available, the best procedure is first to separate the raw material into a number of fractions by flash distillation (*cf.* section 5.4.2) or continuous countercurrent distillation (section 5.2.2). If the cuts are made on the basis of a preliminary distillation the sharpness of this continuous separation need not to be high. The fractions obtained are then further submitted to analytical distillation. An advantage of this method is that the influence exerted by the hold-up is less unfavourable.

Notable examples of analytical distillations of multicomponent mixtures are the separation of a lignite light oil by Kühnhanss and co-workers [17], the investigations of Profft and Buchmann [18], who tried to obtain chinoline bases, and the distillative separation of fatty amine mixtures by Fürst and Schwetlick [19]. Destinorm apparatus has been used, *e.g.*, in the separation of natural amino acid mixtures by means of the countercurrent distillation of the methyl esters of the respective acetyl amino acids [20] and in the isolation of the components of lignite tar oils to establish an element balance [21]. Gutwasser and Müller [22] developed a special thin-film still for the fractionation of spermaceti oil fatty acids at 10^{-1} torr. Mair et al., for example, have demonstrated that a carefully planned combination of normal distillation, azeotropic distillation and the methods of zone melting can lead to a thorough isolation of the components of a petroleum fraction [23].

Unfortunately it often happens that insufficient mixture is available for the isolation of minor components unless special precautions are taken. A column having a very low hold-up, for instance one of the spinning band type (section 7.3.5) may then be chosen. If a packed or plate column is employed, it will be necessary to increase the reflux ratio when the transition fraction starts to pass over, so as to ensure that it will be as small as possible. Bubble cap columns (section 7.3.3) have so far been used relatively little for analytical distillations, though Oldershaw sieve plate columns have been in use for some years. They have the advantage with respect to packed columns of allowing samples to be taken from the upper plates, so that the concentration gradient in the top part of the column may be determined. By doing this it is possible to start increasing the reflux ratio as soon as the concentration on, say, the third plate from the top begins to change. Another method is to separate the mixture as sharply as possible into a number of fractions in a large column, and subsequently to redistil the cuts so made with a smaller column (having a lower hold-up), to obtain the components in a purer state. For very difficult analytical rectifications, requiring 125 or more stages, concentric tube and parallel tube columns (*cf.* section 7.3.1) or columns packed with a wire spiral or wire-gauze elements (section 7.3.4) are the most suitable. HETP values of less than 5 mm are now obtained also with concentric tube columns under vacuum conditions [7].

If an effective type of packing, giving an HETP of at most 2 cm, is not to hand, the construction of a column with a large number of stages may present difficulties of size. In a room 12 feet high the longest column that can be set up will be about 9 feet effective length. Good results have been achieved in such cases by placing two columns in series, as shown in Fig. 134. This method has proved useful, *e.g.*, in analytical distillations of the bases of lignite tar [24]. The distillate from column I is fed continuously at a point above the boiler into column II, which may be smaller in size. The load and the reflux ratio in column II may be different from those in column I. It should be checked that the quantity of liquid in the second boiler remains approximately constant. This method of combining a batch and a continuous procedure saves the time needed for carrying out a second distillation separately. Whilst the contents of the first pot change in composition from beginning to end (say from 50 to 1 mol%), the concentration of the liquid in still pot II is kept within as close limits as possible (*e.g.* between 90 and 95 mol% of light component) by an increase in the reflux ratio in column I, with the result that an almost stationary state corresponding to a continuous process prevails in column II (see chap. 5.2.2). The higher-boiling component concentrates in the second still pot and the transition fraction may consequently be kept very small. After the supply from the first column has been stopped, the liquid in still pot II can be worked up batchwise, or it may be tested for its content of low-boiling component.

An important point in analytical distillation is to use a still head having as low a dead space as possible. By dead space that volume of liquid is denoted which is retained above the column in the still head instead of taking part further in the countercurrent process. The automatic column heads for the partition of vapour or

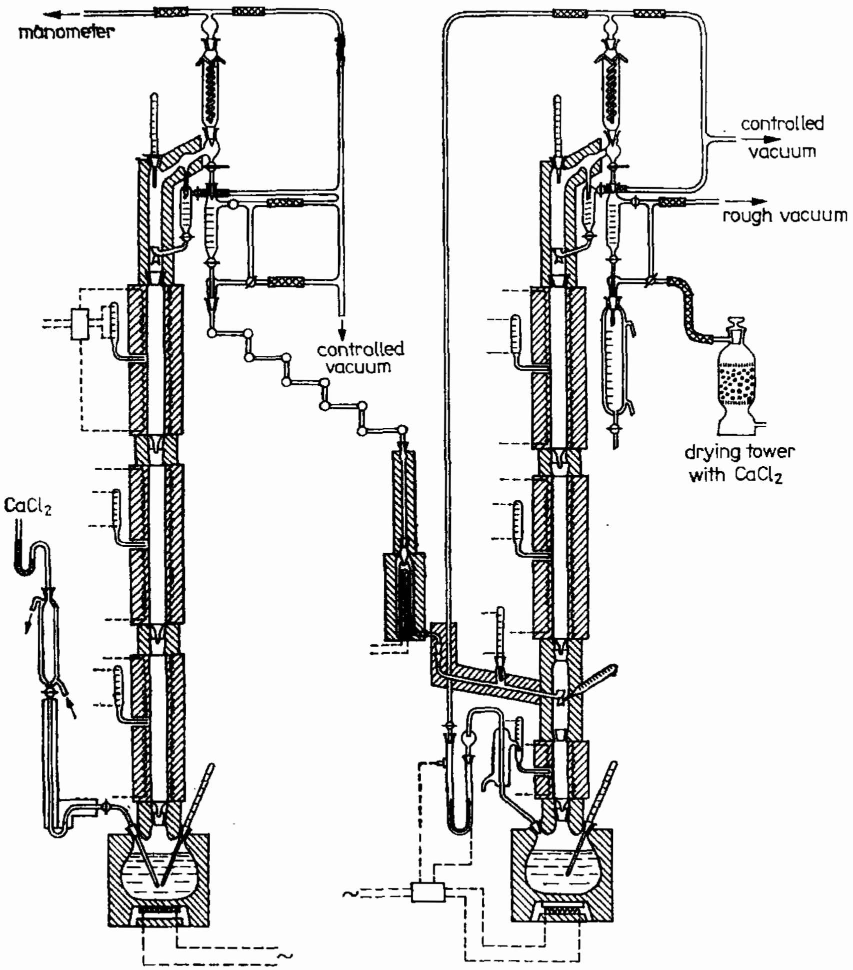


Fig. 134
Combined batch-continuous operation, by the arrangement in series of two Destinorm columns

liquid (section 7.5.3) have the important advantage of possessing almost no dead space. The reader is reminded that the presence of sample taps may cause contamination of the distillate by grease, from which unexpectedly large errors may result. There is consequently a trend towards sampling devices in which the use of taps is avoided (section 4.6.3). Of late automatic column heads (*cf.* section 7.5.3) have been equipped with magnetic valves, which prove to give satisfactory service.

In view of the precision demanded of an analytical distillation it is necessary to examine which of the following two courses is the most favourable: to take off the distillate as a constant fraction of the condensate, or to operate intermittently, *i.e.* to return the condensate to the column entirely as reflux for a certain period and next to remove it completely as distillate for another period. In the latter case the reflux ratio is the quotient of the periods of reflux return and of distillate withdrawal.

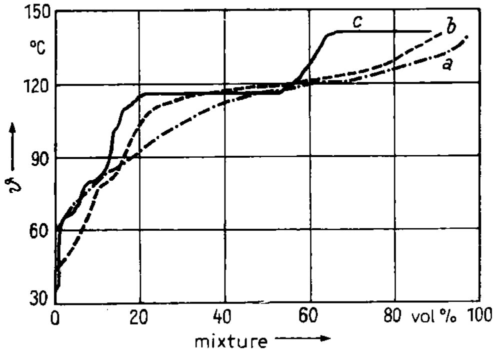


Fig. 135
Distillation diagrams of a solvent mixture
a = Engler distillation,
b = preliminary fractionation,
c = sharp rectification

If the reflux ratio is low, the average sharpness of separation will always be poorer with an intermittent than with a constant take-off. It has been found, however, that with a reflux ratio of about 100:1 the separation is better if the distillate is taken off once an hour than if it is removed every 30 seconds [25]. If the reflux ratio is still higher (*e.g.* 1000:1 to 10,000:1), as in the fractionation of isotopes, intermittent operation will in any case be necessary for technical reasons (chap. 5.1.4).

Boiling point analysis may be carried out with simple apparatus if the components differ considerably in volatility or if a standard record of the boiling range is all that is required. Apparatus for such purposes will be described in chapter 7.2. An exact evaluation of the distillation curve, however, becomes difficult, as appears from Fig. 135, in which the analysis of a solvent mixture is taken as an example. It should be noted in particular that the initial boiling point is very different in the three forms of distillation chosen. This is a result of the differing degrees of separation in the three distillations; the sharp rectification shows initially the boiling point of the most volatile component, 37 °C; the Engler distillation curve starts with the boiling point of a poorly fractionated mixture which naturally has a higher boiling point, 59°; the preliminary fractionation is intermediate in separating power and in initial boiling point, 45°. As the distillations continue, the sharp rectification reflects closely the composition of the mixture, and the distillation curve of this mixture is irregular.

The Engler distillation averages out the boiling points of a sequence of fractions and the curve is therefore smoother.

The considerable expenditure of time for a sharp analytical distillation (*e.g.*, 120 hours for the separation of a petroleum fraction with boiling points in the range from −30 to +260 °C) gave rise to the development of a simulating technique using a special gas-chromatographic apparatus [26]. It gives data comparable to those of a column with about 100 theoretical stages and can be employed for analyses of both crude oils and petroleum fractions in the range of boiling temperatures from C_1 to C_{40}. The Aerograph Simultaneous Still provides boiling point-mass per cent curves. The areas under the gas-chromatographic curves are continuously integrated by computer and recorded as measuring points at 10 second intervals. The time spent on an analysis of the above-mentioned fraction (−30 to +260 °C) amounts to about 1 hour [27].

5.1.3 Preparative and production distillation

If an analytical distillation has shown that a mixture contains certain components, the next step may be to isolate these components in larger amounts. If the differences in their boiling points are large and the purity of the products need not be high, simple stills that can be constructed from standard parts will be adequate. Fig. 136a) illustrates an apparatus of this type that can be equipped with a column if desired (Fig. 136b). Equipment of the kind shown in these two figures, however, operates with an uncontrollable load and "false reflux". For reproducible work it is necessary to use a column head permitting the reflux ratio to be adjusted accurately (*cf.* section 7.5). The Anschütz-Thiele receiver, shown in Fig. 136, though intended for work in vacuum, has also been found convenient for distillation at atmospheric

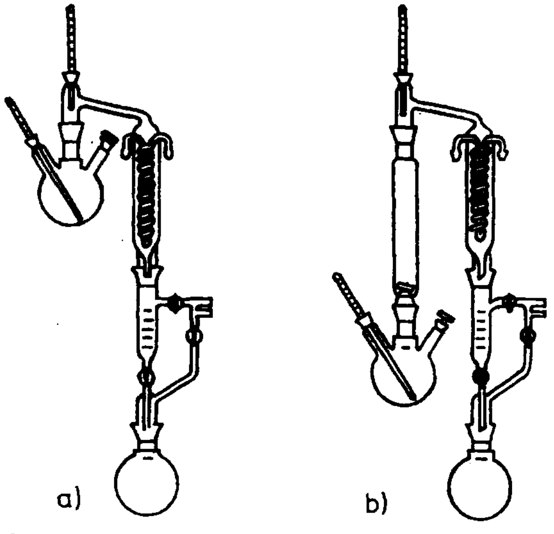


Fig. 136
Apparatus from standard parts for: a) simple distillation, b) rectified distillation

pressure. Besides, high throughputs allow the techniques of partial condensation (chap. 5.2.3) and flash distillation (chap. 5.4.2) to be employed.

Due to the use of standardized ground joints laboratory columns are commonly manufactured up to a ground joint size NS 45. Semi-technical glass columns provided with ball, cone and plane joints have nominal widths up to about 150 mm. In pilot plants columns may be made of glass, ceramics or metal, questions of corrosion possibly determining the choice of material. The nominal diameters are in the range 100 to 400 mm. A survey of apparatus used for preparative separations on a laboratory and semi-technical scale is given by Stage [28].

The preparation of ultra-pure solvents has been thoroughly dealt with by Hampel [29]. He points out that besides extraction, distillation is still one of the most effective methods of purifying solvents up to $> 99.9\%$. With alcohols, ether, benzene, pyridine and a number of hydrocarbons extremely high degrees of purity can be attained, *e.g.*, $< 10^{-4}\%$ absorbing impurities in carbon tetrachloride.

5.1.3.1 Semi-technical columns

The dimensions of the apparatus used should be in accordance with the required rate of throughput and separating effect (section 4.11). Ground joint components are commercially available in sizes NS 10, NS 14.5, NS 29 and NS 45. Arrangements for continuous operation, permitting high distillation rates, are dealt with in sections 5.2.2, 5.4.2 and 5.4.5. For distilling quantities up to 20 l/h the semitechnical Destinorm apparatus, which is made with columns of 50, 70 and 90 mm diameter, was developed. It is designed for work both at atmospheric pressure and reduced pressures down to 1 mm Hg and is largely automatic. Fig. 137 shows a semi-technical apparatus for continuous distillation, put together from standard parts. It allows various arrangements of full-scale plant to be reproduced. The column is connected by means of conical joints; thermometers and tubing carrying liquids are held by NS 14.5 joints, whilst flexibility is obtained in critical places by the use of 35 mm ball joints (chap. 3.1). The column head (Fig. 137) is provided with a multi-channel tap for accurate control of the quantity of distillate; the reflux ratio may be measured and adjusted with the aid of graduated burettes for the reflux and distillate. A condensing coil built into the vapour tube above the column allows the operation to be performed with dephlegmation (partial condensation). The amount of dephlegmate can be calculated from the rise in temperature of the cooling water or measured in a graduated receiver. The semi-technical column is also obtainable with liquid-dividing automatic reflux control (see Fig. 312). In continuous distillation the feed is heated by a preheater, constructed as a U-tube (Fig. 138). When tap *a* is partially closed the liquid level in the preheater rises to the connection *b* and the liquid circulates. By this means the feed can be heated to over 250 °C. Fig. 137 shows only the basic arrangement which may be extended to any degree of automation by adding measuring and control devices (see chap. 8.).

For batch distillation round-bottomed glass flasks were as a rule used only up to a size of 10 l; a larger volume was distilled in a suspension flask (Fig. 316), or a metal still pot with a flat or spherical ground closure, to which the glass apparatus was

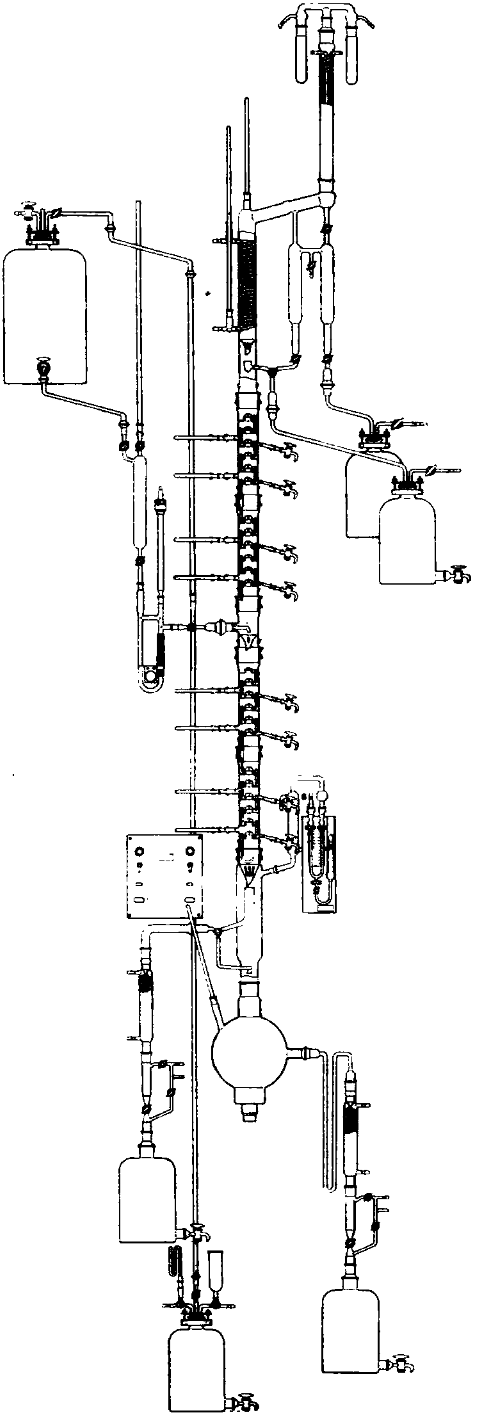


Fig. 137
Semi-technical Destinorm apparatus for throughputs up to 20 l/h

connected. A suitable vessel of 25 l nominal content is a stainless steel still pot, which is equipped with a heating jacket of 3 kW maximum rating, controlled by a 3-heat switch (chap. 7.7.2). An advantage of continuous operation is that even at a throughput of 20 l/h the reboiler need have a capacity of only 2—5 l (*cf.* section 7.6.1).

The plate column (with diameters up to 90 mm) in the author's Destinorm apparatus (Fig. 139), on the other hand, has internal reflux like industrial columns, so that distillations with this form of apparatus are comparable in this respect. The various trays may be provided as required with sampling valves and thermometers, in order that concentration and temperature gradients may be followed during the

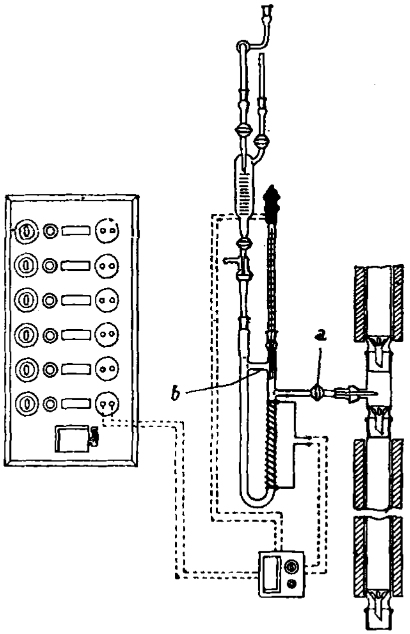


Fig. 138
Preheater for continuous distillation
a = tap, *b* = connecting tube

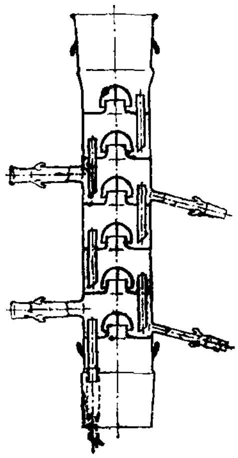


Fig. 139
Krell's plate column with internal reflux
(50, 70 and 90 mm diameter)

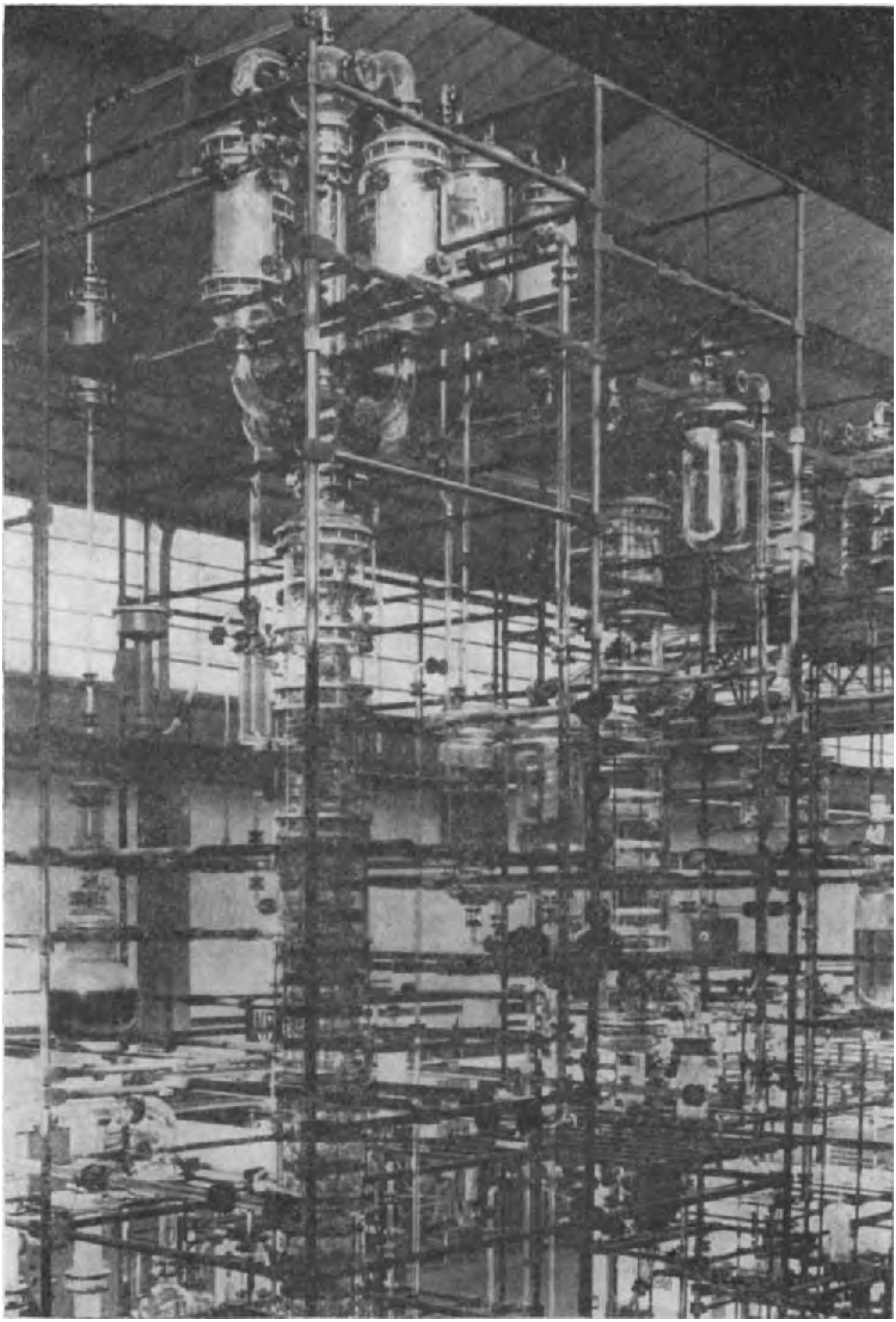


Fig. 140
Distillation plant made of Rasotherm glass, with bubble-cap column NW 400

operation. The Labodest vapour collision plate after Stage (chap. 7.3.3) also operates with internal reflux and is manufactured in sizes up to 100 mm diameter. The dependence of the plate efficiency on the handling of the reflux will be dealt with in chap. 7.3.3.

5.1.3.2 Pilot plants

Glass has proved to be a reliable constructional material in pilot plants for batch and continuous countercurrent distillation as well. It offers the basic advantage that during operation the hydrodynamic processes going on in the column and the other parts can be watched. In addition, the glass manufacturers offer a variety of components with ball or socket shaped tube ends or with plane ground joints [165] by means of which virtually all distillation procedures can be automated to a high extent. The material commonly used is borosilicate glass which is highly resistant to chemicals and can withstand both high temperatures and extreme temperature changes (chap. 7.1). Further details will be exemplified by the glass components made by VEB Jenaer Glaswerk Schott & Gen. of Jena. The material employed is Rasotherm glass of type 320, TGL 7209 [30].

A wall thickness of 5 to 8 mm gives the glass apparatus a sufficient mechanical strength. Due to its low expansion coefficient ($\alpha = 3.3 \times 10^{-6}$) Rasotherm glass displays a high resistance to thermal changes. Pilot plants are mostly made up of standard parts. Examples of such parts are tubes with their fittings, heat exchangers, round-bottomed flasks and cylindrical vessels, bubble-cap plates for nominal widths (NW) of 200, 400 and 500 mm (Fig. 140), column sections up to NW 500 mm, stop-cocks and valves, metering pumps and other components serving measuring and control functions. Besides the standardized plants, which are manufactured serially, such as water processing plants (distillation and ion exchange), circulation stills operating at reduced pressures with throughputs from 5 to 100 l/h (water) (Fig. 141) or plants for the recovery of solvents, special components, such as automatic reflux controllers and pneumatic glass valves, are also made. If a batch distillation requires larger flasks than can be manufactured (the present limit is 200 l) glass columns may be mounted on metal or ceramic flasks (chap. 7.7.2).

Closed tubing systems can be assembled without difficulty on the basis of a system of modules consisting of straight lengths of tubing, fittings, transition pieces, stop-cocks and valves [165]. The tube diameters are graded in the range from NW 15 to NW 500. The individual lengths (at present up to 3 m), are connected by means of loose flanges, the ball and socket-shaped tube ends allowing a deflection up to 3°. There are various other kinds of fittings available for special uses (screwed and flanged fittings for various kinds of tubes). The necessary precautions to achieve more safety in the operation of semi-technical glass apparatus have been reviewed by Winkelsesser [30a]. In particular, the possibility of armouring endangered parts and the prevention of electrostatic charging are discussed. A paper by Pietzsch and Rautenberg [30b] on the uses of glass in the chemical industry gives information about the chemical resistance, surface quality, mechanical and thermal strength of Rasotherm glass and also deals with the question of armouring.

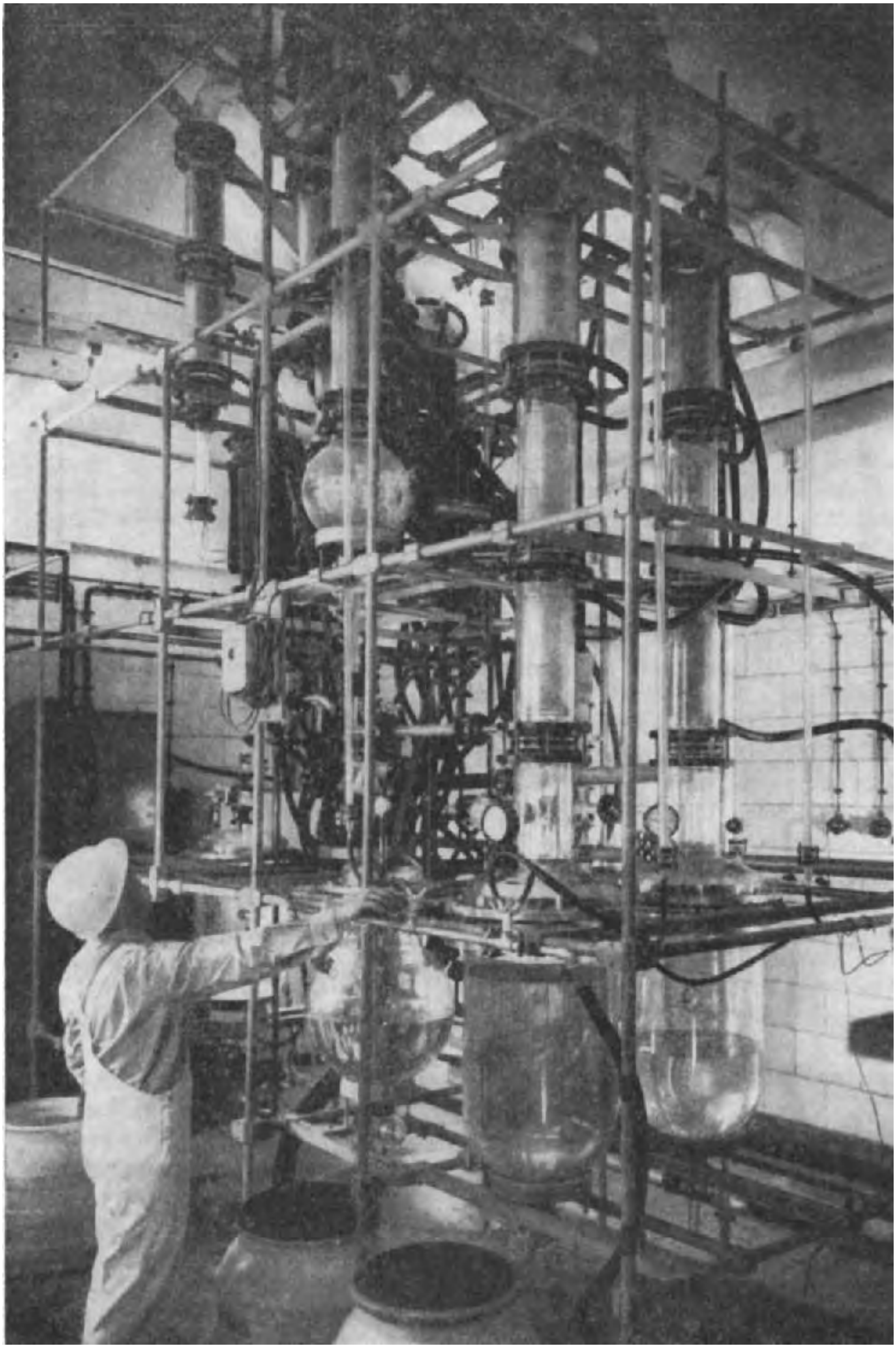


Fig. 141
Circulating-type apparatus for work at reduced pressures, evaporating capacity 100 l/h H_2O

The distillation plants shown in Figs. 140 and 141 (heights up to 14.5 m) are equipped with steam heating elements. The evaporating capacity for each NW 200 or NW 300 element (flattened spirals) at a saturated steam pressure of 2 atm. overpressure is 20 l/h of water. An advantage is that the condensing and heating surfaces

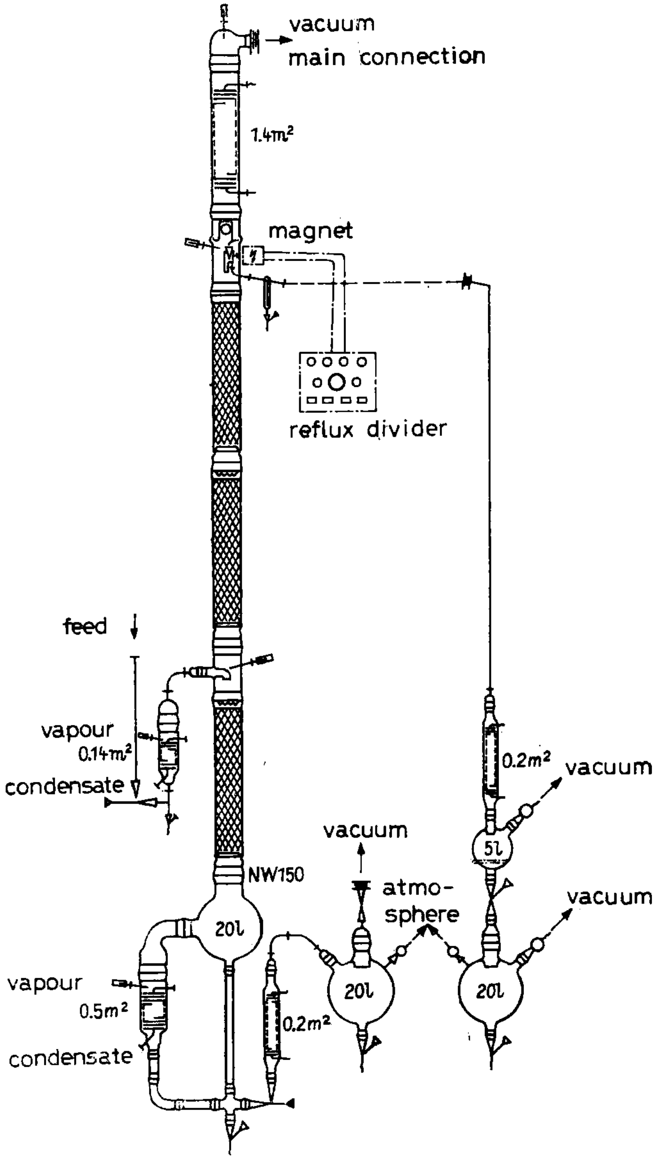


Fig. 142
Apparatus for continuous distillation at reduced pressures, with nominal width of column of 150 mm
Height: 7.2 m, width: 1.9 m

can easily be extended. For heat exchanger calculations the heat transfer coefficient k (kcal/m^2 × h × °C) may be taken to be 400 when liquids are to be heated by steam. For the condensation of vapours by means of condensers and for the cooling of liquids the respective values are $k = 300$ and $k = 150$.

Quickfit glass components, tubing systems and pilot plants are equally well suited to operating at reduced pressures. They contain elements with conical tube ends of nominal widths NW 15 to 600 with plane ground joints and of NW 15 to 225 with ball ground joints. The wall thickness ranges from 2 to 10 mm. All Quickfit components may be protected by a polyester coating which is heat resistant up to 150 °C [165]. For vacuum operation in pilot and small-scale technical plants, Quickfit-Wiegand steam ejectors of glass [128a] (see chapter 5.4.1) are now available.

There is also a tendency to manufacture standardized distillation apparatus, beginning with circulation stills, including also combinations of non-glass flasks and glass columns, and ending up with automatic continuous pilot plants with electromagnetically operated reflux heads, level control and flow control devices (Fig. 142). The maintenance-free operation of such plants requires numerous glass valves.

These will be described in detail in chap. 7.2.1. Further, controlled bottom and feed heating is necessary for the automation of glass-made pilot plants (chap. 7.7.2). The reflux division (chap. 8.4.1 and Fig. 142) and the evaporation rate (chap. 8.4.2) must also be controlled. For the measurement and metering of gas and liquid quantities special glass components for pilot plants were developed (chap. 8.6).

The combination of the constructional materials glass and PTFE is the optimum solution for metering devices for corrosive liquids (temperatures up to 100 °C, kinematic viscosity up to 30 cSt and maximum densities of 2 g/cm^3). VEB Jenaer Glaswerk Schott & Gen. of Jena developed a series of metering pump heads without stuffing boxes (Fig. 143) which are designed to be mounted on the standardized drive of type PAE 32/50 (VEB Pumpenwerk Salzwedel). The nominal capacities range from 63 to 650 l/h at maximum pressures between 3.5 and 2.5 kp/cm^2. The gas flow valve NW 15 mm of the same manufacturer is also highly resistant to corrosion (Fig. 144). The valve chamber is made of glass, the diaphragm and diaphragm support are of PTFE. The valve is closed by spindle lift.

Distillation apparatus made of hard porcelain is used for corroding substances which also attack glass (Fig. 145). Here the smallest still pot volume, however, is 50 l, yet column tube diameters begin at 50 mm nominal width.

Podbielniak Inc., of Chicago, manufacture automatic pilot distillation plants ("Fractioneer" series, Fig. 146) in four types, suitable for batch or continuous operation in the following ranges:

Still charge	45—450 litres
Column diameter	76—304 mm
Column length	1.5—3 m
Distillation pressure	3 mm Hg to 135 atm. abs.
Distillation temperature	—40° to +350 °C

The column packing employed is usually of the Heli-pak or Octa-pak type (section 7.8). Heating can be by electricity, steam or Dowtherm liquid according to choice.

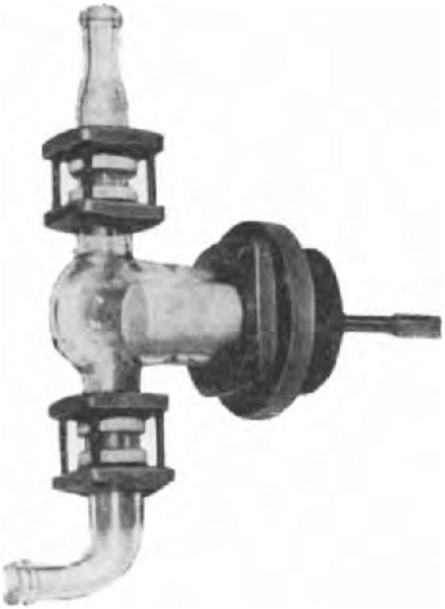


Fig. 143
Metering pump head of glass with Teflon bellows for combination with the standardized drive of type PAE 32/50

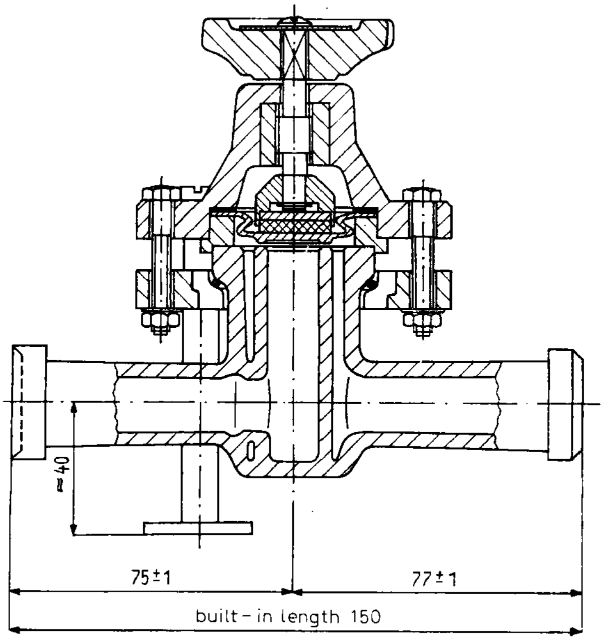


Fig. 144
Gas straight-way valve, NW 15 mm

Suitable components for distillation pilot plants are described by Carpenter and Helwig [31]. Jordan, in his book on chemical pilot plants [32] devotes special attention to the scaling up of results from pilot plant to industrial scale.

Again and again the question arises whether the results of pilot plant experiments could not be replaced by purely arithmetical scaling up. Since, however, there is still no method of precalculating thermal separations available, such experiments will have to continue to provide the data required to scale up separation processes [33]. This is quite obvious in the case of packed columns where the aerodynamic and hydrodynamic parameters are of special importance (chap. 4.2). In addition, as Billet [34] points out, the evaluation of separating columns and hence the minimization of costs involves the exact determination of the dependence of efficiency and pressure drop on the load. Even today this relation has to be determined experimentally for most columns. The same experimental conditions and systems should be chosen so that different column types may be compared (see chap. 4.10 and 4.11).

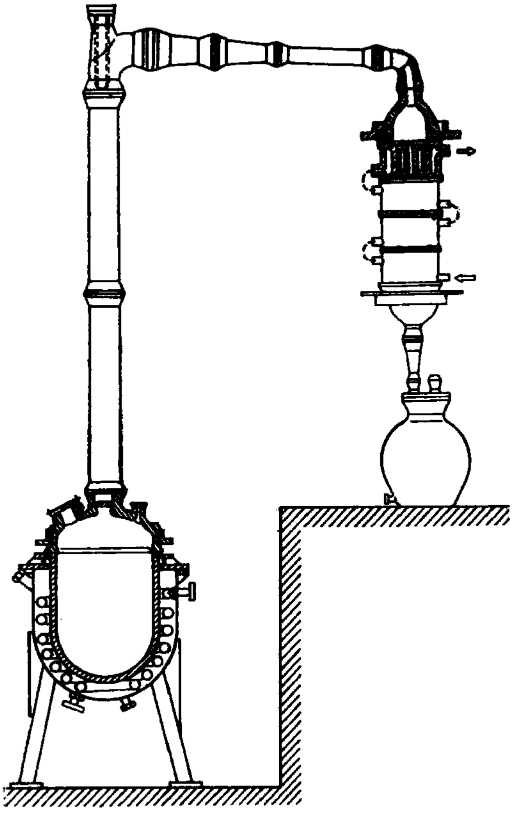


Fig. 145
Semi-technical apparatus for batch distillation made of hard porcelain

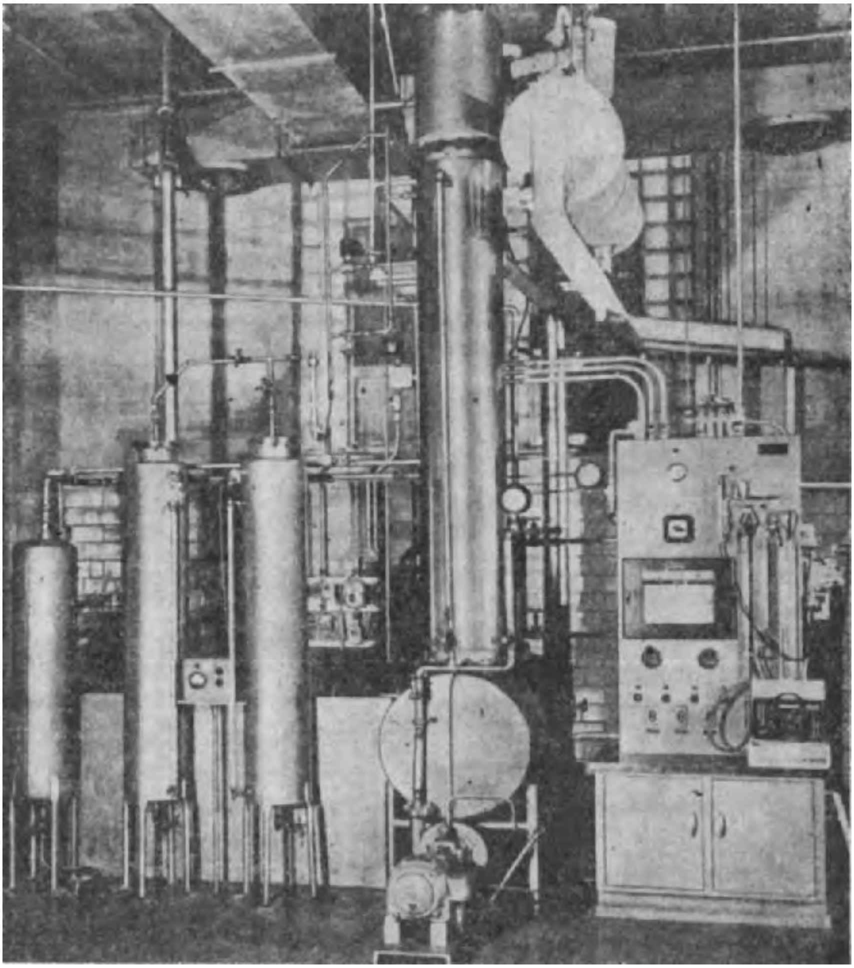


Fig. 146
Podbielniak automatic pilot distillation plant

5.1.3.3 The preparation of distilled water

A typical instance of *production distillation* occurring in the laboratory is the process of making distilled water. This is generally performed continuously. As a rule a constant level is maintained in a water boiler, preheated cooling water is led to it and the surplus is syphoned off continuously. By using quartz glass a high purity of the distillate is ensured (Fig. 147). Moreover, borosilicate glass is now the preferred material. It is attempted to prevent the water from getting into contact with the metal parts.

The multitude of types that are made indicates that the ideal still, from the aspect of economy, has not yet been realized. To achieve better utilization of heat internal

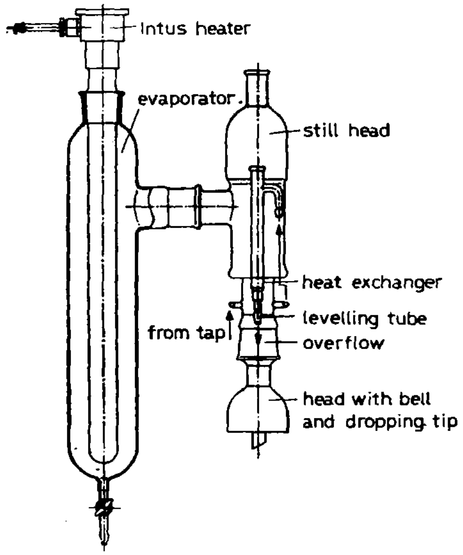


Fig. 147
Water still "Purator", made of quartz glass, with throughput of 2 l/h of distilled water

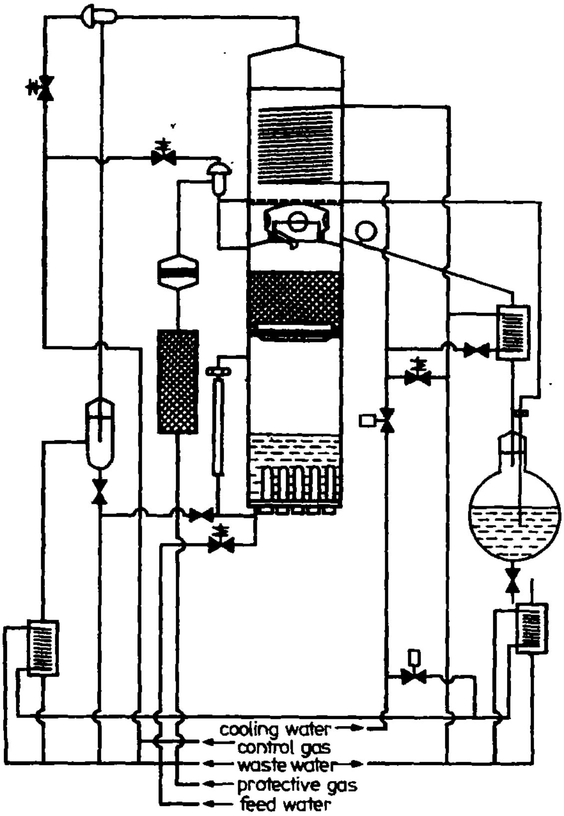


Fig. 148
Automatic water distillation apparatus made of Duran 50
Throughput: 10 to 70 l/h

electric heating is often adopted and the apparatus is provided with efficient insulation. The throughput of laboratory units usually lies in the range of 0.5 to 2 l/h. For throughputs above 2 l/h water stills are also often made of copper, nickel-plated or tinned internally. Such apparatus has the advantage of being unbreakable, but has only a moderate heat efficiency unless the insulation is very thorough.

An electrically heated water still made of Duran 50 was developed by Schott & Gen. of Mainz (Fig. 148). The various designs have throughputs from 10 to 70 l/h of distilled water with a conductivity < 0.5 μS when they are fed with fully desalted water. Apparatus for the single distillation of water with throughputs from 8 to 10 l/h is manufactured by VEB Jenaer Glaswerk Schott & Gen. of Jena. The heating is by electricity or steam. For the electrically heated bidistilling apparatus (8 and 24 l/h) the immersion heater TH Q6 (standard power, 6 kVA) was developed.

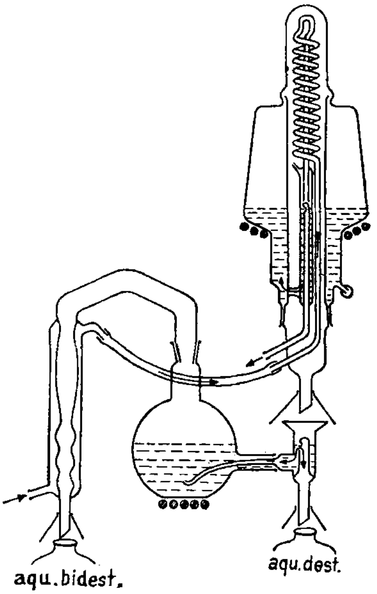


Fig. 149
Apparatus for the simultaneous production of distilled and doubly distilled water (Kullmann)

An interesting form of water still (Fig. 3b) is one employing the "descending" principle of distillation for the more economical utilization of heat. A heat efficiency of 95% is said to be attainable. Kullmann's [35] device operates in a similar way. It yields a highly degassed distillate. An additional unit allows the preparation of doubly distilled water (Fig. 149).

Zellner's "Bidestillator 1600" [36], Fig. 150 which has a throughput of 1.3—1.6 l/h, functions very economically. Heat is supplied only in the first evaporating stage for the production of monodistillate from tap water. The re-evaporation of this distillate takes place at the reduced pressure produced by a water jet pump placed before the condenser, at a temperature of 30°—40 °C, solely by the heat of condensation of the primary vapour. The water used by the pump first functions as cooling medium, and a part of it is finally utilized as feed for the first evaporating stage. Thus, a degassed bidistillate of extreme purity is produced without a residue with the energy supply required for a single distillation and a minimum consumption of tap water.

It seems quite convenient to purify the feed water in an ion exchange filter as is done in the water stills manufactured by Heraeus-Quarzschmelze GmbH of Hanau, which are made of a completely water-resistant quartz. The path of the vapour bubbles is short and yet the liquid surface is large so that spraying of the boiling water and aerosol formation are largely prevented [36a]. The bi-tridistillation apparatus designed by Cammenga et al. [36b] is capable of continuously producing high-purity water of intrinsic conductivity. In routine operation the still yields water of k ≈ 0.06 μS cm^{-1} (20°).

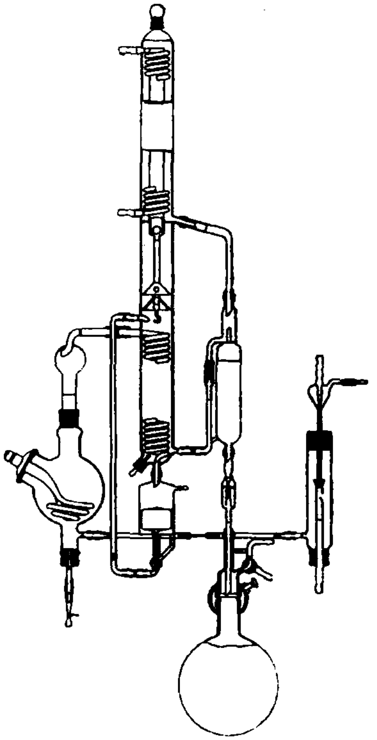


Fig. 150
Zellner's water still 1600

5.1.4 The separation of isotopes

The chemical elements occurring in nature consist for the greater part of mixtures of isotopes. They may be regarded as mixtures, the individual isotopes representing pure components. Isotopes of one element occupy the same position in the periodic system and have the same nuclear charge, but different masses. The carbon isotopes ^{12}C and ^{13}C, for instance, merely differ by having 6 and 7 neutrons in the nucleus, respectively. The atomic weights found for naturally occurring elements are the weighted averages of the atomic weights of the isotopes present.

Isotopes were first discovered in radioactive substances, but the majority of non-radioactive elements also contain a number of (stable) isotopes. Table 38 lists a variety of isotopes, many of which can be obtained by distillation processes [37]. In organic chemistry considerable use is made of "tracer compounds", usually containing heavy isotopes of the elements C, H, O and N. Except for carbon, none of these has a suitable radioactive isotope possessing the requisitely long half-life period, but the stable isotopes ^{2}H, ^{13}C, ^{18}O and ^{15}N are of great importance for chemical research and for biological, medical and geological investigations.

Elements having an odd nuclear charge in general consist of only one or two isotopes with an odd mass number; exceptions are H, Li, B and N. The element Hg, on the other hand, comprises seven stable isotopes with mass numbers of 196 to

Table 38

Some stable isotopes, their relative differences in mass and relative natural abundance

Symbol	Atomic number	Mass number	Relative difference in mass (%)		Relative natural abundance
H (D)	1	1		100	99.9844
		2			0.0156
He	2	3		33.3	1.3×10^{-4}
		4			99.9999
B	5	10		10	18.83
		11			81.17
C	6	12		8.35	98.9
		13			1.1
N	7	14		7.15	99.62
		15			0.365
O	8	16	$^{16}O/^{17}O$	6.25	99.757
		17	$^{17}O/^{18}O$	5.9	0.039
		18	$^{16}O/^{18}O$	12.5	0.204
Ne	10	20	$^{20}Ne/^{21}Ne$	5.0	90.51
		21	$^{21}Ne/^{22}Ne$	4.75	0.28
		22	$^{20}Ne/^{22}Ne$	10	9.21
S	16	32	$^{32}S/^{33}S$	3.13	95.06
		33	$^{33}S/^{34}S$	3.03	0.74
		34	$^{34}S/^{36}S$	5.9	4.18
		36			0.016
Cl	17	35		5.7	75.4
		37			24.6
A	18	36	$^{36}Ar/^{38}Ar$	5.55	0.307
		38	$^{38}Ar/^{40}Ar$	5.25	0.060
		40	$^{36}Ar/^{40}Ar$	11.11	99.633

204, the relative differences in mass being of the order of 0.5%. Since all separating methods for enriching and isolating isotopes depend on difference in mass, which in turn gives rise to some difference in properties, the relative differences in mass provide an indication of the separability. An equally important matter, however, is the relative abundance of the isotopes in the starting material. Among the elements listed in Table 38 the relative natural distribution is particularly suitable in the case of $^{10}B-^{11}B$, $^{20}Ne-^{22}Ne$ and $^{35}Cl-^{37}Cl$.

For the concentration or isolation of isotopes the methods of diffusion, thermal diffusion, electrolysis and exchange reactions are employed. An enrichment can also be attained with the aid of the mass spectrometer and the centrifuge. Distillation procedures are used for obtaining ^4He, ^2H (D), ^{10}B, ^{13}C, ^{15}N, ^{18}O, ^{22}Ne, ^{37}Cl and ^{36}Ar. An extensive survey of the production and use of stable isotopes including the special problems of isotope distillation has been given by Brodsky [38] and by Wetzel [39].

Table 39

Vapour pressure ratios of isotopic systems

System	Temperature (K)	p_{*l}/p_{*s}	References
H_2-D_2	18.65	3.6	[48]
$^3He-^4He$	2.19	5.4	[48]
$^{11}BCl_3-^{10}BCl_3$	260	1.003	[52, 53]
$^{11}BF_3-^{10}BF_3$	170	1.01	[53]
$^{12}C^{16}O-^{13}C^{16}O$	68.2	1.010	[48]
$^{12}C^{16}O-^{13}C^{18}O$	68.2	1.007	[48]
$^{12}C_2H_4-^{12}C^{13}CH_4$	120 169.3	1.0014 1.0019	[54]
$^{12}C_2H_6-^{12}C^{13}CH_6$	130 165	1.0022 1.0006	[54]
$^{12}CH_4-^{13}CH_4$	97.55 111.8	1.0099 1.0070	[54]
$^{14}N_2-^{14}N^{15}N$	63.3	1.006	[48]
$^{14}N_2-^{14}N^{15}N$	71.5	1.005	[55]
$^{14}N^{16}O-^{15}N^{16}O$	117	1.03	[55]
$^{14}N^{16}O-^{14}N^{18}O$	120	1.04	[50]
$^{16}O^{16}O-^{18}O^{18}O$	63.14 74.05	1.01286 1.00912	[49]
$^{20}Ne-^{22}Ne$	24.6	1.043	[48]
$^{36}Ar-^{40}Ar$	83.8	1.006	[48]
$^{128}Xe-^{136}Xe$	161.4	1.000	[48]

p_{*l}/p_{*s} = vapour pressures of compounds with light and heavy isotope, respectively

Of late a combination of chemical exchange and distillation, known as "exchange distillation", has become of increasing importance [40]. The analysis of stable isotopes is done chiefly by mass spectrometry [39]. There are, however, several nonmass-spectrometric techniques used which have been described by Mercea [41] and Müller and Mauersberger [42].

The concentrating of stable isotopes by distillation is particularly suitable for gases and water (the latter as a source of deuterium and ^{18}O). The vapour pressure ratios of such isotopic systems are given in Table 39. Except for the compound BCl_3, the systems require a substantial consumption of cooling agents for separation. Furthermore, the number of separating stages necessary will be in excess of 500 (except in the case of hydrogen and helium) if a reasonable concentration is to be attained. Kuhn et al. [43] determined the separation factors of isotopic compounds with boiling points up to 80 °C by employing an extremely large number of stages.

5.1.4.1 Isotope separation by low-temperature countercurrent distillation

Low-temperature distillation (see section 5.3.1) has been used to separate H—D, ^{10}B—^{11}B, ^{12}C—^{13}C and the isotopes of the noble gases helium, neon and argon.

Due to the great difference in mass and the high vapour pressure ratio the obtaining of deuterium from the gaseous mixture H_2—D_2 by low-temperature distillation appears to be relatively straightforward from a theoretical point of view. In an extensive systematic investigation Sellers and Augood [44] examined the problems involved in the countercurrent distillation of the systems HD—n-H_2, $^{16}O^{18}O$—$^{16}O^{16}O$ and O_2—N_2. They used a bubble-cap column of 27 m height. Further series of experiments on the low-temperature distillation of H—D were performed by Timmerhaus et al. [45] who used a sieve-plate column of 150 mm diameter and determined a number of separating parameters of the system. A small laboratory apparatus for the countercurrent distillation of H_2—HD mixtures is described by Weisser [46]. By now, a number of large-scale plants for the industrial production of heavy water have come into operation [47]. The difficulties, which are considerable, are associated with the apparatus and gas purification. Thus, at present isotope separation at the temperatures of liquid nitrogen and liquid air seem to be too expensive on a laboratory scale. If, however, a distilling plant were connected with an oxygen producing plant having apparatus for the technical decomposition of air, ^{36}Ar, ^{18}O and ^{15}N could be enriched very economically [48, 49]. The low-temperature distillation of NO with the simultaneous separation of ^{15}N and ^{18}O [50], as well as that of CO for the enrichment of ^{13}C [51] appears to be quite promising. Based on these techniques semitechnical processes were developed for enriching the carbon isotopes ^{12}C and ^{13}C, the nitrogen isotopes ^{14}N and ^{15}N and the oxygen isotopes ^{16}O, ^{17}O and ^{18}O [167].

Clusius and Meyer [48] enriched 15 l of argon per day to 0.6% (as compared to 0.307% in naturally occurring Ar) in a low-temperature distillation using 130 theoretical stages. They employed a packed brass column of 12 mm i. d. and 3 m height. The packing consisted of stainless-steel spirals of 2 × 2 mm size. The specially shaped still pot with a volume of 250 ml and the condenser which was cooled with liquid nitrogen are shown in Fig. 151. The separation of the isotopes ^{22}Ne and ^{20}Ne and the enrichment of ^{21}Ne by countercurrent distillation at 28 K are reported by Bewilogua et al. [164].

Mühlenpfordt and collaborators realized an annual production of 4.5 kg of BF_3 containing 83% ^{10}B, using a semi-technical column of 12 mm diameter and 12 m length filled with metal rings of 1.2 mm diameter (Fig. 152). Because of the lower volatility of $^{10}BF_3$ this column has the feed vessel for BF_3 at its upper end and the take-off for the enriched BF_3 at its lower end. The constancy of the liquid BF_3 flow to the upper end of the separating tube, which is a requirement for the success of the separation, was attained by means of a speciallydesigned measuring device.

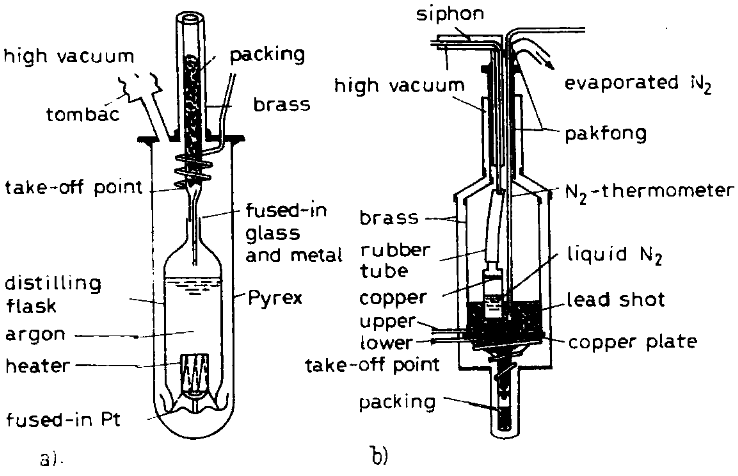


Fig. 151

a) Distilling flask

b) Condenser used in the low-temperature distillation for ^{36}Ar enrichment

5.1.4.2 The preparation of D_2 and $^{18}O_2$ by countercurrent distillation of water

The special circumstances of an isotope separation will be illustrated further by describing the preparation of D_2 and $^{18}O_2$ by the distillation of natural water at normal and reduced pressures.

Hydrogen has three isotopes: ^1H, hydrogen, ^2H or D, deuterium, and ^3H, tritium. The last-mentioned, unstable isotope is almost completely absent from natural compounds. Oxygen occurs in the form of the three isotopes ^{16}O, ^{17}O and ^{18}O, so that, if we disregard tritium, we can formulate water in the nine ways shown in Table 40.

Of these, we are interested only in the compound known as heavy water, $D_2{}^{16}O$ ($^2H_2{}^{16}O$) and the compound $^1H_2{}^{18}O$.

The physical properties of D_2O and H_2O are compared in Table 41 [37, 56].

The difference in boiling point is 1.42 deg. C. Mass spectrometry and the difference in density with respect to natural water are most frequently used for determining the concentration.

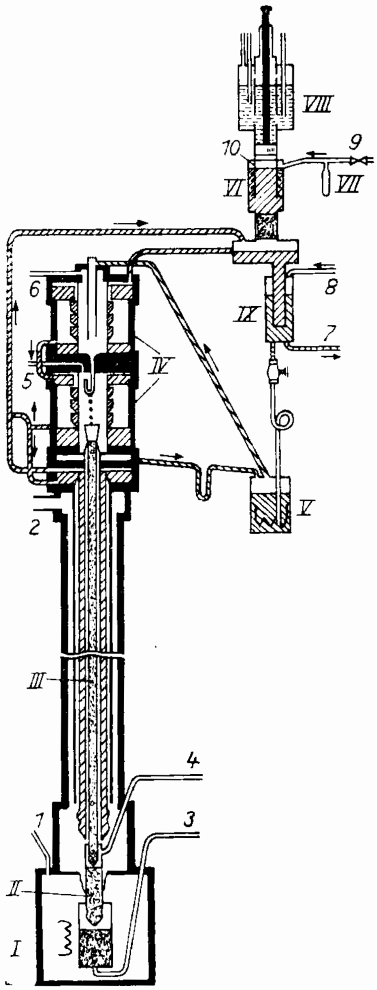


Fig. 152
Distillation column for the production of highly enriched $^{10}BF_3$ (Mühlenpfordt)

I = Evaporator with electric heater, *II* = Column for separating SiF_4 and HF, *III* = Separation tube and packing, *IV* = Double condenser for BF_3, *V* = Feed vessel for liquid BF_3, with electric heater, *VI* = Ethylene condenser, *VII* = Rubber bladder for pressure regulation, *VIII* = Storage vessel for liquid air, *IX* = Auxiliary condenser

1 = To diffusion pump, *2* = To diffusion pump, *3* = Draw-off for impurities, *4* = Take-off for highly enriched $^{10}BF_3$, *5* = Connection to manometer, *6* = Connection to manometer, *7* = Take-off for depleted BF_3, *8* = Inlet for BF_3 feed. *9* = Feed line for ethylene and hydrogen, *10* = Hydrogen gas buffer

Table 40

Theoretically possible isotope forms of water

$^{1}H^{16}O^{1}H$	$\boxed{^{2}H^{16}O^{2}H}$	$^{1}H^{16}O^{2}H$
$^{1}H^{17}O^{1}H$	$^{2}H^{17}O^{2}H$	$^{1}H^{17}O^{2}H$
$\boxed{^{1}H^{18}O^{1}H}$	$^{2}H^{18}O^{2}H$	$^{1}H^{18}O^{2}H$

Table 41

Physical properties of D_2O and H_2O

Property		D_2O	H_2O	Difference
Density ϱ_4^{20}	g/cm^2	1.1059	0.9982	0.1077
Melting point	°C	3.82	0.00	3.82
Boiling point	°C	101.42	100.00	1.42
Temp. of max. density	°C	11.6	4.0	7.6
Viscosity	cp	1.260	1.009	0.251
Surface tension	dynes/cm^2	67.80	72.75	−4.95
Refractive index	n_D^{20}	1.32844	1.33300	−0.00456

The initial material for producing heavy water is natural water, which contains 0.0146 atomic % of D (ratio 1:6850). Rain water has a slightly higher content, 0.0200 at. % (ratio 1:5000) [56]. From the point of view of distillation the main constituents of natural water are H_2O as low-boiling component and D_2O as high-boiling component, but the compound HDO must also be taken into account, so that the separation factor α^* between D and H is given by

$$\alpha^* = \frac{x_{HDO} + 2x_{D_2O}}{2x_{H_2O} + x_{HDO}} \cdot \frac{2y_{H_2O} + y_{HDO}}{y_{HDO} + 2y_{D_2O}}. \tag{168}$$

According to Urey [57], α^* can be expressed in terms of the vapour pressure ratio of the two components as

$$\alpha^* = \sqrt{p_{*H_2O}/p_{*D_2O}}. \tag{169}$$

The latter formula assumes that the solution is an ideal one, that the vapour pressure of HDO is the geometric mean of the vapour pressures of H_2O and D_2O and that the equilibrium constant of the reaction

$$H_2O + D_2O \rightleftarrows 2HDO \tag{170}$$

in the vapour phase has a value of 4.0. In Fig. 153 the values of $\sqrt{p_{*H_2O}/p_{*D_2O}}$ given by Kirschenbaum [56] have been plotted against the temperature.

In theory, therefore, the smallest number of stages would be needed if the separation were carried out at as low a pressure as possible, and at a correspondingly low temperature. These conditions, however, would render condensation difficult and would also limit the throughput owing to the large volume of the vapour. Large pressure differentials and velocities would then result, the time required would become extremely long and the procedure would be uneconomical. As is so often the case in countercurrent distillation, a compromise must be made; as a rule, therefore, the operation is performed at 50 to 125 mm Hg pressure. The value of α^* then lies in the neighbourhood of 1.05—1.06 and the temperature between 40 and 60 °C.

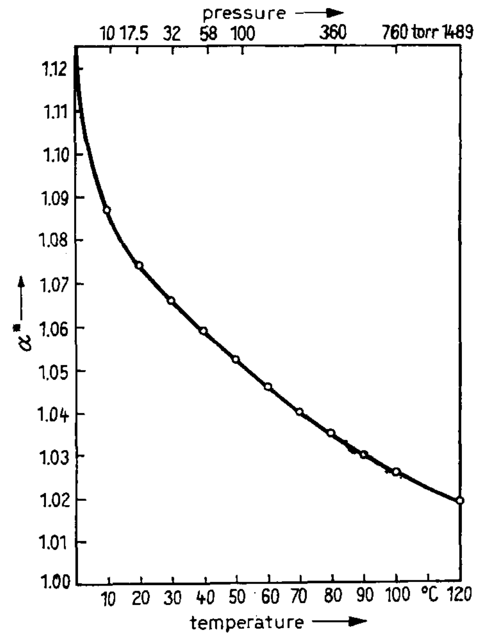


Fig. 153
Values of $\sqrt{p^*_{H_2O}/p^*_{D_2O}}$ as a function of temperature

In this case it is not possible to derive the required number of separating stages by the McCabe-Thiele method because, firstly, the equilibrium curve is too flat and, secondly, extreme concentrations are involved, as shown by the following example:

x_0 = initial concentration = 0.000146 D_2O (atomic fraction);
x_e = final concentration = 0.998 D_2O (atomic fraction)
α^* = 1.059 (at 40 °C and 55.3 mm Hg).

With these figures, the Fenske equation gives the following (very approximate) value for the minimum number of stages required (*i.e.* at total reflux):

$$n_{\min} = \log \frac{x_e(1 - x_0)}{x_0(1 - x_e)} \bigg/ \log \alpha^* = 308. \tag{171}$$

The number of theoretical stages required at the optimum take-off rate will be about 700 [58]. It should be noted that in this case the desired component is the high-boiling compound D_2O, which in batch operation concentrates in the still pot and in continuous operation is drawn off as bottom product. The overhead product is "stripped" water containing less than 0.0146 atomic % of D_2O.

According to Kuhn [59] it is convenient to express the separating effect for such ideal isotopic systems occurring with a single partial evaporation of a mixture of liquids as

$$\frac{\dfrac{y^*}{1-y^*}}{\dfrac{x_0}{1-x_0}} = \mathrm{e}^{\delta}. \tag{172}$$

The quantity δ is characteristic of the binary mixture at a given temperature no matter how large an initial concentration is chosen (*e.g.*, a mole fraction of 0.99 or 0.5 or even 10^{-3}, etc.). It is called separation parameter and can be calculated from the vapour pressure values provided that the mixture in question is athermal, which implies that the heat of mixing is zero:

$$\frac{p_{*1}}{p_{*s}} = \mathrm{e}^{\delta}, \tag{173}$$

where p_{*1} = vapour pressure of the pure low-boiling component,
p_{*s} = vapour pressure of the pure high-boiling component,
or, if the relative difference of the saturation pressures is small:

$$\delta = \frac{p_{*1} - p_{*s}}{p_{*s}}, \tag{174}$$

$$\delta = \alpha - 1. \tag{175}$$

If the mixtures are athermal, as is mostly the case with isotopes, approximate values of δ can be calculated from the formula

$$\delta = 10.7\,\frac{\Delta T}{T_p}, \tag{176}$$

where ΔT = boiling point difference of the two components at normal pressure and T_p = boiling point of the low-boiling component at distillation pressure p.

Another requirement is that Trouton's rule applies to both components and that the temperature dependence of the heat of vaporization is nearly the same for the components. Table 42 shows values of δ thus obtained.

Table 42

Separation parameters δ of isotopic systems

Isotope mixture	Temp. °C	Difference in boiling point, $\Delta\vartheta$ °C	Separation parameter δ	Separation factor α
H_2O/D_2O	70	1.6	0,05	1.05
$H_2{}^{16}O/H_2{}^{18}O$	70	0.165	0.005	1.005
$^{12}CCl_4/^{13}CCl_4$	35	0.036	0.00125	1.00125
$C^{35}Cl_4/C^{37}Cl_4$	35	~ 0.003	0.00010	1.00010

The multiplication of the elementary separating effect in countercurrent columns with a given number of theoretical stages n_{th} leads to an enrichment according to the relation

$$\frac{\dfrac{x_{\mathrm{e}}}{1 - x_{\mathrm{e}}}}{\dfrac{x_{\mathrm{o}}}{1 - x_{\mathrm{o}}}} = \mathrm{e}^{n_{\mathrm{th}}*\delta}, \tag{177}$$

with x_{o} = initial concentration, x_{e} = final concentration. Hence, the number of theoretical stages required for a particular separation which could bring about a change in concentration from x_{o} to x_{e} is

$$n_{\mathrm{o}} = \frac{1}{\delta}\left[\ln\frac{x_{\mathrm{e}}}{1 - x_{\mathrm{e}}} - \ln\frac{x_{\mathrm{o}}}{1 - x_{\mathrm{o}}}\right]. \tag{178}$$

This expression corresponds to the well-known Fenske equation (108b) for $v = \infty$.

To obtain a particular separating effect a minimum reflux ratio is required which to a first approximation is larger than or at least as large as

$$v_{\min} = \frac{Z}{\tau} = \frac{1}{\delta}\,\frac{x_{\mathrm{e}} - x_{\mathrm{o}}}{x_{\mathrm{o}}(1 - x_{\mathrm{o}})}. \tag{179}$$

In the preparation of a concentrate of heavy isotope as the bottom product the minimum reflux ratio (179) is replaced by the maximum bottom take-off ratio:

$$\left(\frac{\tau}{Z}\right)_{\max} = \frac{x_{\mathrm{o}}\delta(1 - x_{\mathrm{o}})}{x_{\mathrm{e}} - x_{\mathrm{o}}}, \tag{180}$$

where Z = amount circulating (reflux) and τ = amount taken off (distillate).

With an amount of take-off calculated according to eq. (180) an infinite number of stages would be necessary. The number of stages n_E required with a finite reflux or take-off ratio may be calculated in the manner described below.

The number of stages n_E necessary at a given take-off ratio τ/Z is given by

$$n_E = n_{\mathrm{o}} + \frac{1}{\delta}\cdot\ln\left[\left\{1 - \frac{x_{\mathrm{e}} - x_{\mathrm{o}}}{1 - x_{\mathrm{o}}}\cdot\frac{\tau}{Z}\cdot\frac{1}{\delta}\right\}\Big/\left\{1 - \frac{x_{\mathrm{e}} - x_{\mathrm{o}}}{x_{\mathrm{o}}(1 - x_{\mathrm{o}})}\cdot\frac{\tau}{Z}\cdot\frac{1}{\delta}\right\}\right]. \tag{181}$$

Fig. 154 shows the number of theoretical stages as a function of the take-off ratio in the preparation of the stable isotope ^{18}O. The three curves represent the following cases (all figures are mole fractions):

Curve I	$x_{\mathrm{o}} = 0.002$ $x_{\mathrm{e}} = 0.015$	$\delta = 0.0045$
Curve II	$x_{\mathrm{o}} = 0.002$ $x_{\mathrm{e}} = 0.020$	$\delta = 0.0045$
Curve III	$x_{\mathrm{e}} = 0.002$ $x_{\mathrm{o}} = 0.020$	$\delta = 0.0065$.

Taking, for example, curve III, we see that an enrichment from 0.2% to 2% of ^{18}O is the possible under the following circumstances:

at a take-off ratio $\tau/Z = 10^{-5}$, with $n = 388$ theoretical stages;
at a take-off ratio $\tau/Z = 10^{-4}$, with $n = 409$ theoretical stages;
at a take-off ratio $\tau/Z = 2 \cdot 10^{-4}$, with $n = 437$ theoretical stages;
at a take-off ratio $\tau/Z = 5 \cdot 10^{-4}$, with $n = 567$ theoretical stages.

Further calculating methods based on nomograms are described by Huber [61] and Hiltbrunner et al. [62].

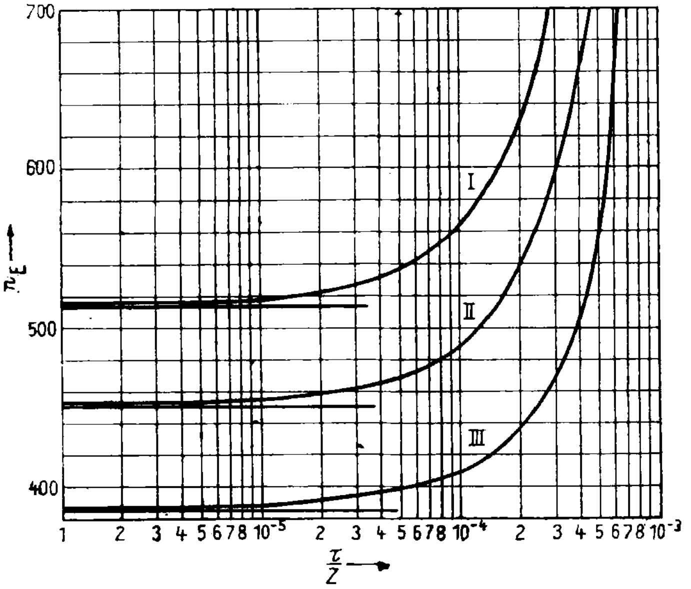


Fig. 154
Relation between the required number of theoretical stages n_E and the take-off ratio τ/Z (Kuhn)

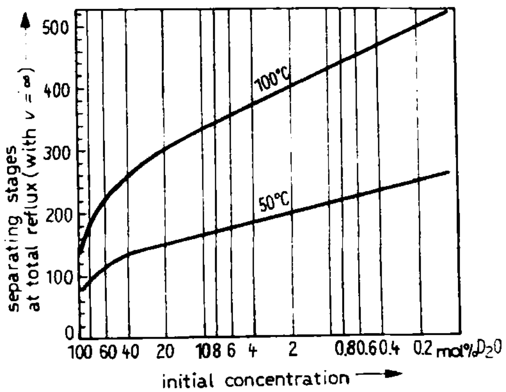


Fig. 155
Number of stages required at $v = \infty$ for preparing D_2O. Pressure 760 torr (100 °C) and 100 torr (50 °C)
$x_0 = 0.1-100$ mol%;
$x_e = 99.8$ mol%

In their preparation of D_2O Kuhn and collaborators [60] began by electrolysing natural water to a D_2O content of 1.0 mol%, and then proceeded by distillation. In industrial operation the opposite route is also followed. Fig. 155 shows the number of stages necessary with an infinite reflux ratio at 50 °C (≡ 100 mm Hg) and at 100 °C (≡ 760 mm Hg) for various initial concentrations and x_e = 99.8 mol% D_2O. The material balance in Kuhn's two-stage operation is represented in Fig. 156, which shows that the take-off ratio in the first stage is 1:1270, in the second stage 1:78.

The realization of these take-off ratios gives rise to some practical difficulty on a laboratory scale. Using Kuhn's apparatus [59] (Fig. 157) as a guide, we shall now

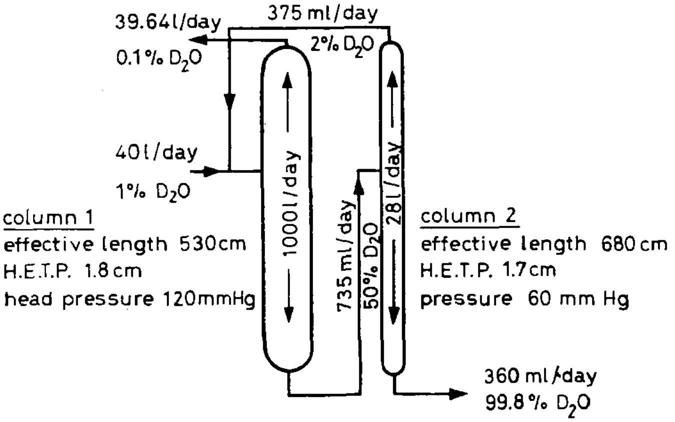


Fig. 156
Material balance in a two-stage process for preparing D_2O (Kuhn)

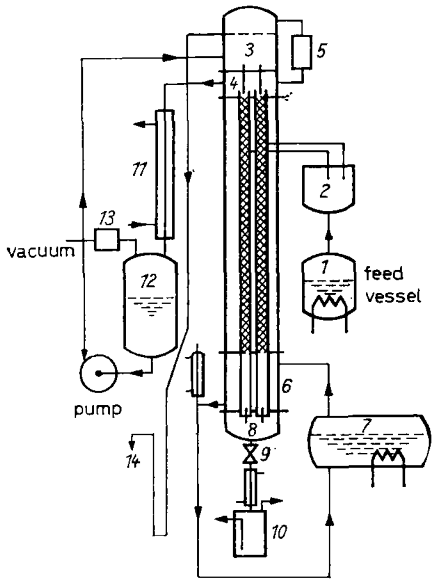


Fig. 157
Diagram of Kuhn's multi-tube column for preparaing D_2O

discuss the operation more fully. The initial mixture is present in the storage vessel *1*; it is evaporated and passes through the superheated capillary tubes *2* at a constant rate into the columns, which are filled with wire-gauze packing. The amount of vapour is controlled by the difference in pressure between points *3* and *4* by means of manometer *5*. The lower part of the columns (zone *6*) is heated by water vapour from *7* so that the total amount of descending liquid evaporates. The base of the columns is constricted by capillary tubes, through which only an amount of vapour corresponding to the take-off ratio is drawn into chamber *8* by a pressure difference. Valve *9* controls the quantity of vapour thus removed; it is condensed and collected in *10*. The vapour ascending in the columns leaves them at *4* and is totally condensed in *11*. The condensate collecting in *12* is pumped back into vessel *3*, from which a controlled amount, exactly corresponding to that introduced at *2*, leaves the column through the barometric overflow *14*. If reduced pressure is employed, vacuum is connected to *13* and to the bottoms receiver *10*.

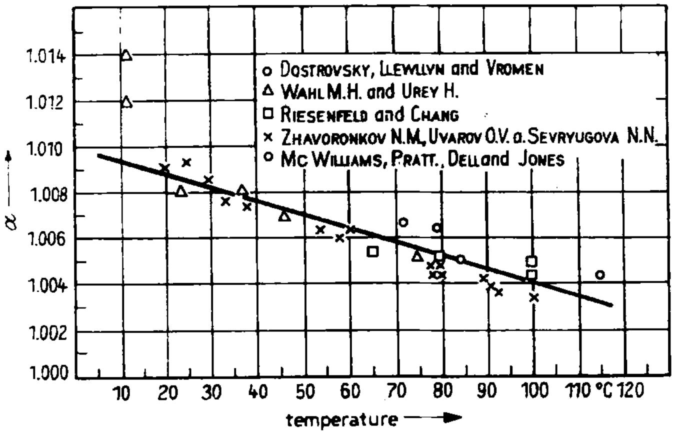


Fig. 158
Vapour pressure ratio α of the system $H_2{}^{16}O/H_2{}^{18}O$ against temperature according to Dostrovsky and Raviv

With this apparatus the throughput of starting material amounted to 1.5 kg/h. The operation was performed in two stages: in the first, D_2O was concentrated from 1.0 to 50 mol%, in the second from 50 to 99.8 mol%. The load was kept at about 10% below the flooding point. With the tubes packed with wire-gauze Raschig (Dixon) rings, the HETP amounted to 1.7 to 1.8 cm. The use of packing was found to be necessary, because empty tubes proved to be wetted irregularly on account of the high surface tension of water. The production of a uniform liquid film on the packing is the crucial problem in the preparation of heavy water (see chap. 4.2). The present state of the large-scale production of heavy water has been reviewed by Lumb [59a].

The normal distribution of the isotopes of oxygen is approximately $^{16}O:^{17}O:^{18}O = 2500:1:5$. During the distillation of natural water ^{18}O concentrates in the bottoms. As can be seen from Fig. 158, however, the value of δ for $H_2{}^{16}O/H_2{}^{18}O$ lies a factor of ten lower than for H_2O/D_2O. At 100°C (760 mm) α is about 1.004 and at 50°C (100 mm) about 1.007. The data presented in Fig. 158 were collected by Dostrovsky and Raviv [53]. The relatively strong scattering of the values is due to the experimental difficulties involved in the determination of α. It is a favourable point, however, that natural water contains 0.204 at. % of ^{18}O, a relatively high concentration.

Kuhn, with his column, reached a concentration of 6 at. % of ^{18}O. Dostrovsky and his collaborators at the Weismann Institute in Israel [53], prepared ^{18}O of about 95% purity and ^{17}O of about 2%. The preliminary concentration from 0.2 to 1.6% of ^{18}O was carried out in 10 columns connected in parallel (diam. 100 mm). The multistage cascade (diam. 80—100 mm) was fed at 800 ml/h and was operated with a take-off ratio of 1.37×10^{-2}. The procedure is to be improved so as to produce a concentration of 99.8%. The highest concentration of ^{17}O is present at the centre of the cascade ($\approx$ 10%). In these separations the Dixon packing, made of 100 mesh phosphor bronze wire gauze in the shape of a Raschig ring with an S-shaped bridge, proved its value [63].

The writer, using a single-stage continuous column (Fig. 160), attained a concentration of 5.25% ^{18}O. The experiments performed with this unit at 300 mm pressure indicated that the most probable value of α at this pressure (76°C) is 1.0068 [64]. Uvarov et al. [54, 65] effected an enrichment from 3 to 24.5% of ^{18}O in a column of 9.5 m effective length and 52 mm diameter, filled with triangular wire spirals (2.0×1.6 mm) and operated batchwise at normal pressure. Their HETP amounted to 1 cm. The high enrichment of the oxygen isotopes by countercurrent distillation of heavy water was studied by Staschewski [70].

Fig. 159 shows a continuous apparatus made of copper. The packing consists of 1.6 mm (1/16 inch) Dixon gauze rings. The columns are extensively automatized; in an auxiliary unit the bottom product enriched with ^{18}O is electrolyzed. The $^{18}O_2$ gas is recombined with hydrogen, which is also obtained by electrolysis. The final products are therefore $H_2{}^{18}O$ and $D_2{}^{16}O$.

Whilst the time for the establishment of a stationary condition in normal distillations varies from a few hours to at most 24, it may amount to weeks or months in the fractionation of isotopes. Since the older formulae for calculating this time proved unreliable, the problem was studied anew. Kuhn and collaborators [59] evolved the following equation for the equilibration time T_b of parallel-tube and packed columns:

$$T_b = H \left\{ \frac{1}{n_{\text{eff}} \cdot \delta} \ln \frac{1 - x_0}{1 - x_e} - x_0 \right\} \bigg/ \{Z \cdot x_0 (1 - x_0)\} \tag{182}$$

with H = hold-up, x_0 = initial concentration, Z = feed rate, x_e = final concentration.

Further contributions to this subject have been made by Jackson and Pigford [67], Rosen [68] and Brodsky [38]. The books of London and Cohen [69] deal with the whole theory of isotope separation. This includes the optimization of cascade arrangements which is of great importance in isotope separation as well as in the separating plants of the chemical industry [71].

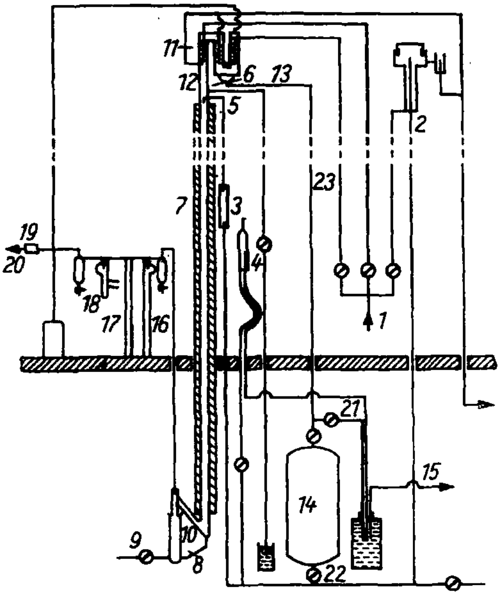


Fig. 159

Metal still for continuous preparation of $H_2{}^{18}O$

1 = Water supply, *2* = Distilled water apparatus, *3* = Flow meter, *4* = Constant level device, *5* = Feed line, *6* = Overflow, *7* = Column, *8* = Boiler, *9* = Product line, *10* = 1-inch copper pipe between boiler and column, *11* = Reflux cooler, *12* & *13* = Main condensers, *14* = Stock tank, *15* = Drain, *16* = Boiler manometer, *17* = Differential manometer, *18* = Manostat, *19* = Magnetic valve, *20* = To pump, *21–23* = Piping

5.1.4.3 The preparation of various isotopes

In addition to the foregoing, some examples may be given of cases in which other isotopes have been concentrated by distillation.

The relative difference in mass and the relative natural abundance are particularly favourable for separating the isotopes of carbon and chlorine:

^{12}C	98.9%	relative difference in mass 8.35%
^{13}C	1.1%	
^{35}Cl	75.4%	relative difference in mass 5.7%.
^{37}Cl	24.6%	

Both pairs of isotopes are separated in the rectification of carbon tetrachloride. Using a parallel-tube column having about 250 effective stages, Kuhn [59] succeeded in concentrating the ^{13}C by about 7% of the original value. (Concentrations were determined by mass spectrometry). An unexpected and interesting result was the observation that heavy carbon (^{13}C) accumulates in the low-boiling overhead fraction, with ^{37}Cl on the other hand in the high-boiling fraction. A similar effect is found with the boron isotopes $^{10}B-{}^{11}B$. Baertschi and Kuhn [72] found that the infrared contri-

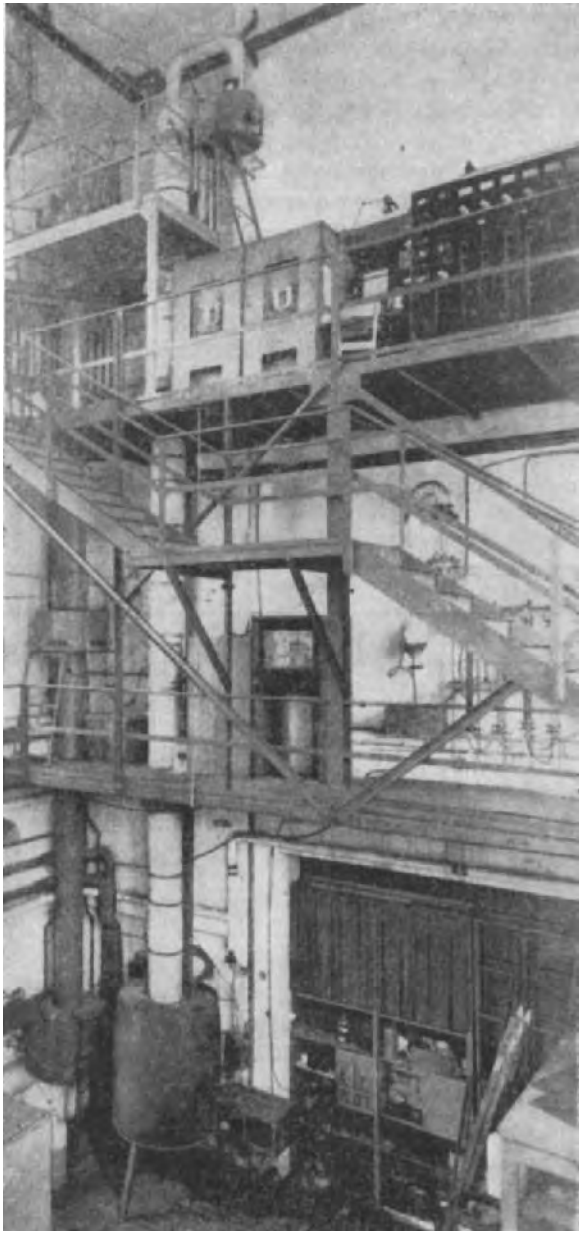


Fig. 160
The author's still for enriching $H_2{}^{18}O$

bution to the dispersion interaction may be considered to be the cause of the greater volatility of the heavy molecules.

In the distillation of CCl_4 a double isotope separation thus takes place. The separation factor of the system $^{12}C-^{13}C$ is about 1.00013, corresponding to a difference in boiling point of approximately 0.036 deg. C (Table 42). The effect referred to above — *i. e.* a concentration of ^{13}C in the overhead product — also occurs in the rectification of chloroform, benzene and methanol. When chloroform is distilled, ^{37}Cl accumulates in the bottoms, and ^{18}O concentrates in the bottoms when methanol is fractionated. Data for such distillations [43] have been collected in Table 43.

Table 43

Single and double isotope concentration by countercurrent distillation

n_{eff} = effective number of stages

p_l, p_s = vapour pressure of the substance with the light (l) and the heavy (p) isotopes at the distillation temperature (34.6 °C)

x_{B1} = concentration at the foot of the column

x_{B2} = concentration at the column head

T_l = boiling point of the substance containing the light isotope

T_s = boiling point of the substance containing the heavy isotope

Substance	n_{eff}	Isotope separation of								
		^{13}C (overhead)			^{37}Cl (in flask)			^{18}O (in flask)		
		$\frac{x_{B1}}{x_{B2}}$	$\frac{p_l - p_s}{p_s}$	$T_l - T_s$ (deg C)	$\frac{x_{B1}}{x_{B2}}$	$\frac{p_l - p_s}{p_s}$	$T_l - T_s$ (deg C)	$\frac{x_{B1}}{x_{B2}}$	$\frac{p_l - p_s}{p_s}$	$T_l - T_s$ (deg C)
Chloroform	610	0.62	-8×10^{-4}	+0.02	1.06	$+10^{-5}$	−0.003			
Carbon-tetrachloride	80	0.90	-1.3×10^{-4}	+0.033	1.003	$+3 \times 10^{-4}$	−0.001			
Methanol	140	0.97	-2×10^{-4}	+0.0055				1.50	3×10^{-3}	−0.07
Benzene	80	0.98	-2.5×10^{-4}	+0.006						

Trauser and co-workers investigated the application of molecular or short-path distillation in the enrichment of the lithium isotopes. They developed single and multi-stage apparatus and found separation factors between 1.052 and 1.064 for one stage in the temperature range from 535 to 627 °C. In a similar way the mercury isotopes were separated.

5.2 Methods of operation

Although simple and rectified batch distillation are the methods most used in the laboratory, they are not the only ones. Procedures employed mainly in industry have also been added to the laboratory repertoire. In order to increase output, semicontinuous and continuous processes have been adopted, whilst in certain cases partial condensation also presents advantages.

5.2.1 Batch and semi-continuous distillation

The basic difference between batch and continuous distillation is that the composition of the liquid in the still pot and that of the distillate change progressively during the former operation, but are constant during the latter.

In batch distillation (whether of the simple or countercurrent type) a definite charge is put into the still and treated. A distinction should be made between fractional and unfractionated distillation. In the latter, the whole distillate is collected in one lot, and the initial material is thus separated into two fractions: the distillate and the residue. In fractional distillation, on the other hand, the distillate is collected in a number of successive portions. In an interesting paper Block et al. [168] have investigated the influence of the operating variables on the result of a separation for discontinuous operation. A small total hold-up is particularly favourable for substances a small proportion of which is contained in the flask.

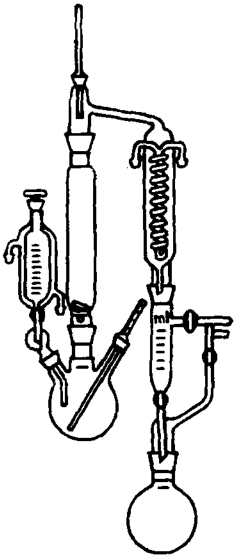


Fig. 161
Apparatus for semi-continuous vacuum distillation with column and heating of the feed

In certain cases a semi-continuous procedure is to be recommended owing to the higher throughput and the better heat economy that can be attained. The procedure is to supplement the contents of the still pot with feedstock at the same rate at which distillate is removed. The feedstock may be admitted either directly into the still pot or at some point in the column and should previously have been heated nearly to its boiling point (Fig. 138). The flask must be large enough to contain the residue from the quantity of feedstock to be introduced. This method is chiefly employed for separating a low-boiling preliminary fraction or for concentrating a mixture containing a high proportion of solids. In the latter case the continuous admission of feedstock prevents the contents of the still from becoming too viscous or even solid.

After a certain time the feed is stopped and the liquid in the boiler is further evaporated batchwise, or drawn off. Continuous withdrawal is impossible since the feed steadily introduces low-boiling material which has to be evaporated before the residue is drawn off. The apparatus illustrated in Fig. 161 is built up from standard parts, is provided with a column and allows the feedstock to be preheated in a jacketed vessel.

5.2.2 Continuous distillation

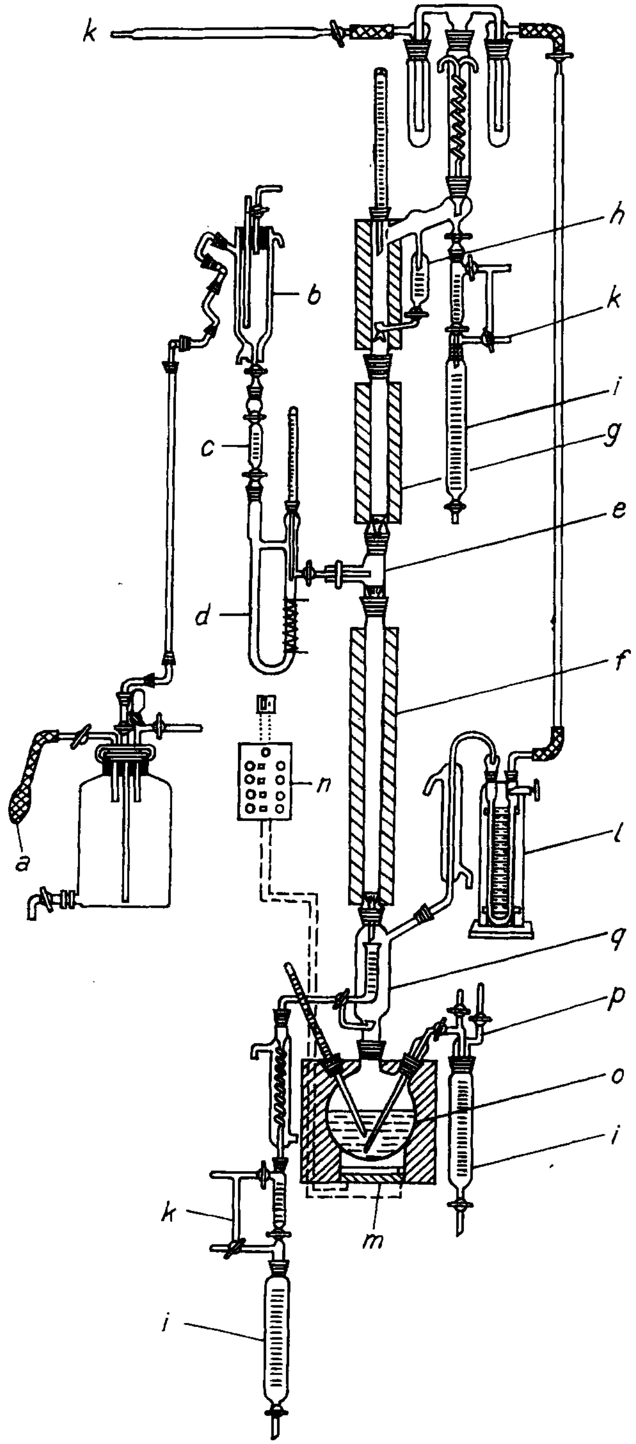
In continuous distillation the feedstock — usually preheated to a certain degree — is uninterruptedly passed into the apparatus and is separated into an overhead distillate and a bottom product, both of which are continuously removed from the process. After the ratio and compositions of these two products, and other predetermined conditions, have become established, they should not change during the further course of the operation (see chap. 4.7.2). Continuous countercurrent distillation, like the corresponding batch process, is carried out with a column, and the feed is usually fed into the column at some point between its base and top (Fig. 162).

The advantages of continuous, as opposed to batch and semi-continuous distillation [28], are the less severe thermal treatment to which the material is submitted and the higher throughput that can often be realized. In this respect the results of the process on the laboratory scale may frequently equal those of semi-technical batch distillation. Such continuous distillation can, in fact, be used in many cases for preparative purposes (with a throughput of, say, 10—20 kg a day), *e.g.* for the production of temperature-sensitive pharmaceutical substances or for the recovery of solvents. Throughputs in the laboratory mostly range from 0.5 to 5 l/h. Corrosive substances attacking the more common metals may, with a few exceptions, be distilled continuously in glass; on an industrial scale these substances would require the use of glass-lined plants or plants of porcelain or special metals. Further basic features are that with uniform column operation top and bottom products of constant composition may be obtained and that the heat consumption of a continuous distillation is appreciably lower than that of a batch process so that time and energy are saved. An important requirement of a continuous method — constant composition of the raw material — can easily be realized in the laboratory and this composition may readily be determined in advance by a preliminary distillation (section 7.2).

→

Fig. 162
Destinorm apparatus for continuous vacuum distillation

a = filling device, b = heated feed vessel, c = graduated pipette, d = heating tube for feed, e = connecting tube with feed inlet, f = lower column part, g = coil, h = column head with graduated pipette, i = graduated pipette, k = vacuum connection, l = contact manometer, m = flask heater, n = switchboard, o = bottom, p = sampling point, q = bottoms reflux meter


k
h
b
k
i
c
g
e
d
f
n
a
l
q
p
o
i
k
m
i

5.2.2.1 Applications

The principal applications of continuous laboratory distillation may be classified as follows:

For comparison with industrial operations

a) The development of a process to be converted to a semi-technical or industrial scale;
b) The establishment of a small-scale distillation comparable with one on an industrial scale;
c) Demonstrations for training purposes.

The preliminary fractionation of mixtures in quantities of, say, 50 to 100 l.

a) The removal of a low-boiling fraction;
b) The separation of a medium-boiling cut;
c) The separation of high-boiling material.

Production distillation for amounts up to 20 kg a day (see chap. 5.1.3)

a) The separation of temperature-sensitive materials, e.g., essential oils, scents;
b) The isolation of pure substances from crude mixtures;
c) The purification of starting materials and solvents;
d) The production of pharmaceutical substances.

There is a marked tendency in industrial distillation practice to convert batch operations into continuous ones, and it is important, therefore, that laboratory distillation should be able to follow suit. It is becoming more and more necessary for industrial processes to be developed first with corresponding apparatus on a small scale. In the case of multicomponent mixtures, in particular, information may be obtained more rapidly by experiment than by calculation. Trials in the laboratory are, of course, far more economical than experiments on an industrial scale, since they save material, power and time, and by the introduction of standard laboratory components it has become easy to construct small distillation equipment in accordance with the flow diagram of an industrial plant. The distillation tests described in section 5.2.2.4 for example, were all performed with industrial application in mind. In the same way it is now also possible to evolve laboratory tests for checking processes that have already found application on a large scale, with the object of finding the causes of malfunctioning or irregularities that may occur [73]. Thus, *e.g.*, the lay-out of columns for the sharp fractionation of isoprene on an industrial scale was prepared by semi-technical test distillations. The concentration profiles obtained from a test column were checked with a computer programme. The agreement was found to be close. This enabled an optimum lay-out of the industrial columns (see chap. 4.15; [73a]).

The advantages of continuous distillation are particularly clear for binary mixtures of components having a large difference in boiling point. The apparatus can then be relatively simple and can run for days on end without interruption; even in glass equipment a considerable throughput can be obtained, both at normal and reduced pressures. By the use of a second column, ternary mixtures can also be separated continuously (chap. 4.9). In theory a mixture of n constituents can be separated by means of $(n - 1)$ columns, but in practice a mixture containing more than three components is unlikely to be dealt with in one operation, since the process tends to become complicated. In such a case it is usually preferable to separate the mixture first into two or three fractions continuously, and then to fractionate each of these separately in batch into its constituents.

If the mixture to be fractionated contains a large high-boiling "tail" it is advisable to remove the latter first by thin-film distillation (*cf.* section 5.4.3) since high-molecular-weight substances can often give rise to decomposition and polymerization. A preliminary removal of the high-boiling fraction by a thermally mild method allows the yield of distillate to be increased appreciably. Low-boiling "tops" may be separated from a product at a high rate (up to 3 l/h) by flash distillation (section 5.4.2). If both of these procedures are applied, a residue-free main fraction is obtained which can then be split up into fractions by continuous countercurrent distillation. To illustrate this sequence of operations, Fig. 163 gives a scheme for the separation of a multicomponent mixture ranging from C_1 to C_{20}.

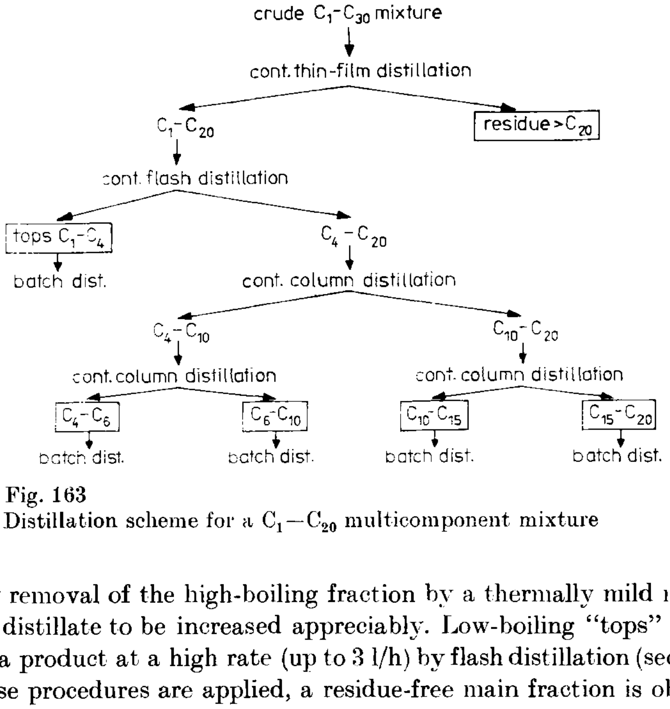


Fig. 163
Distillation scheme for a C_1—C_{20} multicomponent mixture

5.2.2.2 Calculation

As with distillation in batch, it is necessary before undertaking a continuous rectification to select the conditions, namely:

1. The pressure, atmospheric or reduced;
2. The number of theoretical stages required;
3. The minimum reflux ratio;
4. The temperature of the feed;
5. The amount of heat necessary.

Prior to every continuous distillation, an ASTM-type distillation — or, preferably, a sharp rectification — in batch should be performed, and this will usually give the information needed.

The question of the distillation pressure will be fully discussed in section 5.4. The number of stages and the minimum reflux ratio are calculated as described in 4.7.2; the temperature of the feedstock is usually kept as near as possible to its boiling point. The dimensions of the column and the heat requirements can be found as detailed in sections 4.11 and 4.12, respectively. When calculating the column diameter one should remember that the lower half-column is loaded with an amount of reflux exceeding that in the upper half-column by the high-boiling part of the feedstock. If little distillate is to be taken off — say 10 or 20% — it is advisable to make the lower column wider than indicated by the calculation described, which applies only to the upper column half.

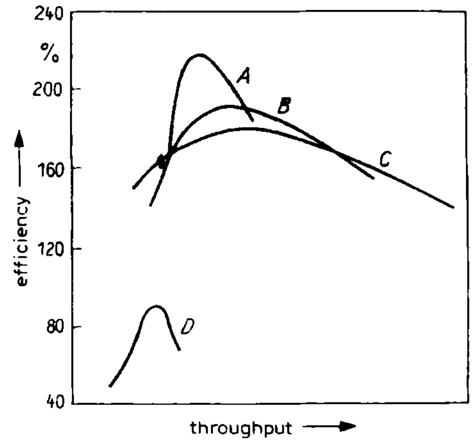


Fig. 164
Plate efficiency as a function of the load (McWhirter and Lloyd) [76]

A, *B*, *C* = cyclical operation with three different divisions of the cycle, *D* = continuous operation

Here the possibility of cyclic operation should be mentioned, which was studied by Gelbin [74]. Thus, according to Cannon [75], the vapour flow from the boiler to the column may be controlled such that a cycle consists of a three-second flow followed by a one-second interruption. McWhirter and Lloyd [76] used a combined plate and packed column in which each of the five plates carried a layer of packing. With the mixture methyl cyclohexane-toluene they increased the column efficiency considerably by means of cyclic operation, the optimum depending on the timing of the cycle and the shape of the quantity-time curve during metering. Fig. 164 illustrates the astonishingly high plate efficiencies with cyclic operation.

5.2.2.3 Apparatus for continuous column distillation

For laboratory and semi-technical operation the packed column is the type chiefly employed; in special cases use is made of plate columns constructed of glass, which, owing to the resistance of the material, are also suitable for the distillation of corrosive substances.

An all-metal laboratory apparatus with a tubular heater was described as early as 1931 by Burstin and Winkler [77]. It was designed for distilling crude mineral oil residues at atmospheric and reduced pressures and has also proved convenient for treating readily decomposable or foaming liquids, since it operates on the principle of thin-film distillation. It may be noted that this unit (Fig. 165) corresponds to industrial installations of the same period and could thus be used for solving problems encountered in large-scale practice. The control systems for continuous laboratory columns described by Kolling and Tramm [78] are intended to provide automatic operation. Fig. 166 shows the arrangement used for distillation at atmospheric pressure.

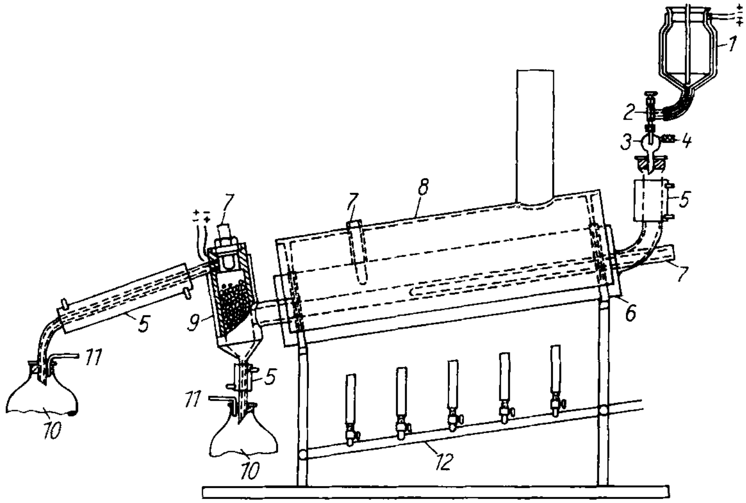


Fig. 165
Apparatus for continuous distillation with tubular heater (Burstin and Winkler)

1 = Constant level vessel, *2* = Needle valve, *3* = Observation bulb, *4* = Vacuum connection, *5* = Condensers, *6* = Metal block, *7* = Thermometer wells, *8* = Insulated jacket, *9* = Dephlegmator, *10* = Receivers, *11* = Vacuum connections, *12* = Burners

Further details of a Destinorm apparatus for continuous distillation at reduced pressures (Fig. 162) will be discussed in chap. 5.2.2.5. A continuous plate column is exemplified in Fig. 167 by a Labodest apparatus which can operate from atmospheric pressure down to about 20 torr. It is provided with vapour-collision bubble-cap plates of glass (chap. 7.3.3) having an efficiency between 80 and 100%. Their mode of operation is identical with that of industrial plates so that the test results can be transferred directly. Besides, they are well suited to demonstrations since the gradual exchange process can be observed. This type of column is built with lengths between 600 and 1300 mm and column diameters between 30 and 120 mm and has between 5 and 28 plates depending on the distance between the plates (35 to 150 mm).

A remarkable feature of the apparatus of Fig. 167 is the boiler with circulatory heating (4) which imitates the industrial construction. The switch cupboard (20) contains all the measuring and control devices.

This is a good illustration of the general trend to learn from industry and to shape laboratory and pilot plant methods according to large-scale processes [79].

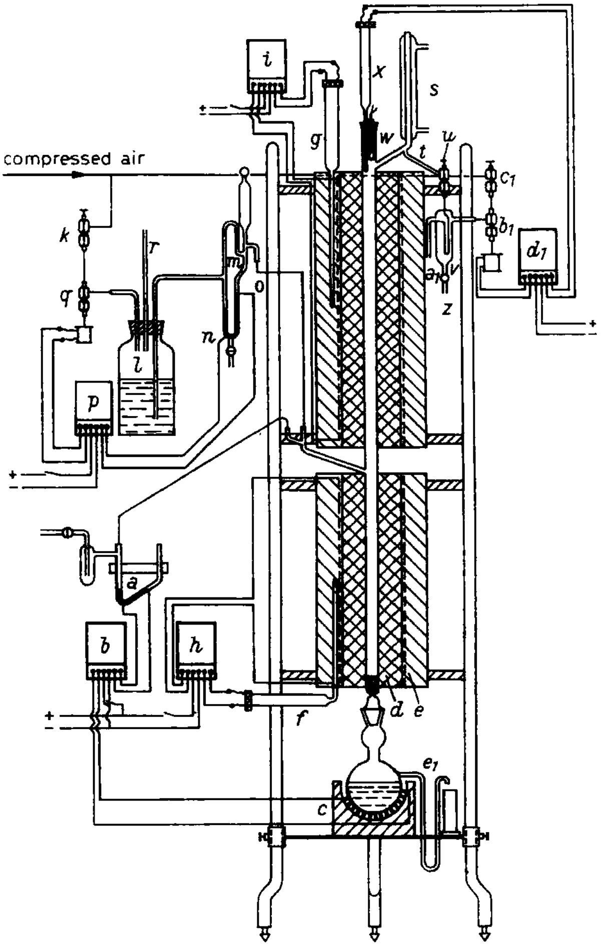


Fig. 166

Arrangement of an automatic apparatus for continuous distillation at atmospheric pressure used by Kolling and Tramm

a = Contact manometer, b = Relay, c = Electric heater, d = Insulating jacket, e = Heating jacket, f/g = Contact thermometers, h/i = Relays, k = Valve, l = Storage vessel, m = Flowmeter, n/o = Electric contacts of flowmeter, p = Relay, q = Electromagnetic valve, r = Resistance capillary, s = Total condenser, t = Capillary tube, u = Needle valve, v = Receiving vessel, w = Thermometer, x = Contact thermometer, y = Syphon-shaped tube, z = Draw-off cock, a_1 = Capillary tube, b_1 = Electromagnetic valve, c_1 = Needle valve, d_1 = Relay, e_1 = Overflow

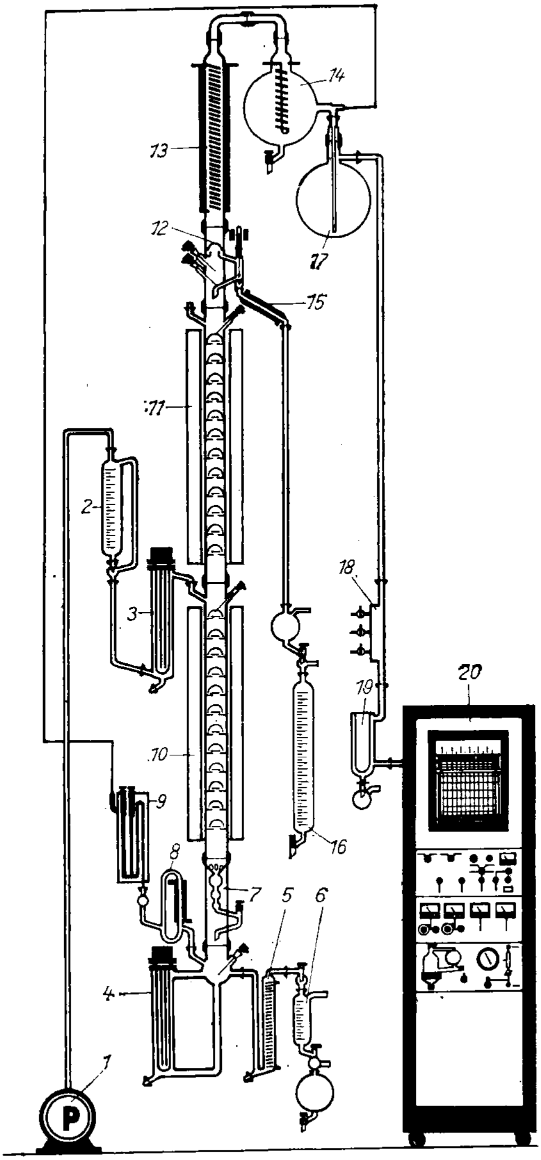


Fig. 167
Labodest bubble-cap column with vapour collision plates made of glass for continuous operation at 760 to 20 torr (Stage)

1 = pump, *2* = feed vessel, *3* = feed heater, *4* = circulating evaporator, *5* = bottoms condenser, *6* = bottoms receiver, *7* = reflux meter, *8* = safety device, *9* = differential pressure controller, *10/11* = plate columns with heating jacket, *12* = column head, *13* = condenser, *14* = expansion vessel, *15* = distillate condenser, *16* = exchangeable receiver for distillate, *17* = buffer volume, *18* = tap distribution, *19* = cold trap, *20* = switch cupboard

The importance of keeping the equipment as simple as possible was soon recognized, and accordingly the Labodest apparatus after Stage [80] as well as the series of components manufactured by Fischer Labor- und Verfahrenstechnik of Bonn-Bad Godesberg and by several other firms were designed. This is true also for the Destinorm equipment of VEB Kombinat Technisches Glas of Ilmenau, and the components made by VEB Jenaer Glaswerk Schott & Gen. of Jena. Standardized components enable fractured parts to be replaced promptly. Further, all kinds of problems may be tackled as regards equipment, and large-scale plants may be copied to a large extent.

5.2.2.4 Examples of application from laboratory practice

With the aid of the columns and other apparatus described it is possible to separate liquid mixtures continuously at normal and reduced pressures as well as at small overpressures (chap. 5.4.5) as sharply as in batch distillation. This is clear from the distillation curves of the products obtained in the continuous distillation of a mixture of crude fatty acids in the C_4 to C_{19} range (Fig. 168). A further example shows that by the use of control devices it was possible to separate a mixture of phenols into its main components with great constancy. Fig. 169 illustrates the results of the first separation in this sequence, which was made between the *ortho-* and *meta/para-*cresol fractions.

120 samples were taken during the run for determination of the density of the bottoms and the solidification point of the tops. As the diagram shows, there were negligible variations in the temperatures of the feed, the head and the bottom, and

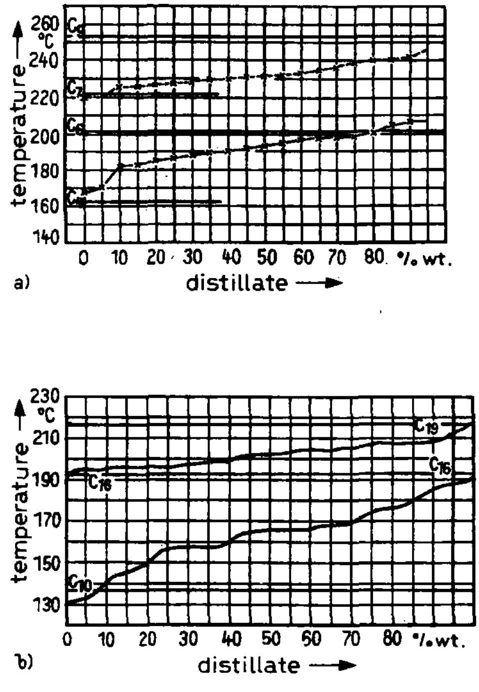


Fig. 168
Distillation curves of products prepared by continuous laboratory distillation from a C_4-C_{19} mixture of fatty acids

a) $C_4 \cdots C_9$
b) $C_{10} \cdots C_{19}$

in the physical properties in the course of 22 hours. The vacuum, also, could be kept constant by the control mechanism. In a similar way a phenol fraction, solidifying at 37.0 °C, could be worked up continuously to an overhead of pure phenol, solidifying at 40.3 °C (purity 99.2%), by the use of a reflux ratio of 10:1 at 60 mm pressure. The bottom product was continuously withdrawn so that its residence time in the still was considerably shorter than with batch operation. Thus, decomposition of the bottom product was largely prevented. Further continuous methods, including azeotropic and extractive distillation, flash distillation, thin-film distillation and molecular distillation will be discussed in sections 6.2, 5.4.2, 5.4.3 and 5.4.4 respectively.

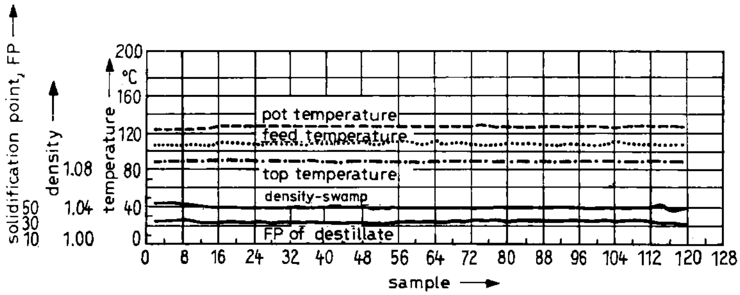


Fig. 169
Continuous rectification of crude phenols. Pressure: 30 torr; duration of run: 22 hours
Distillate: phenol + o-cresol; bottoms: m/p-cresol + xylenols and higher

5.2.2.5 Starting up continuous distillations

The function of the various control devices has been discussed in section 5.2.2.3 we need therefore deal only with a few points concerning the operation of the process (Fig. 162). The mixture charged to the reboiler *o* should have the expected composition of the bottom product, so that long equilibration times are avoided. In order to wet the packing properly at the same time, this reboiler charge may be prepared batchwise, by distilling off the required amount of material. Then the supply of feedstock is started (*e*), after first heating it to the required temperature in the storage vessel d. The feed rate is regulated by means of the measuring burette *c* and the reflux ratio is adjusted at the column head *h*. The load on the column depends on the feed rate and is in addition governed by the contact manometer *l*. It is obvious that the adjustment must be such that the feed rate is the sum of the overhead and bottom take-off rates. The valves on the distillate *h* and bottoms receivers *i* are therefore so regulated that the proper ratio is obtained. As an example we can take the separation of a benzene-toluene mixture containing 20% of benzene. At a feed rate of 500 ml/h we must take off 100 ml/h at the head and 400 ml/h from the bottoms. If the reflux ratio is to be adjusted to 2:1, the vapour load will have to be regulated at 300 ml/h. The reflux will be 200 ml/h above the feed point and 700 ml/h below the feed. Equilibration will probably require $^1/_2$ to 1hour and its progress can be judged by variations in the top and bottom temperatures (Fig. 169). As soon as the feed temperature has also become constant, the apparatus should operate without further adjustment. The operator's attention can then be confined to checking the quantities of feed and take-off and to recording the experimental data.

5.2.3 Separation by partial condensation

The term partial condensation is used to denote the liquefaction of a fraction from a flow of vapour. It can be brought about deliberately by interposing a special condenser — a so-called *dephlegmator* — in the vapour line, and it also occurs as an undesired effect by loss of heat from an insufficiently insulated column (Fig. 170a).

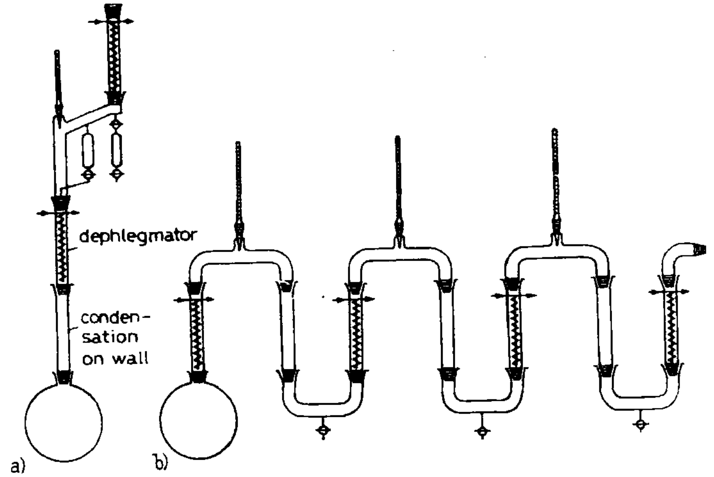


Fig. 170
Partial condensation

a) Dephlegmator (Labodest, type III of Stage) and lateral condensation
b) fractional partial condensation

The gradual dephlegmation of a vapour flow in a tube system consisting of sections with progressively falling temperatures serves for preliminary separations which give various fractions in the case of components with great differences in boiling point (Fig. 170b). Examples of calculations applicable to such partial condensation (assuming the condensate to be drawn off immediately) have been given by Sigwart [81]. The enrichment achieved by partial condensation can be increased appreciably by employing the countercurrent principle [82].

The flows of vapour leaving the column have to be in a particular ratio depending on the object of the distillation. In industry it is common to make a dephlegmator produce the reflux and cool the distillate to be drawn off in a production condenser. The aim is to use the amplifying effect of the dephlegmator which is due to the partial condensation of the high-boiling components. Partial condensation is employed especially in the low-temperature separation of gas mixtures. Otto [83] has reported the partial condensation of binary mixtures in vertical tubes.

The performance depends on the nature of the mixture to be separated [84]. Another advantage is the low hold-up. In Table 44 two examples concerning mixtures of technical importance are given.

The calculation of the enrichment caused by a dephlegmator can be carried out with a formula due to Fabuss:

$$\log (V_l + 1) = \frac{1}{\alpha - 1}\left(\alpha \log \frac{y^2}{y_1} + \log \frac{1 - y_1}{1 - y_2}\right) \tag{183}$$

in which

V_l = the internal reflux ratio $= \dfrac{\text{amount of condensate}}{\text{amount of vapour feed}}$ (both in moles/h);

y_1 = mole fraction of vapour feed;

y_2 = mole fraction of residual vapour.

Table 44

Separating action of a dephlegmator

Mixture	x_1 Concentration before the dephlegmator	x_2 Concentration after the dephlegmator	v Reflux ratio	n_{th} Number of theoretical stages
Ethanol-water	67 mol%	78 mol%	5	3
Benzene-toluene	63 mol%	80 mol%	5	1

A nomogram has been developed for the solution of this equation [85]. An equation for the calculation of residual vapour and condensate concentrations of a dephlegmator in multicomponent separation is given by Fischer [86]. On the basis of extensive experiments Herrmann [87] has tried to disentangle some points of the complicated problem of partial condensation. Although the study deals with industrial dephlegmators Herrmann's findings are of use for the laboratory and pilot plant scales as well. Further methods of calculating the separating efficiency of a partial condenser have been reported by Tröster [88]. Wondrak [88a] is credited with having pointed out that the optimum fields of application of distillation and partial condensation are quite different. Consistent treatment of simple thermodynamic model concepts reveals the functional relations between the two separating processes for ideal binary mixtures.

In analytical and preparative distillations in the laboratory total condensation is generally used, and dephlegmation is employed only when the simulation of an industrial plant is required. In this case a dephlegmator (Fig. 170a) is inserted above the column. Total condensation has the advantage that it is relatively easy to process the liquid condensate in a certain ratio whereas the establishment of a definite reflux ratio from a dephlegmator is difficult, since small variations in the amount and temperature of the cooling water are sufficient to cause large changes in the quantity and composition of the reflux and residual vapour. On an industrial scale it is the practice not to measure the quantity of reflux in a partial condenser, but to regulate it only by controlling the temperature at the head. If the quantity and temperatures of the cooling water entering and leaving the dephlegmator are measured, the quantity of reflux can be calculated roughly from the heat of evaporation of the distillate. In cases where the products are more or less constant, as generally occurs in manufacture, this procedure may be adequate, but when mixtures of varying composition have to be dealt with the calculation becomes very uncertain.

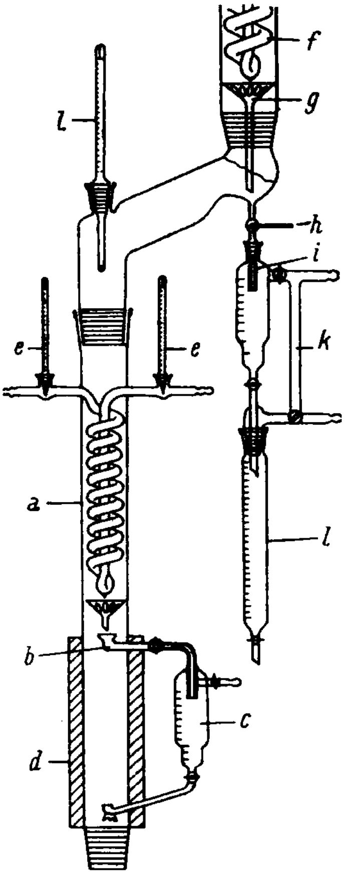


Fig. 171
Destinorm column head for partial condensation with capillary take-off tubes

a = Dephlegmator, *b* = Collecting funnel,
c = Measuring pipette,
d = Glass wool insulation,
e = Thermometers, *f* = Condenser,
g = Perforated funnel, *h* = Cock,
i = Capillary distillate take-off,
k = Receiver, *l* = Measuring pipette

In laboratory experiments utilizing partial condensation to imitate a technical process, a special form of the author's Destinorm column head, shown in Fig. 171, may be used. The ascending vapour is partially condensed in dephlegmator *a* and the resulting condensate is passed into measuring pipette *c* through the collecting funnel *b*; pipette *c* is provided with a capillary inlet, so that the amount of reflux can be observed at any moment. The section between the funnel and the column is insulated by the glass wool jacket *d*. The temperatures of the incoming and outgoing water are read off on thermometers *e*. The uncondensed vapour flows upwards to condenser *f*, where it is completely liquefied. The condensate is collected by the perforated funnel *g* and when cock h is opened it passes down through capillary tube *i* into receiver *k*. A cooler may, if desired, be interposed between k and the receiving vessel *l*.

As the separating effect of a dephlegmator is relatively low and its control on a laboratory scale presents difficulties it will, as has already been said, be employed mainly for comparative distillations. Partial condensation in stages may, however, be applied for the preliminary separation of mixtures with large differences in boiling point, especially for the removal of water or some other low-boiling fraction. The column is then replaced by a system of tubes (Fig. 170b) containing condensers at progressively decreasing temperatures. In this way it is, for instance, possible to split up a mixture of crude fatty acids (up to C_{20}) fairly rapidly into the fractions C_1—C_4, C_4—C_9, and C_9 to C_{20}.

According to Junge [89] a proper application of partial condensation within a column can increase its efficiency. The effect in question is a partial wall condensation due to a heat loss in the column, *i.e.*, to non-adiabatic operation. Trenne [90] has reported a similar process. On the other hand the extensive calculations of Kuhn [91] promote the view that the most effective procedure is to avoid all condensation except at the upper end of the column. Von Weber [92] has pointed out that partial condensation offers advantages if it is applied in connection with a column narrowing towards its top (see Fig. 172). Owing to the increase in concentration

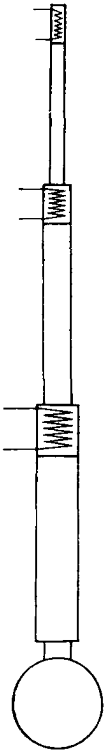


Fig. 172
Partial condensation in countercurrent distillation [92]

in the upper part of the column there is an advantage in reducing its hold-up. On the other hand the required reflux flow becomes smaller towards the top. On this account the column cross-section may be reduced in proportion to the enrichment and a dephlegmator incorporated in order to reduce the throughput at the upper end. Voigt [93] has shown on theoretical grounds that the separating effect may be improved appreciably if heat is withdrawn, not only in certain sections, but from the whole of the column's surface. This produces an improvement only as regards the enrichment of the low-boiling components. If, on the other hand, the concentration of the high-boiling constituents is to be increased (as, for instance, in the isolation of stable isotopes) it will conversely be necessary to introduce heat into the lower part of the column, so as to reduce the throughput in this region (*cf.* 5.1.4; [93a, b]). Recent investigations by Blaß and Sauer [93d] of the partial condensation and nonadiabatic rectification of binary mixtures in packed tubes point to ways of improving separation effects for particular ratios of tube length to diameter.

5.3 Temperature

In the most commonly occurring forms of distillation the temperatures lie within the range of about 20 to 250 °C. If the boiling points of the components to be separated are below room temperature it becomes necessary to employ one of the special methods of low-temperature distillation, in which additional cooling agents are required for condensation. Distillations involving temperatures in the range of 250—400 °C may be termed high-temperature distillations. A distillation performed isothermally by keeping the temperature constant and varying the pressure is also conceivable.

5.3.1 Low-temperature distillation

Mixtures of low-boiling substances, for example light hydrocarbons and gases such as H_2, N_2, O_2 and CO can be fractionated either at atmospheric pressure, with the aid of cooling agents, or under pressure. In the latter case the use of pressure establishes overhead temperatures above those of the usual cooling media (section 5.4.5). Since pressure distillation involves difficulties with apparatus, low-temperature distillation is generally preferred in the laboratory and in pilot plants. The technique of low-temperature distillation has evolved to a high degree of perfection, and completely automatic apparatus suitable for the temperature range of —190° to 20 °C has been developed. Various types of columns — empty or packed — are used.

For analytical purposes low-temperature distillation has now to some extent been superseded by gas chromatography (chap. 5.1.2). If, however, the object is to prepare a considerable quantity of a pure gas or to effect a comparison with a large-scale installation, low-temperature distillation is still the best method. This applies especially to industrial waste gases without hydrogen concentrations and, more recently, to natural gas. For example, the separation of helium and nitrogen from natural gas is still a difficult problem. The separation of fission rare gases from the used air of nuclear plants is now gaining importance. After the removal of accompanying components the task is to separate the mixture $Kr/Xe/N_2$ with radioactive krypton and xenon isotopes by means of low-temperature distillation [93c].

The basic work on the analytical distillation of gases (comprising the permanent gases, the gaseous and lower liquid hydrocarbons) was carried out by Podbielniak [94], who for this purpose developed an effective column containing a closely-wound wire spiral known as Heli-grid packing (see chap. 7.3.4), which has also proved its worth for normal distillations.

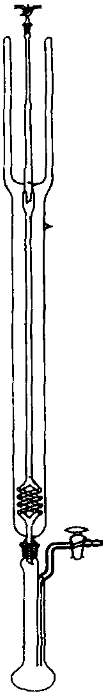


Fig. 173
Low-temperature column with fused-on dephlegmator (Grosse-Oetringhaus)

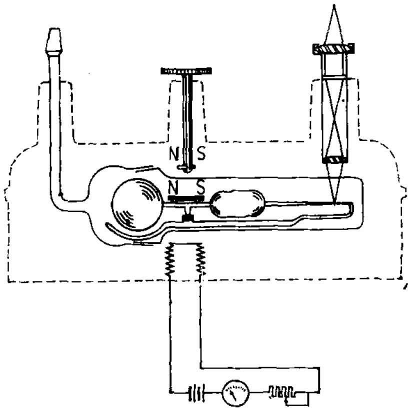


Fig. 174
Gas density balance after Stock

Grosse-Oetringhaus [95] gives detailed methods for performing low-temperature distillations. To start with, the taking of samples requires great care. Semi-automatic and automatic apparatus for drawing instantaneous and continuous samples have been devised. *The actual separation is carried out in the following manner. First,* those components not condensed by liquid nitrogen (—195.8 °C) are removed and analysed in an Orsat absorption apparatus. The condensable components are treated as gas in washing bottles for the removal of CO_2, H_2S and NH_3 and then again liquefied. The distillation is performed in a packed column insulated by a silvered vacuum jacket (Fig. 173); the column has spiral sections to take up strains. The dephlegmator with its conical tube is either fused to the column or connected to it by a ground joint. It has a vessel for the cooling medium which again is surrounded by a vacuum jacket. The column and the dephlegmator are filled with $2 \times 2 \times 0.2$ mm stainless steel spirals. The apparatus has been rendered largely automatic by the

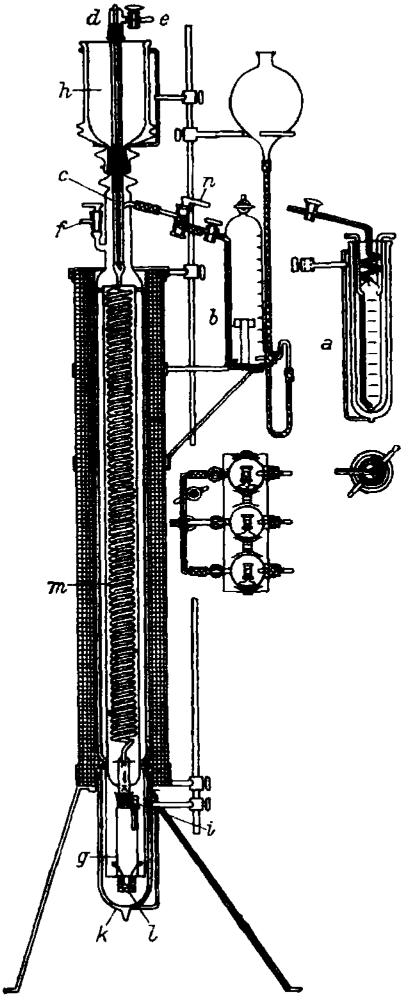


Fig. 175
Low-temperature column (Koch and Hilberath)

incorporation of various control devices, including a manometer with automatic pressure control and an arrangement for maintaining the temperature of the cooling bath. An ingenious set-up for cooling the column head to a constant temperature has also been described by Stokes and Hauptschein and Drawin [97]. The molecular weights of gases may be determined by means of Stock's balance (Fig. 174) [98]. Vapour pressure measurements (see chap. 4.4.1) are used to determine n-butane and isobutane contents. A useful summary of gas-handling techniques has been given by

Miller [99]. In their book on high-purity gases Müller and Gnauck [100] deal with the production and use of equipment for work on gases and with gas analysis, separation and purification.

The low-temperature column of Koch and Hilberath [101], which is very simple to operate, will be taken as an example to describe the procedure. The column has been given the form of a spiral, like Jantzen's column shown in Fig. 7b, and it consequently has a low hold-up (3—4 ml), so that a charge of 15—25 g is sufficient (Fig. 175). It functions in the same manner as a distillation apparatus at normal temperature. By the production of total condensation any desired reflux ratio may be obtained. The distillate may be taken off as gas or as liquid.

Thermometer *c* is suspended from a thin wire and the capillary opening d is closed with picein. The side-tube *e* of the ground-on cap is connected to a small drying tube.

The degree of vacuum in the insulating jacket should be checked at intervals by means of a high-frequency vacuum tester. In a darkened room no lighting up of the gas space should be noticeable, at most a wavering green fluorescence of the glass walls. If the gas space lights up, the jacket must be exhausted anew. This is done by means of a three-stage mercury diffusion pump, with a cooled adsorption vessel containing active charcoal or silica gel between the pump and the jacket in order to freeze out mercury vapour. Cocks are greased with high-vacuum grease (section 9.4). When the requisite vacuum (10^{-5} mm Hg or better) has been reached, the Schiff valve *f* is closed.

The boiling tube *g* is now cooled with a solid-CO_2-methanol slurry or another suitable cooling mixture to the required temperature. Condenser *h* is filled with its cooling agent. Liquid air or liquid nitrogen may be used. Alternatively, a salt solution may be used and the cooling temperature be kept constant by means of a cryostat. The dried gas sample (if necessary freed from CO_2) is then condensed into the boiling tube *g*, which for this purpose can be removed at a ground joint *i*. Instead of the cooling bath a Dewar vessel *k* is now placed so far around the boiling tube that its upper end is in contact with the bottom of the stand. The evaporation of the charge in *g* is then brought about as usual by the heat from an electric resistance element *l*. The vapours pass up the spiral column *m*, which is surrounded by the silvered insulating vessel and by a glass-wool jacket. The temperature is measured at the column head in a well that prevents the thermometer *c* from being cooled by the condensate. The distillate is drawn off below the condenser through the regulating valve *n*.

In order that the distillate may, if desired, be collected as liquid, a spiral tube leads down to a fused-on, graduated receiver and the whole is surrounded by a Dewar vessel containing a cooling medium in which the distillate is liquefied. The weight of the liquid condensing in the spiral yields sufficient suction at the regulating valve to draw off the vapour from the column. If the distillate is to be collected as gas, it can be passed from the valve to a vessel *b* in which it displaces a suitable liquid. The necessary suction is then produced by a difference in level between the gas entry and the liquid overflow.

If the boiling and solidifying points of the distillate lie close together the temperature in the condenser has to be controlled exactly. For preparative purposes a low-temperature column was developed by Stage [102] in which the coolant temperature is controlled automatically (Fig. 176). This refers to the liquid in both the condenser and the still pot which is cooled by a stream of evaporating liquid air. When the temperature reaches the minimum value pre-set on a contact thermometer a magnetic valve opens and admits atmospheric air. The distillate is also drawn off through magnetic valves. The low-temperature still after Grosse-Oetringhaus (Fig. 177) is used for the distillation of low-boiling liquids or liquids containing dissolved gases. The vapours or gases which cannot be condensed in the first condenser will undergo condensation in the low-temperature condenser of the receiver. This is filled with a suitable cooling agent.

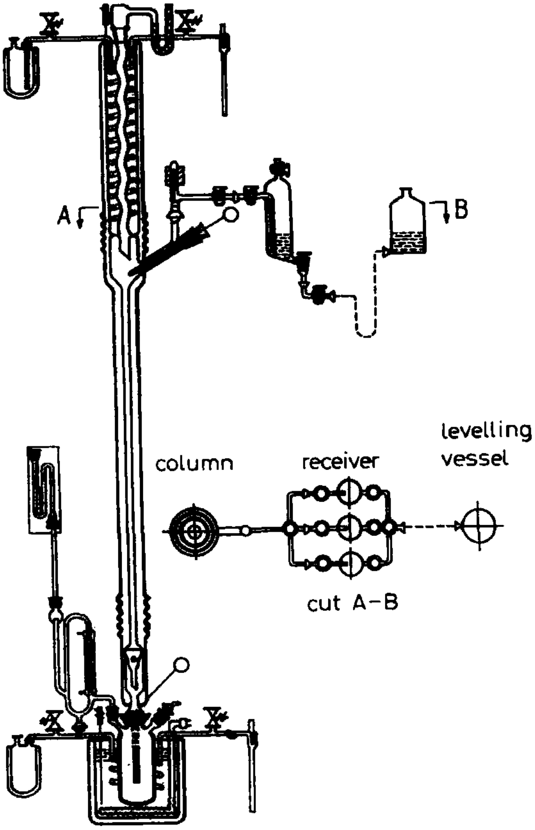


Fig. 176
Packed column for preparative low-temperature distillation (Stage)

The latest development in the field of low-temperature distillation is illustrated by the fully automatic apparatus of Podbielniak. The "Thermocon" model, series

8700, is designed to operate in the temperature range of —200 to 20 °C (Fig. 178 [104]; *cf.* section 8.1).

A modified Podbielniak apparatus, the "Ruhrgas" model, employs charges of 3—4 l of gas (at normal pressure). A distillation takes 2 hours; the introduction of the charge by condensation requires about the same time. The built-in recorders continuously register the temperature of the still head. Fig. 179 gives an example of such a distillation curve [105].

Low-temperature distillations of very small amounts of liquefied gases (about 5 ml) may be carried out with the apparatus of Simons [106], which fits into a Dewar vessel (Fig. 180).

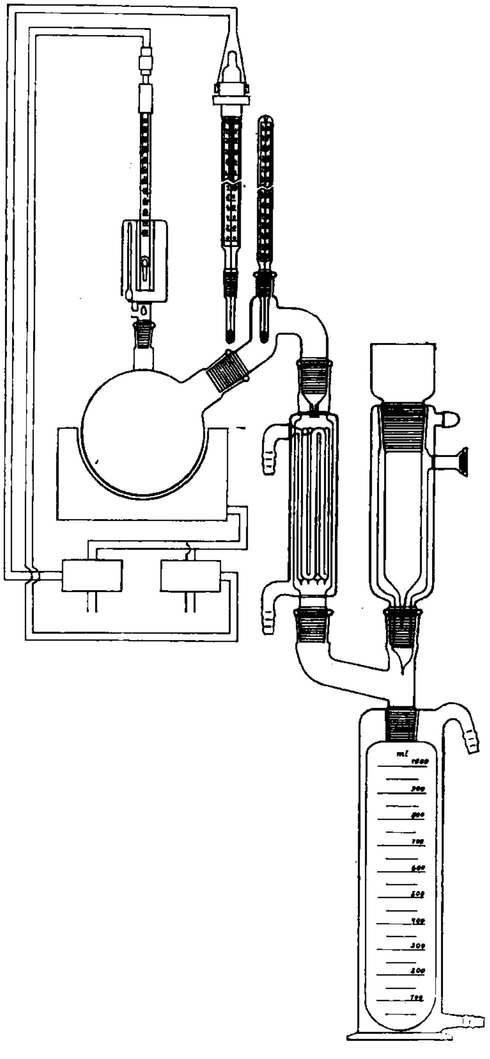


Fig. 177
Low-temperature distillation apparatus (Grosse-Oetringhaus)

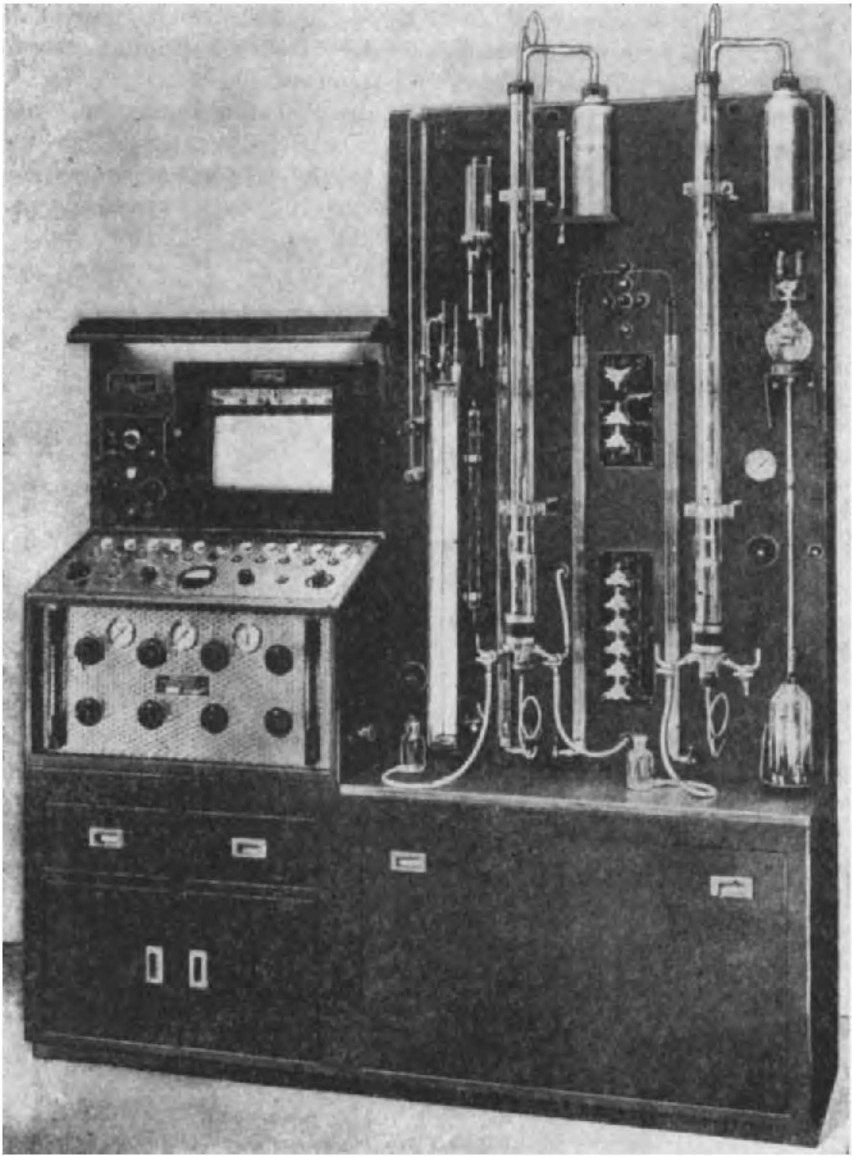


Fig. 178
Fully automatic low-temperature distillation apparatus of Podbielniak

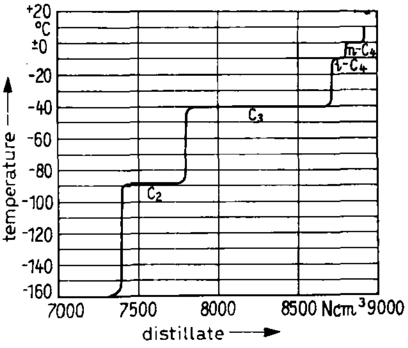


Fig. 179
Boiling curve obtained with the "Ruhrgas" low-temperature apparatus

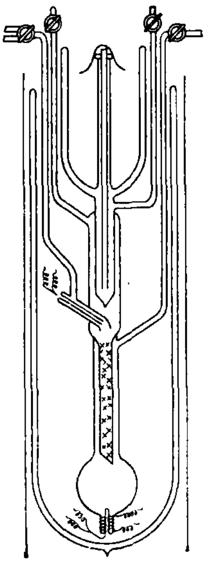


Fig. 180
Low-temperature micro-column (Simons)

The minimum reflux ratio required in a low-temperature distillation may be calculated approximately by a formula due to Podbielniak [107], which assumes the concentration of the charge to be 50 mol%:

$$v_{\min} = \left\{x_E - \frac{\alpha}{\alpha - 1}\right\} \left\{\frac{1}{1 - x_B}\right\} \left\{\frac{x_E}{\alpha - 1}\right\} \left\{\frac{1}{x_B(1 - x_B)}\right\} \qquad (184)$$

(x_E = mol. fraction of low-boiling component in distillate;
x_B = mol. fraction of low-boiling component in still pot).

For calculating the minimum number of stages in a low-temperature distillation at infinite reflux ratio, the nomogram of Fig. 181 after Podbielniak [107], may be used. The diagram again assumes that the concentration of the charge is 50 mol%, but takes account of the relative volatility of the mixture and the desired concentration of the distillate. Firstly, the relative volatility of the gas mixture to be separated is determined from vapour pressure values, as described in section 4.4.4. From this value of α one proceeds vertically to the curve corresponding to the required purity of the distillate (80—99.9 mol%). From the intersection with this curve a horizontal line is followed to the scale for the number of theoretical stages. For a rough guide Table 45 [108] gives the minimum stage number for a few commonly occurring mixtures of low-boiling hydrocarbons at infinite and minimum reflux ratios.

It can be seen from the table that the separation of low-bolling mixtures is relatively straightforward. Thus, it is usually sufficient to have columns with low efficiency. It has to be borne in mind, of course, that the data given refer to $v = \infty$. For finite reflux ratios the requirements have to be altered appropriately.

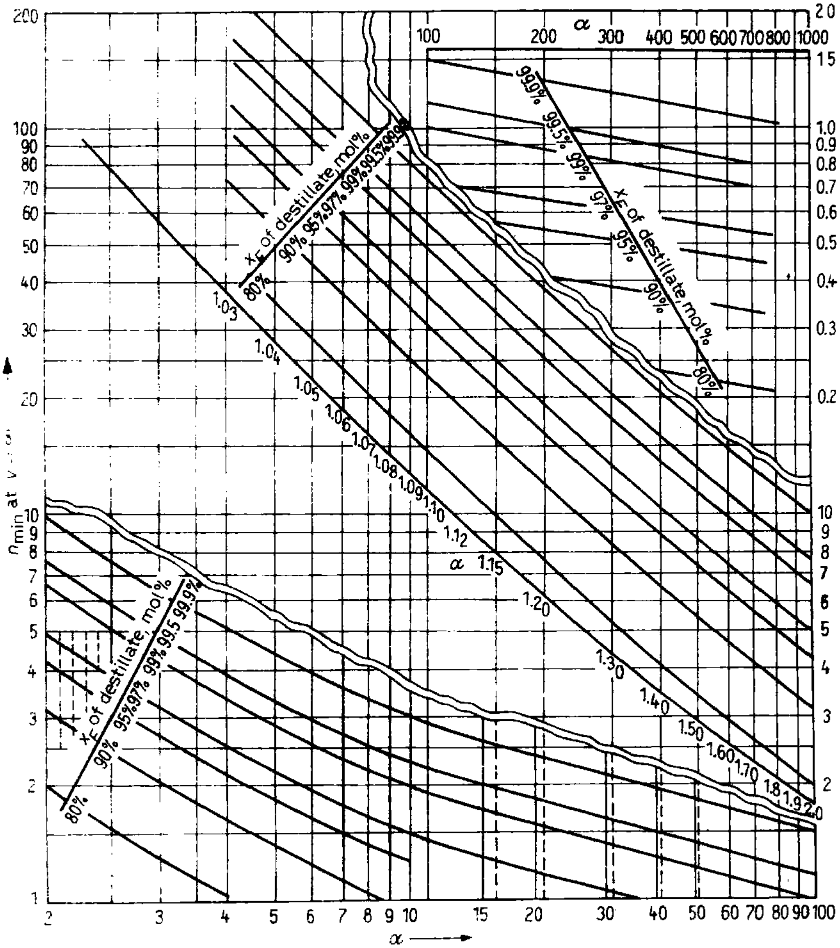


Fig. 181
Nomogram for the determination of the minimum plate number n_{min} for low-temperature distillation at $v = \infty$

Table 45

Minimum numbers of stages and reflux ratios required for the separation of various low-boiling binary mixtures

Mixture	α	A	B	C	D
Methane-ethylene	61.2	1.32	1.82	0.03	0.164
Methane-ethane	107.0	1.14	1.60	0.018	0.093
Ethylene-ethane	2.3	6.5	9.2	1.60	7.95
Ethane-propylene	8.1	2.52	3.57	0.27	1.4
Ethane-propane	9.3	2.38	3.36	0.23	1.2
Propylene-propane	1.3	20.2	28.6	6.65	33.0
Propane-isobutane	3.3	4.6	6.5	0.89	4.5
Isobutane-n-butane	1.5	13.0	18.4	3.99	20.0
Isobutane-isobutylene	1.2	28.8	40.8	10.0	50.0
Isobutylene-1-butylene	1.03	25.5	36.0	8.98	43.5
n-Butane-isopentane	2.8	5.3	7.5	1.16	5.8
Isopentane-n-pentane	1.33	18.6	26.3	6.25	30.1
n-Pentane-n-hexane	3.0	4.9	6.95	1.04	5.25

A = number of stages required with $x_B = 50$ mol%, $x_E = 99.5$ mol% and $v = \infty$
B = number of stages required with $x_B = 10$ mol%, $x_E = 99.5$ mol% and $v = \infty$
C = minimum reflux ratio for a mixture with $x_B = 50$ mol% and $x_E = 100$ mol%
D = minimum reflux ratio for a mixture with $x_B = 10$ mol% and $x_E = 100$ mol%

5.3.2 High-temperature and isothermal distillation

Temperatures above 250 °C may cause some decomposition in organic compounds and the range of 250 to 400 °C is therefore avoided if possible in the laboratory. The necessity may, however, arise in determinations of boiling range of mixtures of low volatility at atmospheric pressure, as with tars or high-molecular-weight waxes. Crude waxes are often purposely distilled destructively to obtain fractions of low molecular weight [109]. On the other hand inhibitors are sometimes added in an attempt to reduce decomposition and polymerization [110].

In the distillation of substances of low volatility at atmospheric and reduced pressures a short column is all that is employed and its function is mainly to act as spray trap. Coarse packing, placed on a gauze support, is used; plate columns are unsuited for such purposes. It is obvious that the column should be provided with a heating jacket and that no part of the apparatus, from the still pot to the condenser, should be unheated, so that there may be no partial condensation. The receivers should also be capable of being warmed. A useful measure is to heat the take-off valve by radiation from an infrared source or by a hot air blower (hair dryer), so as to prevent it from sticking. Better still is the use of magnetic valves.

In laboratory high-temperature distillation the boiler is as a rule heated indirectly by an oil, Wood's metal or molten salt bath [111], controlled by a contact thermometer. (The maintenance of a constant high temperature in such a bath is, however, usually not an easy matter.) Table 46 shows the temperatures that are attainable with various baths (*cf.* section 7.7).

A molten salt bath has the advantage that it can be used over a wide temperature range and that it does not give rise to objectionable vapours. However, the flask must be removed from the bath when heating is stopped and the adhering salt washed off with water.

In high-temperature distillation cooling sometimes poses serious problems in that the condenser cross-section must be prevented from being narrowed or even blocked by solidifying (or subliming) matter. By means of circulatory thermostats and with water or glycol as warming agent the required condensation temperatures can be set and kept. Another simple possibility is offered by the boiling condenser which consists of two concentric tubes. The inner tube contains the liquid whose boiling point lies somewhat above the solidifying point of the distillate but below the boiling point of the latter. The distillate vapours heat the liquid and cause it to evaporate. The distillate condenses on the outer wall of the cooling tube. Fig. 182 shows a distillation apparatus with a simple boiling condenser after Stage as presented in [112]. In that paper, further arrangements for the distillation of high-melting, subliming materials, partly with the addition of solvents, are described.

Table 46

Heating baths for high-temperature distillation

Medium	Temperature range (°C)
Glycerin	up to about 160
Sulphuric acid	up to about 250
Poly-glycols	up to about 300
Paraffin wax, melting point 30°–60 °C	up to about 300
Mineral oil	up to about 330
Mixture of 40% wt. $NaNO_2$, 53% wt. KNO_3 and 7% wt. $NaNO_3$	150–500
Wood's metal	70–300

Of late the purification of metals by distillation has become important, for example with the mixtures Al–Zn, Al–Mg, Pb–Zn, Ag–Zn and Ag–Pb [113]. Vapour pressure data for metals can be found in Leybold's handbook [114]. The investigation of such problems on a laboratory scale, with small amounts of material, may become common in the near future. Fig. 183 shows two forms of apparatus suitable for this purpose, having the flow of vapour directed sideways in the one case and downwards in the other [115]. An extensive account of the vacuum distillation of non-ferrous metals and alloys on a laboratory scale has been published by Spendlove [116]. Horsley [117] has described an apparatus for the distillation of alkali metals. The metal is melted in vacuum, filtered and distilled at 10^{-4} mm pressure. The rubber gaskets are protected from excessive heat by cooling coils. The metal vapour is condensed on a surface cooled by circulating oil. The chloride $TaCl_5$ ($Kp._{760} = 240\,°C$) was used by Parker and Wilson [118] for the purification of tantalum. Bezobrazov et al. [118a] developed an apparatus made of quartz for the

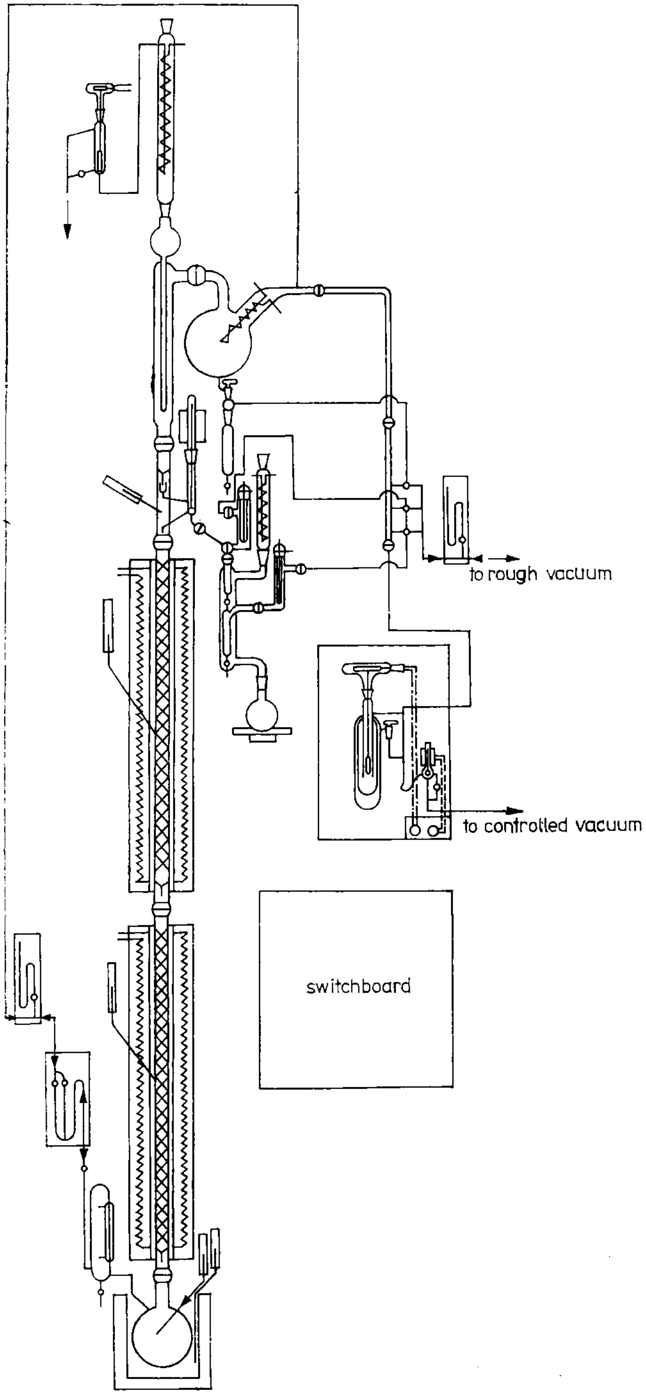


Fig. 182
Apparatus for high-temperature distillation with boiling condenser (Stage)

continuous distillation of high-boiling substances up to 1000 °C (*e.g.*, sulphur, selenium, tellurium, zinc, cadmium, arsenic sulphide).

An operation frequently occurring in the laboratory is the (unrectified) *distillation of mercury* to remove tin, cadmium and noble metals. Generally, a preliminary chemical purification is carried out so that there remain, in addition, traces of the purifying agents in the mercury. In general the evaporation process exhibits nonstationary and strongly pulsating states, which have been analyzed by Schmücker and Grigull [118b].

The apparatus, which is constructed of silica or high-melting glass, is often designed so as to operate continuously on the principle of the Sprengel pump: after a preliminary pumping-out the apparatus evacuates itself further continuously during its operation [119]. Fig. 184 illustrates the apparatus diagrammatically. For the self-pumping action to be effective, the condensed mercury must flow down through a capillary tube of about 1.5 mm bore. A better procedure, however, is to evacuate the apparatus first with a mercury diffusion pump and to close valve *H* after 1 to 2 hours' distillation, reopening it only when evacuation is again necessary.

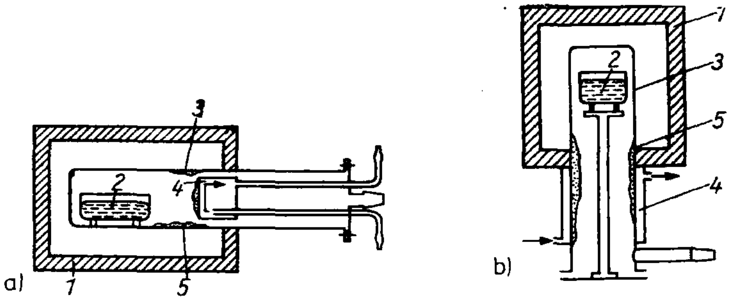


Fig. 183
Unit for metal distillation
a) with horizontal vapour flow
b) with downward vapour flow
1 = furnace, *2* = melt, *3* = receiver, *4* = condenser, *5* = condensate

Since very pure mercury is required in increasing quantities a mercury bidistillation apparatus as shown in Fig. 185 was evolved by VEB Jenaer Glaswerk Schott & Gen. of Jena. After vacuum evaporation in the first stage the condensate is passed through a tube bridge into the second stage where it is again subjected to evaporation. The distillate then flows through a tube working on the barometric principle to the receiver. At a pressure of 1 torr about 2 kg/h distillate may be obtained with a heating power of 300 VA for each distillation stage. According to spectral analysis results, the mercury thus obtained has a very high degree of purity. This is partly due to the use of precision ball ground joints which need no vacuum grease.

In isobaric distillation — the form normally practised — the pressure is kept constant and the distillate passes over with rising temperature. In *isothermal distillation* the still pot temperature is kept constant by a thermostat and the pressure is pro-

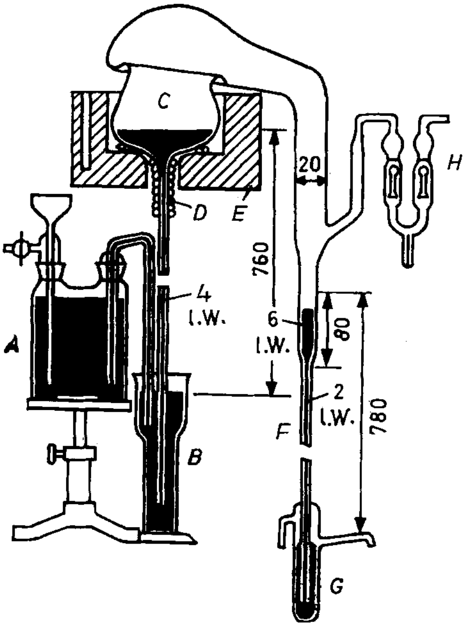


Fig. 184
Apparatus for the distillation of mercury (dimensions in mm)

A = Storage vessel for intake, B = Riser tube, C = Distillation vessel, D = Electrical heater, E = Aluminium block, F = Descending capillary tube, G = Receiver with overflow, H = Mercury float valve with connection to diffusion pump

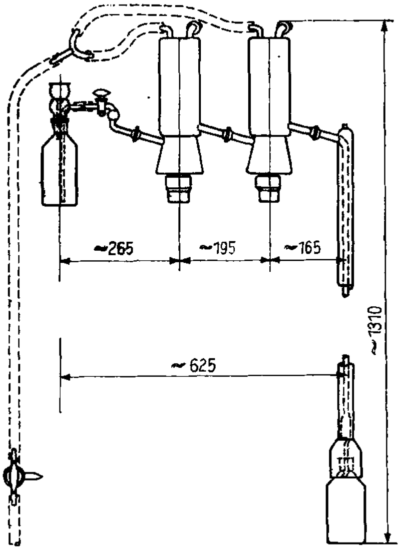


Fig. 185
Mercury bidistilling unit

gressively reduced. One can then construct a diagram for the temperature in question by plotting the pressure along one axis and the amount of distillate along the other. This method is applied when it is necessary to know the pressure at which a definite percentage will be evaporated from a multicomponent mixture at a particular temperature, for instance in the case where steam at a certain pressure (corresponding to a particular temperature) is available as heating medium. By means of isothermal distillation Echols and Gelus [120] determined the properties of the residue of a mixture which at a constant temperature corresponded to a particular pressure. Equilibrium curves may also be determined isothermally. The theory of isothermal distillation as compared to isobaric distillation has been discussed by Ulusoy and Sakaloz [121]. According to their findings isothermal distillation may be the more favourable method in some cases.

5.4 Distillation pressure

An important point to be considered prior to every distillation is the pressure at which the separation is best performed. If there are no objections to its use, normal atmospheric pressure will generally be chosen, since a reduced or increased pressure involves complications in the apparatus and a vacuum distillation gives a lower throughput.

As a rule gas mixtures containing low-boiling hydrocarbons are distilled at atmospheric pressure (*i.e.* at low temperatures) or at an increased pressure, whilst easily decomposable or high-boiling organic substances are distilled at a reduced pressure in order to prevent overheating. High throughputs may be realized with flash distillation at 20 to 1 mm Hg pressure, whilst temperature-sensitive compounds, which cannot be distilled from a flask, may be separated by the mild process of thin-film distillation at 20 to 10^{-1} mm. For the distillation of substances of low vapour pressure and high molecular weight (20—1200) the method of molecular distillation was developed, in which — by the use of pressures of 10^{-3} to 10^{-6} mm — the mean free paths of the molecules are of the same magnitude as the distances travelled by the vapour in the apparatus. Experience gathered in the simple and countercurrent distillations of sensitive substances under reduced pressure and methods evolved for such procedures have been reviewed extensively by Frank and Kutsche in their book on mild distillation [122].

5.4.1 Simple and countercurrent distillation under reduced pressure

Rectified distillation, with a column, may be carried out at pressures down to about 0.5 mm Hg. At lower pressures special forms of apparatus must be employed.

The basic advantage associated with the use of reduced pressure in distillation is the lowering of the boiling point and the consequent possibility of separating compounds below the temperature at which they decompose or undergo chemical alteration, such as polymerization. Examples from industry that may be quoted are the distillation of lubricating oils, the fractionation of crude phenols (which is performed at 20—60 mm pressure) and that of synthetic fatty acids (carried out at 1—20 mm). Reduced pressures are also employed for distillation where, although no direct danger of chemical change is present, the boiling points lie so high at normal pressure that it is profitable to reduce them for reasons of heat economy, as with certain ethereal oils. A further advantage of a reduced pressure in distillation is the fact that the equilibria are often more favourable for the operation than at atmospheric pressure.

An *azeotrope* frequently becomes richer in the low-boiling component as the pressure is reduced. By continuing the reduction, a pressure is reached at which the azeotropic point vanishes. As an example, the mixture ethanol-water may be quoted; at 70 mm Hg this system no longer has an azeotropic point (*cf.* section 6.2.1). Hence it is possible to prepare absolute alcohol by the distillation of dilute spirits at a pressure below 70 mm, without the addition of auxiliary substances. The boiling point, however, is then rather low (28 °C). In this connection it is obvious that the choice of distillation pressure may also depend on the temperature of the cooling medium.

Another motive for using reduced pressure in distillation — especially on an industrial scale — may be that low-pressure steam is to be used as heating agent and that its temperature would be too low for distillation at normal pressure. In practice, furthermore, the corrosion of a metal still can be an important consideration, and on this account it may be necessary not to exceed a certain temperature.

It thus appears that there are numerous technical and economic factors to be considered in choosing the distillation pressure.

Billet and Raichle [123] described a method of calculating column dimensions which optimizes a vacuum distillation in terms of minimum total pressure drop. The reader will recall that in chap. 4.6.2 and 4.10.6 it was attempted to clarify, from various points of view, to what extent reduced pressure influences the efficiency of a column. Gelbe [124] has pointed out that the findings of the various authors are still contradictory. Using a column of 45.7 mm diameter and 500 mm length (4 mm spaced helices) he found that with constant throughput the efficiency is practically independent of pressure between 10 and 100 torr. As the pressure is raised to 740 torr the number of transfer units gradually increases due to the increase of the relative velocity. In experiments with n-decane-trans-decaline he observed an increase by about 15% (cf. Fig. 97). According to Gelbe the contradictions found in the literature are due to column flooding being carried out differently or in some cases even being omitted. In chap. 4.10.8 this was already mentioned and a method of flooding described. In his distillations with operating pressures below 100 torr Gelbe employed a higher initial pressure to obtain a higher reflux rate. What was important was that the bubbling layer moved steadily upward from the column base through the packing. The layer of liquid formed at the head was pressed through the packing several times, then the pressure was lowered with the column remaining in the state of bubbling. The optimum wetting of the packing thus achieved is clearly shown in Fig. 186. The straight line f corresponds to the optimum flooding conditions described.

The calculation of the column dimensions has been dealt within section 4.11. It is important to ensure that the vacuum lines are sufficiently wide. The drop in pressure in a vacuum line can be calculated by Poiseuille's law if the pressure is not too low and the tube has a diameter of less than 200 mm:

$$\Delta p = \frac{8 V \eta l}{\pi r^4 t} \tag{185}$$

where p = the pressure drop in kg/cm² (1 atm. = 1.03 kg/cm²);
V = the gas flow rate, cm³/sec;
η = the dynamic viscosity of the gas in kg · sec/cm² (1 kg · sec/cm² = 1.02 poises);
l = the length of the tube, cm;
r = its radius, cm;
t = time, sec.

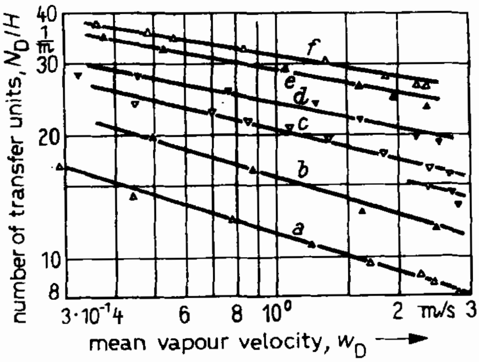


Fig. 186
Influence of flooding at 20 torr (Gelbe [124])

A useful nomogram (Fig. 187) interrelating these variables has been published by Harries [125]. It assumes that the suction is not choked more than 30%. The following examples explain its use.

1. Calculation of the maximum pump capacity

a) Connect points on scale d and l to intersect A at A_1.
b) Connect A_1 with p_1 and produce the line to meet scale s_2.
c) The reading on scale s_2 is the maximum pump capacity.

2. Calculation of the smallest allowable diameter of tubing

a) Connect the point p_0 on scale p_1, representing the maximum allowable pressure drop, and the point on scale s_2, representing the gas flow rate, by a line intersecting scale A at A_1. Scale A shows a function of the resistance of the tubing to gas flow.
b) Connect A_1 and the point on scale l corresponding to the length of the tube, and produce it to meet scale d. The reading on scale d is the smallest allowable diameter.

3. Calculation of the maximum length of vacuum line

a) Connect points on scale p_1 and s_2 to intersect scale A, as in 2a.
b) Connect the point A with the point on scale *d* showing the diameter of the tubing, and produce the line to intersect scale *2*. The reading on *l* shows the maximum allowable length of vacuum line.

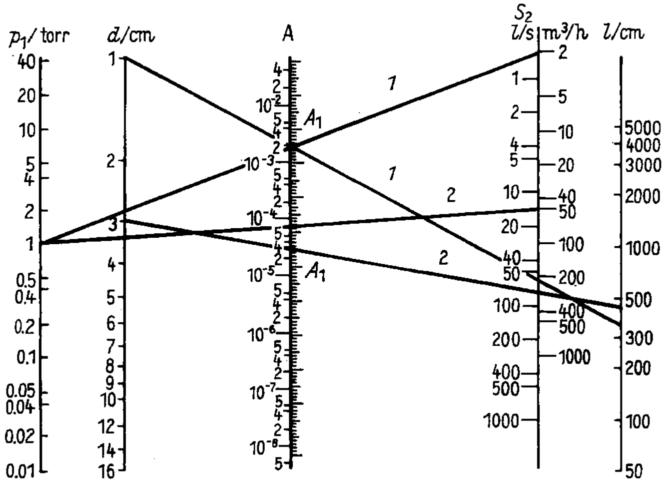


Fig. 187
Nomogram for the sizing of vacuum lines (Harries)

		Example 1	Example 2
p_1 = pressure in vacuum vessel,	mm Hg	1.0	1.0
d = diameter of line	cm	1.0	3.0
S_2 = gas flow rate	m³/h	2.0	50.0
l = length of line	cm	350	450

In example 2 the intersection of p_1—S_2 with *A* is 6.5 scale divisions above that of *d*—*l* with *A*. The vacuum line therefore has some capacity in reserve

The intersection of the two straight lines in example 1 corresponds to an efficiency of 41%:

$$N = \sqrt{1 + (p_0/p_1)^2} - p_0/p_1, \tag{186}$$

where p_0 represents the minimum pressure at which a vacuum apparatus can be run with sufficient efficiency.

For checking an existing vacuum lay-out it suffices to connect points p_1 — s_2 and d — l, respectively, by straight lines and to find the points of intersection of these lines with scale A. If the point of intersection of p_1 — s_2 is situated above that of d — l the vacuum installation is adequate. For more detailed calculations the reader is referred to the original paper [125]. A vacuum system constructed of 20—30 mm I.D. glass tubing is in general satisfactory in distillation laboratories; it may be built up of 1—2 m lengths of such pipe, connected by short pieces of rubber vacuum tube or, better, by ball and socket joints.

The apparatus for simple or countercurrent distillation at reduced pressures differs from that used at atmospheric pressure only by its wider dimensions (*cf.* section 4.11). A few additional components are necessary, such as a vacuum connection, which is generally provided with a cold trap (Fig. 188). Besides packed columns, empty columns (chap. 7.3.1) and columns with stationary (chap. 7.3.4) and rotating elements (chap. 7.3.5) are especially suited for distillation under reduced pressure. The optimum ratio between the diameters of the inner and the outer tube of a cold trap is 1.6. Furthermore, special vacuum receivers are required (section 7.6). It is important to measure pressure directly after the vacuum connection and to ensure that there is no loss in pressure between this point and that where vapour temperature is observed. To be on the safe side, a differential manometer can be connected between these two points (*cf.* section 8.3).

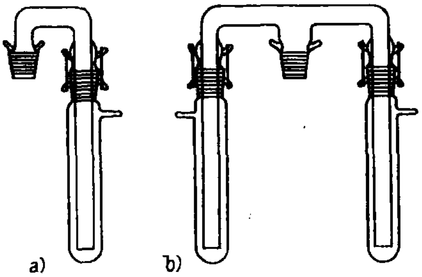


Fig. 188
Vacuum connection with cold trap
a) For apparatus without control by pressure drop
b) for apparatus with control by pressure drop

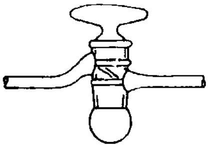


Fig. 189
Vacuum tap having body closed on one side

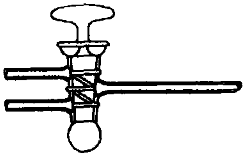


Fig. 190
Vacuum tap with mercury pocket

The standard ground joints normally employed for vacuum work are those of series 1; in cases where the grease is rapidly dissolved away or high vacuum is required series 0 is also employed, which might be called high-vacuum ground joints (chap. 3.1). Because normal glass taps are subject to leakage, special types have been evolved for vacuum work. Fig. 189 shows a tap with the body closed on the one side and Fig. 190 a similar type with a mercury pocket. Further special taps and valves for vacuum work will be described in chap. 7.2.1.

Reduced pressure is produced by means of water-jet (filter) pumps, ejectors, and various types of electrically driven mechanical pumps; for high vacuum, mercury and oil diffusion pumps are used. A description of these adjuncts would take us outside the scope of the book. The reader is therefore referred to relevant books [113, 114, 119, 122, 126, 127]. Leybold's book [124] discusses the principle underlying the choice of pumps, and von Ardenne [128] reviews the operating ranges and the characteristics of the more important pump types. All-glass Quickfit-Wiegand steam ejectors [128a] have now become available. The main advantages of these pumps are corrosion resistance and transparence. Two types are provided for operation with or without water circulation. They require a saturation vapour and water pressure of 3 bar. Two steam jets in series effect compression from 1 torr and 2.5 torr to about 120 torr with types G. 01.1 and G. 01.1—K (0.1 kg/h air) and G. 05.2 and G.05.2—K (0.5 kg/h air), resp. The water jet condenser condenses the working vapour and compresses air, gases and noncondensable vapours to atmospheric pressure.

Fig. 191
High-frequency leak detector with brush electrode and ratio shielding

After the vacuum system has been assembled it is necessary to test it for efficiency and leaks. Testing should be carried out systematically and should start with the pump, the capacity of which may be checked by connecting it to a buffer vessel of 5—10 l volume. Valves and ground joints are then tested, passing on to the individual components, where fused connections often prove to be the cause of leakage. It is useful — by including taps at suitable points — to construct the apparatus in such a way that various sections may be tested separately for leakage. Testing for leaks can be carried out with the aid of a high-frequency tester with a brush electrode working according to the Tesla principle (Fig. 191). At points where air is drawn in a luminous spark breaks through. Leaks can also be detected aurally with a stethoscope; another method is to apply a pressure of about half an atmosphere and dab soap solution with a brush on suspected spots. An elegant method is to paint a weakly alkaline, methanolic solution of fluorescein or eosin onto the apparatus while it is under vacuum; if it is then irradiated with ultra-violet light in a darkened room, the leakages become apparent by fluorescence.

For special high-vacuum testing methods see the books of Laporte [119] and Mönch [126].

Devices for hunting leaks in vacuum and pressure equipment may be purchased. Halogen leak detectors operate with Refrigerant 12 (CF_2Cl_2) as test gas. The principle of operation is that incandescent platinum, in the presence of halogens, emits ions. If an apparatus under vacuum is to be tested it is connected to the detector tube and the apparatus is sprayed on the outside with the test gas. If the gas penetrates at any point this is indicated by a deflection on an indicator or by the emission of a signal. For testing pressure apparatus the test gas is introduced into the equipment and it is examined externally with the detector. The smallest leak that can be detected is about 10^{-6} mm Hg l/sec (see eq. (187) below). Other devices employ hydrogen or coal gas as testing medium and have the same sensitivity. The helium leak detectors function according to the principle of the mass spectrometer and indicate leaks down to 10^{-10} mm Hg l/sec [129].

The degree of tightness *Di* of an evacuated apparatus with the pump shut off can be expressed by the formula

$$Di = \frac{V \cdot \Delta p}{t} \text{ mm Hg} \cdot \text{l/sec.} \tag{187}$$

in which Δp = the change in pressure in mm Hg;
V = the volume of the apparatus in litres;
t = the time of observation (in sec).

The value of *Di* should not be greater than 10^{-3} to 10^{-5}.

5.4.2 Continuous equilibrium vaporisation (flash distillation)

One of the continuous processes employed on an industrial scale is continuous equilibrium vaporisation — generally known as flash distillation. In spite of its advantages this procedure has not been widely used in the laboratory and in pilot plants. A glass apparatus developed for this purpose by the author is illustrated in Fig. 192 [130]. The most important component is the flask a of 250—500 ml capacity, provided with a ground-in thermometer. It is placed in a thickly-lagged vessel and is heated to a constant temperature, regulated by means of a contact thermometer. Into the centre of the flask there projects an interchangeable injection capillary *b*, which may be observed through a small window and is illuminated behind by a lamp. The mixture to be distilled is forced from bottle *c* into the storage vessel *d* (operating on the principle of the Mariotte bottle) and is brought to the required temperature by the thermostatically controlled jacket. The feed rate may be checked in the measuring burette *e*. The feedstock is heated further in heat exchanger *f* by a liquid at constant temperature or by steam. The temperature of the heating agent is controlled by contact thermometer *g*.

The preheated feedstock passes at a definite rate through the fine control valve *h*, is sprayed into flask *a* (in which a reduced pressure is maintained), and forms a thin film on its walls. The release of pressure causes the low-boiling fractions to vaporise preferentially at once. Furthermore the walls of *a* (which can be heated to a higher temperature if desired) have a large surface, so that more of the light components evaporate after a very brief interval of heating. The vapour passes through the insulated tube *i* to condenser *k*, then as liquid, via the Anschütz-Thiele vacuum receiver *m* to the collecting bottle *l*. The vacuum pump is connected to *n*; the pressure is kept constant by a controller (*cf.* section 8.3). The high-boiling fraction flowing down from the flask is distributed by a perforated funnel in a short column *o*, equipped with a heating jacket. Any low-boiling constituents remaining in the residue are removed in this column, which is supplied with heat for this purpose. The heating jacket of the column is regulated by contact thermometer *p*. The bottom product runs continuously into bottle *q* through the measuring device *r*.

Flash distillation has proved particularly convenient for distilling off low-boiling "tops"; at a pressure of 1 to 20 mm Hg a throughput of 800 to 1500 g/h may be attained. In the separation, for instance, of a crude fatty acid mixture, a C_4—C_{10} fraction could be taken off with a feed rate of 1200 g/h at 15 mm pressure.

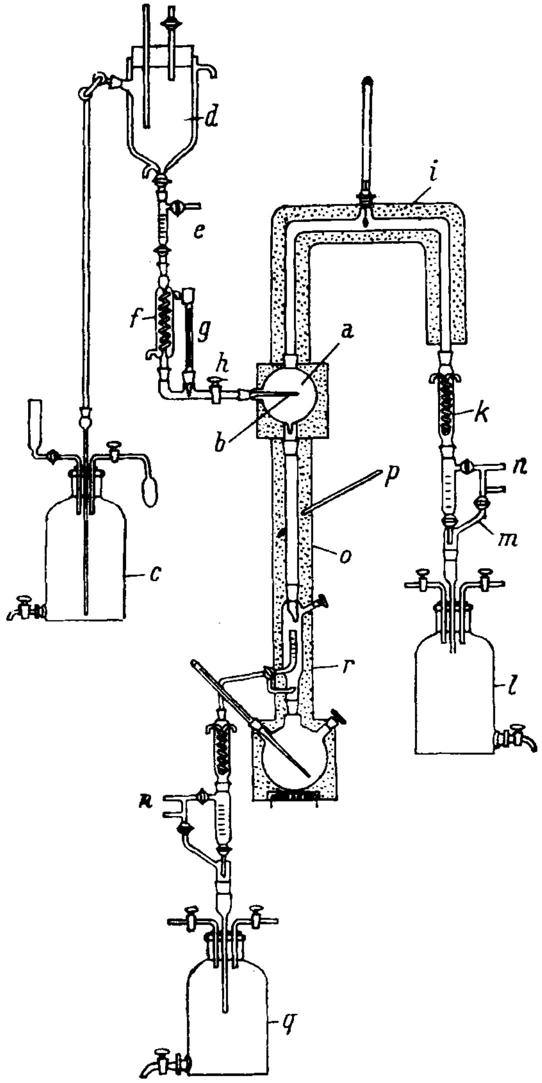


Fig. 192
Apparatus for flash distillation (Krell)

Fig. 193 shows the distillation analyses of the distillate and residue obtained in this separation. A satisfactory cut proves to have been effected at C_{10}. The preliminary fractionation of large amounts of a phenol oil total distillate was also carried out by flash distillation. The cut was intended to lie between 210 and 230 °C (normal pressure). The result is given in Fig. 194. The separation performed in three stages under different conditions yielded an overlap of about 15 °C, as shown by the top and bottom products analyzed in a test distillation at normal pressure. If the mixture to be separated contains fractions having large differences in boiling point, even higher rates of throughput, up to about 3 l/h, may be realized.

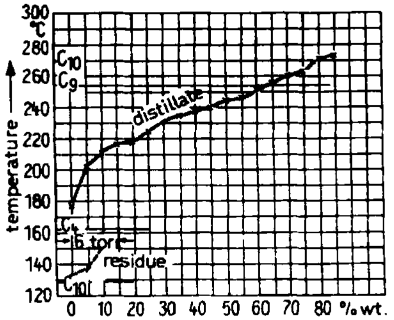


Fig. 193
Distillation analyses of the top and bottom products from a flash distillation of crude fatty acids at 15 torr

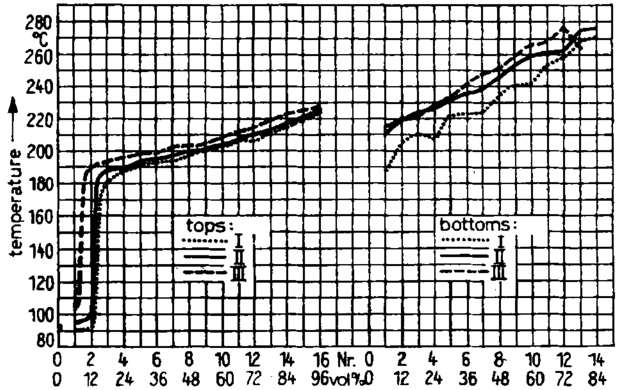


Fig. 194
Flash distillation of a phenol oil total distillate. Analyses of the top and bottom products

A mixture of phenol containing 9% of water could be dehydrated in the same apparatus, with the omission of the column below the flash vessel. At a pressure of 23 mm and a feed temperature of 80 °C the optimum rate of input proved to be 4 l/h. Such a large throughput could scarcely be attained in the laboratory by the normal method of distillation from a flask, if only on account of foaming.

Flash distillation has proved valuable in preparative work as a preliminary operation in the separation of multicomponent mixtures into their constituents.

Quantities of feedstock up to 100 l may be split up in this way, at a high rate and without thermal ill-treatment, into fractions suitable for subsequent batch rectification.

5.4.3 Thin-film distillation

In the method to be described now the crude material is not submitted to distillation in the form of a thick layer of liquid (as is done in a boiler) but as a thin flowing film; the thermal treatment it undergoes is consequently very mild, both as regards time and temperature. The procedure may be regarded as a one-stage simple distillation with a maximum efficiency of one theoretical stage. Arranging several stills in series increases the efficiency. According to the author's experiments the procedure can frequently be utilized with advantage at any pressure in the range from atmospheric down to 0.1–0.2 mm Hg [130]. Its favourable features can be demonstrated by means of an example. Suppose that a mixture of saturated straight-chain alcohols, C_{10}—C_{18}, is to be distilled at 1 mm pressure. If the mixture were put into a 1-litre still pot and the depth of the charge were 54 mm, the pressures would be as shown in Fig. 195. There would be a pressure of 1 mm Hg only at the surface of the liquid, whilst at the bottom of the still pot this would be increased hydrostatically by an amount of about 54/13.5 = 4 mm, *i.e.* to a total of 5 mm. At the beginning of distillation C_{10} would evaporate under 1 mm pressure at 76 °C, but the temperature in the bottom of the flask would be 142 °C. In thin-film distillation no appreciable hydrostatic pressure exists. A heated surface having a temperature of about 78 °C is hence sufficient to vaporise the first component. This example shows that thin-film distillation reduces thermal hazards, so that the method is suitable for effecting an initial separation of temperature-sensitive substances.

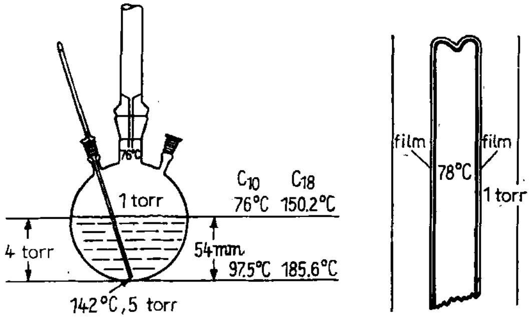


Fig. 195
Pressures in a still pot and in thin-film distillation

When a high-boiling mixture contains a small amount of a volatile component it is often impossible, when a conventional still is used, to remove all the light fraction, even by an increase in temperature. If the pressure is reduced to prevent decomposition there is the danger that the volatile constituent will escape uncondensed. This danger can be avoided by the use of thin-film distillation at atmospheric pressure.

The applications of thin-film distillation may be summarized as follows (cf. also [122], chap. 5 and 6).

1. For a "mild" continuous distillation of temperature-sensitive materials.
2. For the distillation of high-boiling mixtures that cannot be separated in a normal still.
3. For the continuous separation of mixtures containing a low-boiling fraction and a very high-boiling main fraction.
4. For the continuous degassing of liquids.
5. For the continuous evaporation of liquids.
6. For the continuous distillation of easily foaming substances.

The following types of evaporators for thin-film distillation or rather, evaporation have to be distinguished.

1. Falling-film evaporators
   - with vertical heated tubes, straight or spiral-shaped, down the outer walls of which the liquid flows (Figs. 196, 198, 199, 212);
   - with rotating elements for film circulation in the form of fractionating brushes (Fig. 201), glass spirals (Fig. 210) or wiper systems consisting of brushes, lamellae or rolls (Figs. 201, 202, 211).
2. Evaporating dishes, horizontal or inclined as used particularly for molecular distillation (Figs. 205, 209).
3. Spraying stills, such as the one described in the section on flash distillation (Fig. 192).
4. Rotating stills
   - apparatus with rotating still pots (Fig. 203);
   - mixed-film drums (Fig. 200);
   - rotating-disk apparatus with centrifugal distribution (Fig. 213).

An exhaustive discussion of all the problems associated with thin-film and flash evaporation as well as falling-film columns illustrated with numerous constructional examples has been presented by Gemmeker and Stage [132]. Furthermore, the reader is referred to chap. 2 (secs. 1 to 8) of [122]. A review of the present state of thin-film stills for laboratory and experimental use by Stage and Fischer [166] is accompanied by impressive illustrations. The paper indicates the large variety of applications of thin-film distillation.

Thin-film distillation is used for both the evaporation of solid solutions and the partial separation of liquid mixtures. As shown by Wilhelm and Miß [132a] the two methods can be combined in special cases. The possible combinations are compared concerning the separating efficiency and heat requirement on the basis of an ideal phase equilibrium of the volatile components.

The author's thin-film apparatus, as developed further by VEB Glaswerk Stützerbach and illustrated in Fig. 196, was adapted from the early types of molecular stills operating with a falling film. It contains two concentric tubes. The inner tube, which is interchangeable by the provision of a ground joint, can be heated by an element a and functions as a surface for evaporation. The outer tube acts as condensing surface.

As pointed out by Utzinger [133] the production of a uniformly thin, downflowing film is a matter of considerable difficulty (see Chap. 4.2). The author has avoided channelling on the evaporator by introducing the feed into a weir, which distributes it evenly over the periphery of the cylinder. The end of the feed tube can be submerged below the surface in this weir, so that the liquid is not broken up into drops. The surface of the evaporating tube is roughened by sand-blasting, a condition also favouring an even film. Moveable metal rings *b* round the heating cylinder serve to mix up the downflowing film; a protective funnel *c* over the distributing weir prevents the liquid from spraying onto the condensing surface.

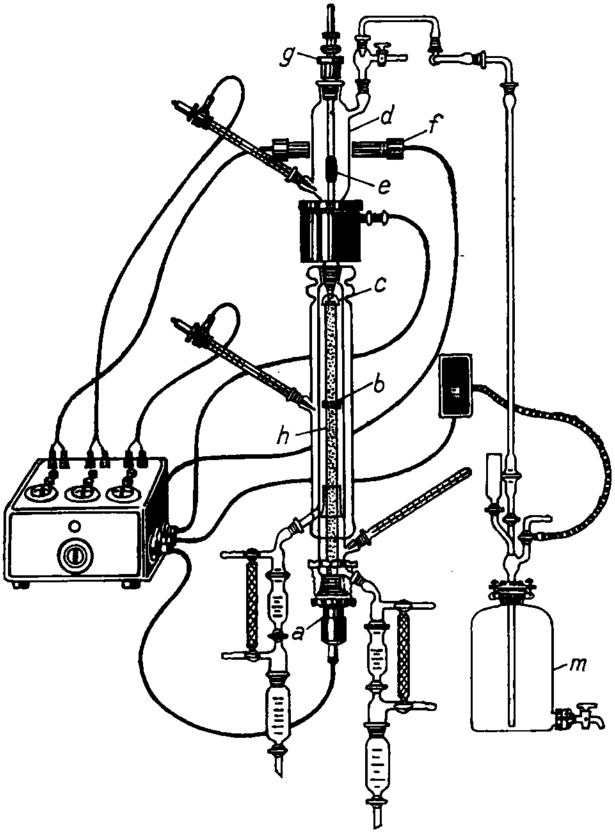


Fig. 196
Krell's thin-film distillation apparatus

The apparatus is equipped with photo-electric control of the feed rate; the temperature of evaporation is regulated by a contact thermometer. The distillation area is surrounded by a cooled jacket, so that the procedure may also be employed for substances of relatively low boiling point. The whole apparatus is operated from a central panel. The material to be distilled is contained in bottle *m* of about 10 l capacity. It is forced by air pressure through tubing to the supply vessel *d*, where it is preheated. The feed rate is controlled by a float *e* which, by means of a photoelectric cell, switches the pump off and on as necessary. A fine-control valve *g* on the supply vessel allows the feed rate to be adjusted accurately. The distillate and residue may be withdrawn from their respective receivers without interrupting the operation. The apparatus can be used at normal and reduced pressures.

Experiments have shown that the rate at which the mixture is introduced, at a given temperature and pressure, has a great influence on the result. It the feed rate is increased, the percentage of bottoms becomes larger, whilst if it is reduced the amount of distillate rises and the separation becomes sharper. The best conditions may be found in each case by keeping the pressure constant and varying the temperature of distillation.

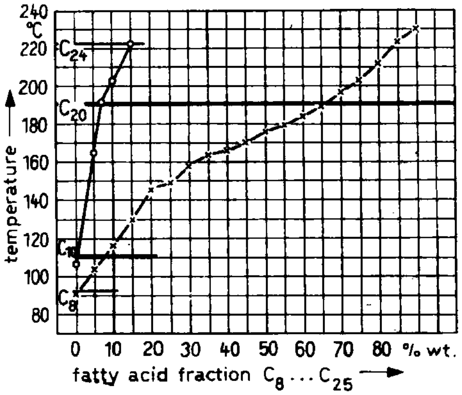


Fig. 197
Fractionation of products obtained in a continuous thin-film distillation of a $C_8 \cdots C_{25}$ fatty acid fraction
× = distillate, ○ = residue

If the composition of the mixture is known, the feed rate may be so adjusted that the yields of distillate and residue correspond to the desired division. It is found, however, to be preferable to work in two stages. In the first thin-film distillation the cut is purposely placed somewhat too high, so that the residue is free from the desired distillate fractions. The tops are distilled in the same way a second time; the high-boiling components carried over in the first operation then remain in the bottoms and the distillate obtained is very pure. By the use of the graduated receivers the separation ratios can be watched at frequent intervals (Fig. 197).

By continuous thin-film distillation fatty acid fractions up to an acid value of 90 could be separated off, so that the distillates were higher than C_{30}. The thin-film procedure has also proved to be very suitable for fractionating silicone oils (which are distributed with great uniformity on the heater) and for distilling waxes. Gutwasser and Müller [22] developed a thin-film evaporator which has been successfully used for the distillation of spermaceti-oil fatty acids. Fig. 198 shows the whole apparatus.

The principle of thin-film distillation has been developed further by Messrs. Leybold-Heraeus GmbH, Cologne, to a so-called "mixed-film distillation procedure". This process takes place at pressures of 1 mm or less on a large evaporating surface, with special precautions to ensure that the film is energetically mixed, so as to renew

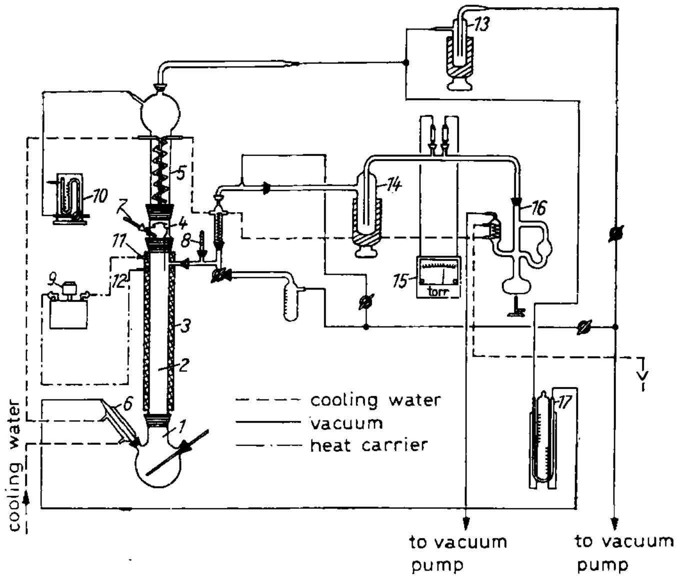


Fig. 198a)
Apparatus for thin-film distillation (Gutwasser and Möller [22])

1 = still pot, *2* = thin-film evaporator, *3* = heating jacket, *4* = vapour-liquid distributor, *5* = overhead condenser, *6* = safety condenser, *7*, *8* = thermometers, *9* = thermostat, *10* = vacuum gauge, *11*, *12* = connections to thermostat, *13*, *14* = cold traps, *15* = ionization gauge, *16* = mercury diffusion pump, *17* = oil manometer

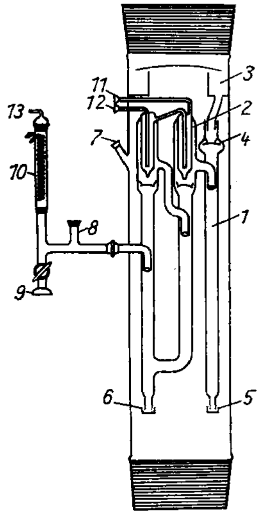


Fig. 198b)
Thin-film evaporator with standard ground joint NS 70

1 = main evaporator tube, *2* = condensers with additional evaporators, *3* = distributor for top product, *4* = glass disc for distribution, *5*, *6* = seals, *7*, *8* = temperature measuring points,
9 = ball joint for receiver, *10* = condenser for distillate, *11*, *12* = connections to thermostat,
13 = vacuum connection

the "active" surface. The following are the main forms of apparatus that have been evolved.

1. A "mixed-film" column (Fig. 199),
   intended for liquids giving a residue that is still capable of flowing at the distillation temperature e. g. high-molecular-weight esters and mineral oil fractions, scents, monoglycerides, plant extracts etc. It should be noted that the vapour is taken off at right angles to the direction of liquid flow. The trickle evaporator II is employed in cases where the product tends to cause caking of the column packing.

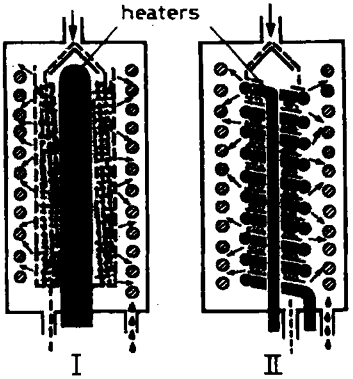


Fig. 199
Mixed-film columns

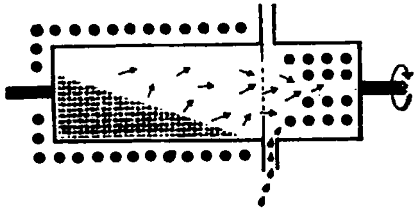


Fig. 200
Mixed-film drum

2. A "mixed-film drum", (Fig. 200),
   which can be used for substances with viscous to solid residues, such as coal tar pitch, natural and synthetic waxes, shale oils etc.
3. A "fractionating brush" (Fig. 201),
   intended for substances giving residues with a viscosity up to 800 cP at the temperature of distillation, or distillates with the same viscosity at the temperature of condensation, for instance tallow oil, chlorinated di- and terphenyls, wool grease [146].

For these main forms components were designed which may be assembled to give multistage thin-film distillation apparatus for degassing and distillation at various temperatures. Further development has led to short-path distillation units with internal condensation and rotating wipers, which may also be combined to operate as multistage apparatus (see chap. 5.4.4).

Falling-film evaporators with rotating elements resemble columns with rotating elements (chap. 7.3.5). The basic difference is that with columns evaporation takes place in a normal manner in a flask and there exists a countercurrent of vapour and liquid for material transfer so that a considerably higher separating efficiency can be obtained with these columns. In both cases, however, the liquid film is made to circulate by the rotational motions. Thus, the low-boiling component is prevented from being depleted at the film surface. The problem of mechanically induced areal turbulence in thin films of liquid was dealt with by Janosfia [134].

Falling-film evaporators may be used for simple and countercurrent distillation as well as for short-path evaporation (see chap. 5.4.4). Heating is mostly done via the outer wall (Figs. 198, 200, 201, 202, 203, 211) but the opposite design is also employed (Figs. 196, 199, 210, 212).

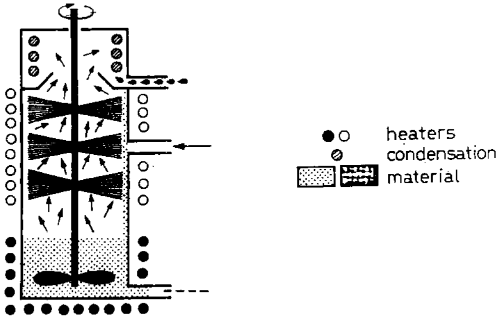


Fig. 201
Fractionating brush

Thin-film evaporators have proved particularly useful on a semi-technical scale [135]. The performance of various types of evaporators with rotors and the causes and degrees of resistance to mass transfer were studied by Dieter [136]. Billet has reported methods for the mathematical treatment of the distillation process in thin-film evaporators with rotating elements [137].

Fig. 202 shows the Sambay glass-made evaporator of QVF-Glastechnik, Wiesbaden-Schierstein, as an example of a falling-film apparatus with rotating wipers.

The feed is supplied to the evaporator from a jacketed dropping funnel (*A*). The feed rate can be controlled exactly by means of a needle valve (*B*) and the funnel itself which works on the principle of the Mariotte bottle. Before entering the evaporation zone the feed is passed through a heated coil (*C*) and heated to about boiling temperature. Thus, full use can be made of the evaporation zone for actual evaporation. Besides, the product is already degassed in the coil and spraying in the evaporator tube is avoided.

The liquid film is formed on the calibrated inner glass tube (*D*) by the action of the rotating wiper system having movable lamellae (*E*). (For corrosion resistance these metal parts are made of tantalum or special steel.) The rotor is operated via a magnetic coupling (*F*) by a variably controllable drive (*G*). Thus the disadvantages of a stuffing box are avoided. The lower bearing is of the pendulum type with a Teflon ball placed in a glass bearing. It is lubricated by the bottom product. Heating is done by an electrically heated circulatory thermostat (1.5 or 2 kW) (*H*), using paraffin oil (up to 200 °C) or silicone oil (above 200 °C) as heating agents. Both oils are completely transparent.

The apparatus is completed by a receiver for the bottoms (*J*) and a transition piece (*K*) with a connection to the vacuum gauge. For deodorization work or for the processing of mixtures with a small proportion of low-boiling material the transition piece (*K*) is replaced by the deodorization piece (*O*). Through the lateral inlet the vapour of a low-boiling product can be passed counter to the falling liquid film in order to enhance the flow toward the condenser and to prevent recondensation of the distillate. A siphon prevents condensation in the bottoms receiver.

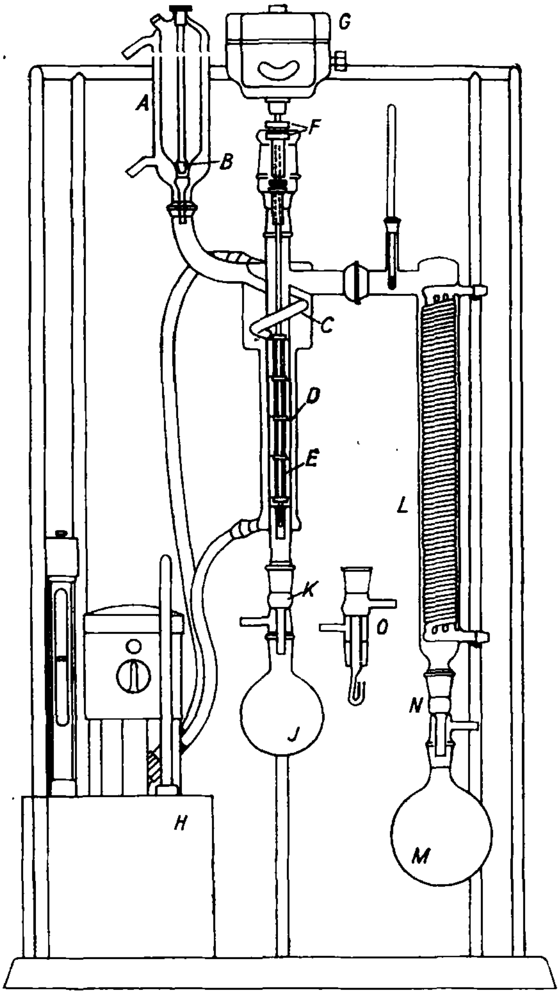


Fig. 202
Sambay distillation apparatus made of glass

The low-boiling phase is condensed in a large-dimensioned condenser (*L*) and collected in a receiver (*M*). A transition piece (*N*) provides the vacuum connection.

The heating surface area of the apparatus is 0.016 m^2, the condensing surface area of the condenser is 0.2 m^2. The maximum working temperature lies around 220 °C so that at 25 torr the maximum rate of evaporation is 480 g/h.

On account of its flexibility, apparatus with rotating evaporators has become standard equipment for laboratory and semi-technical work, particularly because its throughput actually covers the range from micro to pilot-plant scale. Thus there are rotating bulb tubes (chap. 5.1.1) for < 1 ml and 100 l still pots for operation on a semi-technical scale. Besides the degassing of oils and resins, units with rotating evaporators are preferably used for the mild separation of solvents and are especially suited for foaming substances. Fig. 203 shows the operating principle, and Egli's [138] paper offers a discussion of constructional details and applications. The evaporator 1 is variably controlled in the range of about 10 to 220 r.p.m. It is provided with mechanical rapid siphons and automatic siphons. Kramer [138a] has discussed the possible applications of a system of rotating evaporator components. Sorbe [138b] describes the IKA-DEST system which opens up a wide field of applications through manifold combinations of various condensers.

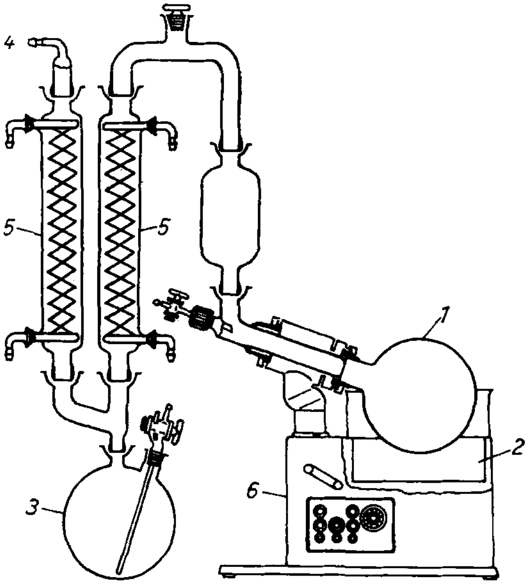


Fig. 203
Rotating evaporator "Rotavapor" R-10

1 = rotating still pot, *2* = heating bath, *3* = distillate receiving flask, *4* = vacuum connection, *5* = condensers, *6* = switchboard

The LRV 2 laboratory rotating evaporator of VEB Carl Zeiss, Jena, can be provided with still pots of 500 to 2000 ml capacity. The heating bath can reach 90 °C.

5.4.4 Molecular distillation

In molecular distillation, which is applied to high-boiling substances (mainly of a temperature-sensitive nature), the material is distilled at a pressure $< 10^{-3}$ torr in apparatus constructed in such a way that the distance travelled by the molecules between the evaporating and condensing surfaces is shorter than their mean free path. The purpose of this arrangement is that the majority of the evaporated molecules reach the condensing surface without being deflected on collision with foreign gas molecules. The mean free path is the theoretical concept of the distance a molecule can travel without colliding with another molecule. For the normal triglyceride fats with a molecular weight of 800, *e.g.*, it assumes these values [141]:

distillation pressure	mean free path
8×10^{-3} torr	7 mm
3×10^{-3} torr	25 mm
1×10^{-3} torr	50 mm.

The process going on in molecular distillation is not the normal ebullition; it might be called "molar evaporation". The equilibrium between evaporated molecules and the liquid is continually disturbed by condensation so that, in accordance with physical laws, equilibrium has to be re-established. This means, however, that more molecules will evaporate from the liquid surface. Thus, we have a true example of a simple distillation which is also termed "one-way evaporation" [141]. The whole field of molecular distillation is covered by the books of Burrows and Holó et al. [139]. Ridgway-Watt [140] presents an introductory survey of apparatus from the micro to the technical scale. In addition, the reader is referred to chap. 1.5 of [122] and some more review articles [108, 131, 145, 156, 157].

The rate of evaporation depends on the vapour pressure p_* of the substance at the temperature of the evaporating surface T, and on the molecular weight M of the substance to be distilled.

This relationship is expressed in Langmuir's equation for the rate of evaporation [142]:

$$D = 0.0583\, p_* \sqrt{M/T} \tag{188}$$

in which

D = the rate of evaporation ($\mathrm{g \cdot cm^{-2} \cdot sec^{-1}}$);
T = the temperature of the surface (K);
p_* = the vapour pressure of the substance (mm Hg) at T;
M = the molecular weight.

This equation assumes that evaporation is not impeded by foreign gas molecules. Since it is inevitable that some evaporated molecules will collide with those of residual gas before arriving at the condensing surface, the value of D given by this formula is not normally attained. It is therefore necessary to correct D by multiplying it by a factor a, which approaches unity the more closely, the lower the pressure of the residual gas. This factor a can amount to 0.9 in modern industrial apparatus.

The validity of equation (188) has been examined by Burrows [143], who has derived a number of semi-empirical formulae giving better agreement in various practical conditions.

The amounts of distillate theoretically obtainable are quite small, as will be apparent from the figures given as examples [108] in Table 47.

If we take the correction factor a to be 0.8 and multiply the figures of the third column by 3.6×10^5 (to give the amount of distillate in one hour from an evaporating surface of 100 cm^2), we obtain quantities in the range of 15 to 22 grams. To realize a higher throughput, Utzinger's method of "short-path distillation" [133] or, Jaeckel's "free-path distillation" [144] are suitable, (the latter of which is chiefly utilized on a semi-technical or industrial scale) with pressures higher than 10^{-3} mm. These processes rely on the increase in distillation rate brought about by a higher pressure, which is shown by Langmuir's equation, and compensate for the shortened mean free path by appropriate design of the apparatus.

Table 47

Theoretically obtainable amounts of distillate, at a saturation pressure of 10^{-3} torr, from substances with molecular weights of 284 to 891

Substance	Mol. wt	D by formula (188) ($g \cdot cm^{-2} \cdot sec^{-1}$)	D by formula (188) ($mol \cdot cm^{-2} \cdot sec^{-1}$)	p_* at 120°C (torr)	$\sqrt{M/T}$ at 10^{-3} (torr)	$p_*/\sqrt{M}$ at 120°C
Stearic acid	284	0.52×10^{-4}	0.21×10^{-6}	35.0	0.90	2.07
Cholesterin	387	0.56×10^{-4}	0.14×10^{-6}	0.5	0.97	0.025
Tristearin	891	0.76×10^{-4}	0.09×10^{-6}	10^{-4}	1.32	—

It should be noted that a pressure of less than 10^{-3}, quoted as being necessary for molecular distillation, applies only to the residual gas. The vapour pressure of the substance distilling may be considerably higher, up to about 1 mm. Only the molecules of the residual gas rebound from the condensing surface; the molecules of the vapour are retained by this surface [145].

The applications of molecular distillation are numerous and lie chiefly in the field of temperature-sensitive substances having molecular weights of 250 to 1200. The following examples have been chosen from the many that might have been given (*cf.* [122], chap. 5 and 6 and [158]):

the preparation of vacuum pump oils and viscous lubricants with a flat viscosity curve;

the investigation of triglycerides (oils and fats) and high-molecular-weight fatty acids, fatty alcohols, waxes and residues;

the separation of vitamin and hormone concentrates;

the purification of plasticizers and other substances of low volatility;

the purification of essential oils and scents;

the deodorization of materials of high molecular weight.

Of late molecular distillation has been employed for the investigation of the high-molecular-weight components present in the residues of crude oils and similar materials. Recycling is employed to improve distillate purities. A survey of apparatus and methods used in the molecular distillation of fatty acids and lipids has been given by Perry [145]. Frank [146] deals with special problems and, in particular, describes multistage stills.

An essential feature of molecular distillation is that it is capable of separating substances having the same vapour pressure, but differing in molecular weight. If we examine Langmuir's original equation

$$D = \frac{p}{\sqrt{2\pi MRT}} \tag{189}$$

in which D = the maximum amount that can be evaporated, in moles · cm^{-2} · sec^{-1};
p = the vapour pressure, dynes · cm^{-2};
M = the molecular weight;
R = the gas constant, 8.3 × 10^7 ergs/K · mole;
T = the temperature, K,

we observe that at constant temperature the amount evaporated is dependent only on $p/\sqrt{M}$. By analogy to the relative volatility we can therefore write the relative quantities that can be evaporated as

$$D_1/D_2 = \left(p_1/\sqrt{M_1}\right)/\left(p_2/\sqrt{M_2}\right) \tag{190}$$

where p_1 and p_2 represent the partial pressures of the components [108]. Substances for which p_1 and p_2 are identical can therefore be separated if M_1 and M_2 have different values.

The apparatus employed for molecular distillation should comply with the following requirements:

1. the vacuum system should be wide in bore, so that pressure differentials are avoided (see chap. 5.4.1);
2. the liquid should be evenly distributed as a thin film and its residence time (*cf.* chap. 5.4.3) should be short;
3. the distance between the evaporating and condensing surfaces should not be greater than the mean free path (1—2 cm); the condensation temperature should be about 50—100 °C below that of evaporation;
4. the substance to be distilled should undergo a preliminary degassing to minimize the amount of uncondensable gas present.

The types of apparatus that have been developed so far may be divided into the following groups according to their principle of operation:

a) flat-bottomed stills containing a thin film;
b) apparatus having horizontal or inclined trays as evaporating surfaces;
c) apparatus with a film descending vertically;
d) centrifugal apparatus.

It should be observed that recycling can be practised in all these forms of apparatus in order to separate low-boiling components effectively; this is often necessary in view of the fact that molecular distillation effectively corresponds to a single equilibrium stage. We must not forget, however, that in a distillation from a flask entrainment may constitute a complication; in molecular distillation, on the other hand, evaporation takes place at the surface only, so that the molecules can leave it selectively without mechanical disturbance [147].

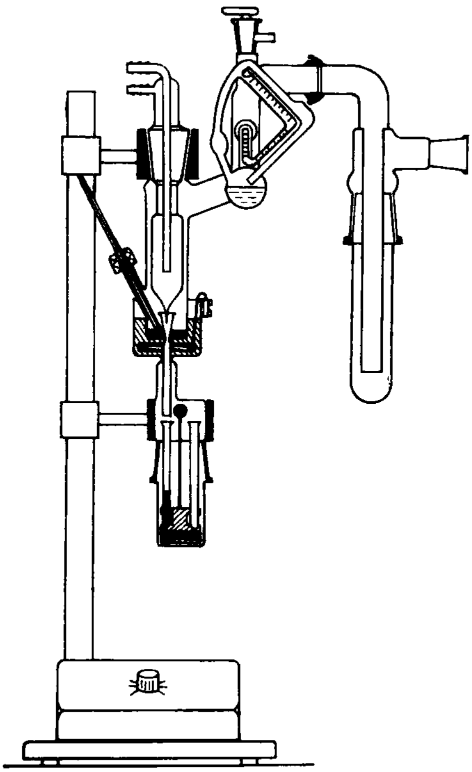


Fig. 204
High-vacuum molecular still for charges of 2, 5 or 10 ml, temperature range 20 to 200 °C, vacuum to about 10^4 torr, with support and temperature control device

The oldest forms of apparatus are those having a flat-bottomed still pot containing a thin film of liquid. Fig. 204 shows a modern construction developed by Fischer. This type of still is well suited for dealing with substances having molecular weights up to 300, and are mainly used for obtaining preliminary data on the boiling range and the tendency to decomposition of the material in question. Methods employed in micromolecular distillation based on the cold-finger and the falling film principle for throughputs of 0.5 to 5.0 g were described in chap. 5.1.1 (Figs. 131 to 136).

A good example of an apparatus in which the evaporation takes place from a tray is the arrangement of Utzinger [133, 147], who employs the term "short-path distillation" for one-way distillation at pressures above 10^{-3} mm Hg. The apparatus, dating from 1943, has been developed further for continuous fractionation. Fig. 205 shows it in a recent form.

The previously degassed feedstock emerges from the degassing flask through a capillary tube into the "still" and flows as a thin film over a tray of adjustable slope, heated by the circulation of high-boiling mineral oil. A temperature gradient is here established, the temperature increasing in the direction of flow. The vapours are condensed by a cooler surrounding the tray, inclined at the same angle as the latter.

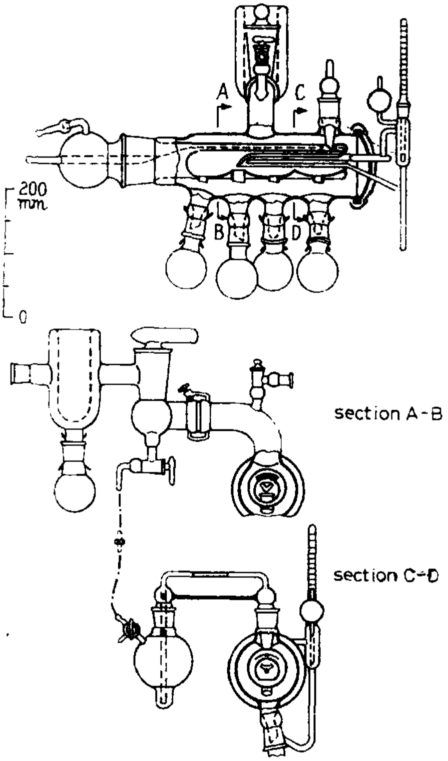


Fig. 205
Short-path distillation apparatus for three distillate fractions (Utzinger)

The condenser is subdivided into three sections and there are take-off tubes, three for distillate fractions and one for the residue.

A small difference in pressure between the degassing flask and the distillation space — both of which are initially connected to the same pump — allows the tray to be charged with feedstock and the rate of admission to be adjusted as required. Furthermore, the rate of flow of the liquid on the tray can be controlled, even during distillation, by altering the slope; to do this, it is rotated around a conical ground joint. These two variables are necessary for establishing the desired fractionating ratio.

The heating medium is brought into circulation and warmed by heating the tube leading to the entry jet with a Bunsen burner or electric element. The temperature gradient in the tray depends on the rate of circulation of the heating oil, on the feed rate, the downflow rate on the tray, the composition of the feedstock and the pumping system. In the glass apparatus described here temperature differences of 10 to 20 deg. C occur between the beginning and end of the tray. The distillation temperature is measured indirectly by submitting small samples of the feedstock to the usual boiling point determination at the same pressure. The temperature of the heating medium usually lies about 60 to 80 deg. C above this distillation temperature; the evaporation in the film is thus accompanied by a marked cooling effect. The average throughput is approximately 100 ml/h if 50—70 ml/h of distillate is taken off.

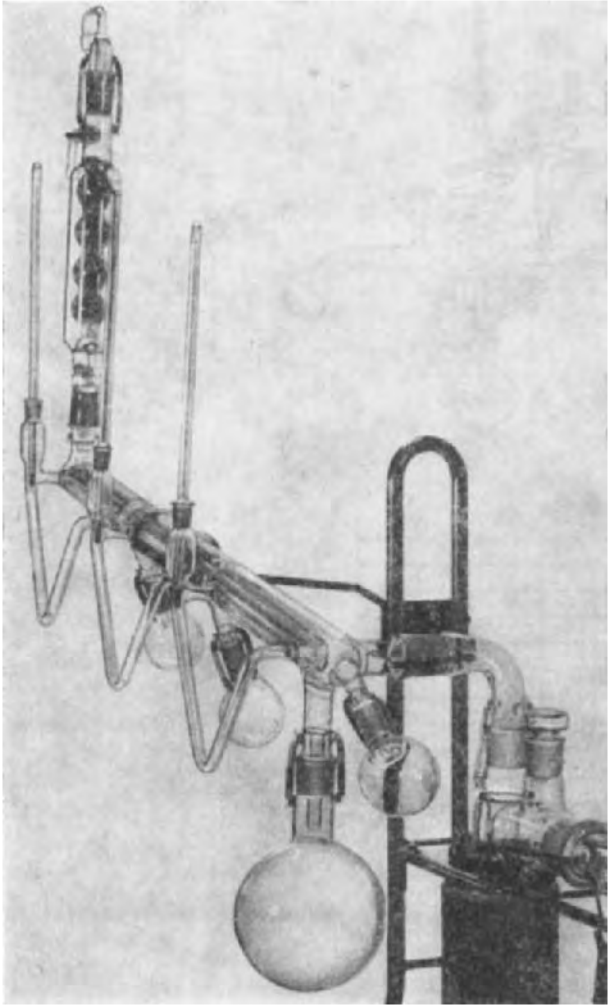


Fig. 206
Micro-cascade apparatus for short-path and molecular distillation

Utzinger's device has been developed further by the VEB Jenaer Glaswerk Schott & Gen., Jena, Germany, who have constructed a macro- and micro-cascade apparatus (Fig. 206). Since this device is built up of separate parts it can be set up for any number of fractions. Every step of the cascade may be adjusted to a different temperature by means of its circulatory heater. Degassing is carried out independently in the apparatus shown in Fig. 207. In this way account is taken of the fact that degassing and the actual distillation frequently have to be performed at different rates.

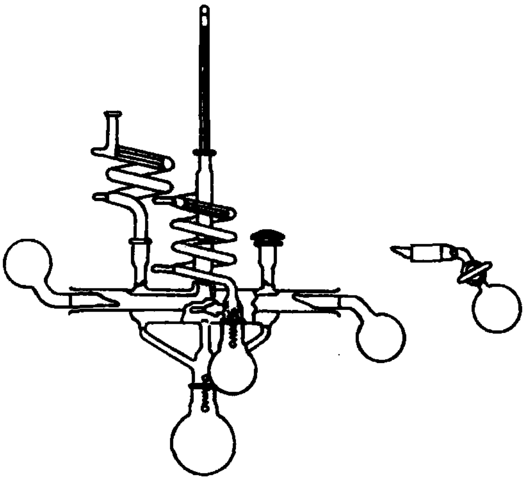


Fig. 207
Utzinger's degasser

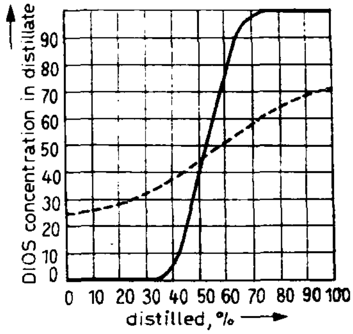


Fig. 208
Comparison of separating efficiencies according to Frank [146]

Molecular distillation with the test mixture:

di-(iso-octyl-)sebacate (DIOS), molecular weight 426
di-(iso-octyl-)phthalate (DIOP), molecular weight 391
Single-stage apparatus: — — — — —
Ten-stage apparatus: ————

Melpolder et al. [148] have evolved a 20-stage apparatus for molecular countercurrent distillation, intended for the separation of high-boiling components of petroleum. A 10-stage still described by Ridgway-Watt [140] rotates slowly in an inclined position. Thus the product is distributed over the whole evaporator surface. After condensation in the first condenser stage it is fed into the second, and so forth until the product is withdrawn. Fig. 208 [146] demonstrates the separating efficiency of a single-stage still (Fig. 204) as compared with that of a 10-stage apparatus after [140]. Methods for calculating the number of theoretical stages in multi-stage devices have been worked out by Malyusov et al. [149] and Shavoronkov et al. [150]. Fig. 209 shows the apparatus used by those authors.

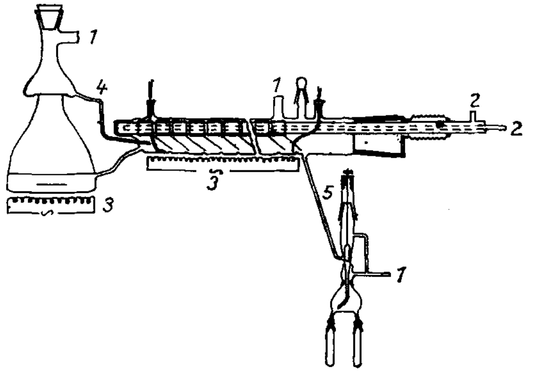


Fig. 209
Multi-stage apparatus for molecular distillation (Malyusov and Shavoronkov [150])
1 = tube vacuum, *2* = cooling water, *3* = electric heater, *4* = product feed, *5* = distillate removal

The principle of the *falling film* is that which has been most generally utilized (*cf.* section 5.4.3). The very short residence time of such a falling film — amounting to 3—4 seconds in laboratory apparatus and as little as 1/1000th of a second in some industrial installations — ensures a very "mild" thermal treatment of the substance being distilled. In laboratory molecular stills the thickness of a falling film may be of the order of 0.1 to 0.2 mm, corresponding to 50,000 molecular layers, whilst film thicknesses down to 0.001—0.005 mm (around 400 molecular layers) can be established in large-scale units. The ideal solution would be mono-layers.

Important factors in molecular distillation are the character of the evaporating surface and, of course, the distance between this latter and the condensing surface. For falling-film apparatus a good wetting of the evaporator surface and effective circulation of the liquid film are achieved by means of the same constructional measures as those described on p. 286 [122].

As an example of a spiral still Fig. 210 represents apparatus for molecular distillation manufactured by VEB Jenaer Glaswerk Schott & Gen., Jena. The glass spiral 3 rotates around the heater 2. Thus a film thickness of about 0.1 mm and a good circu-

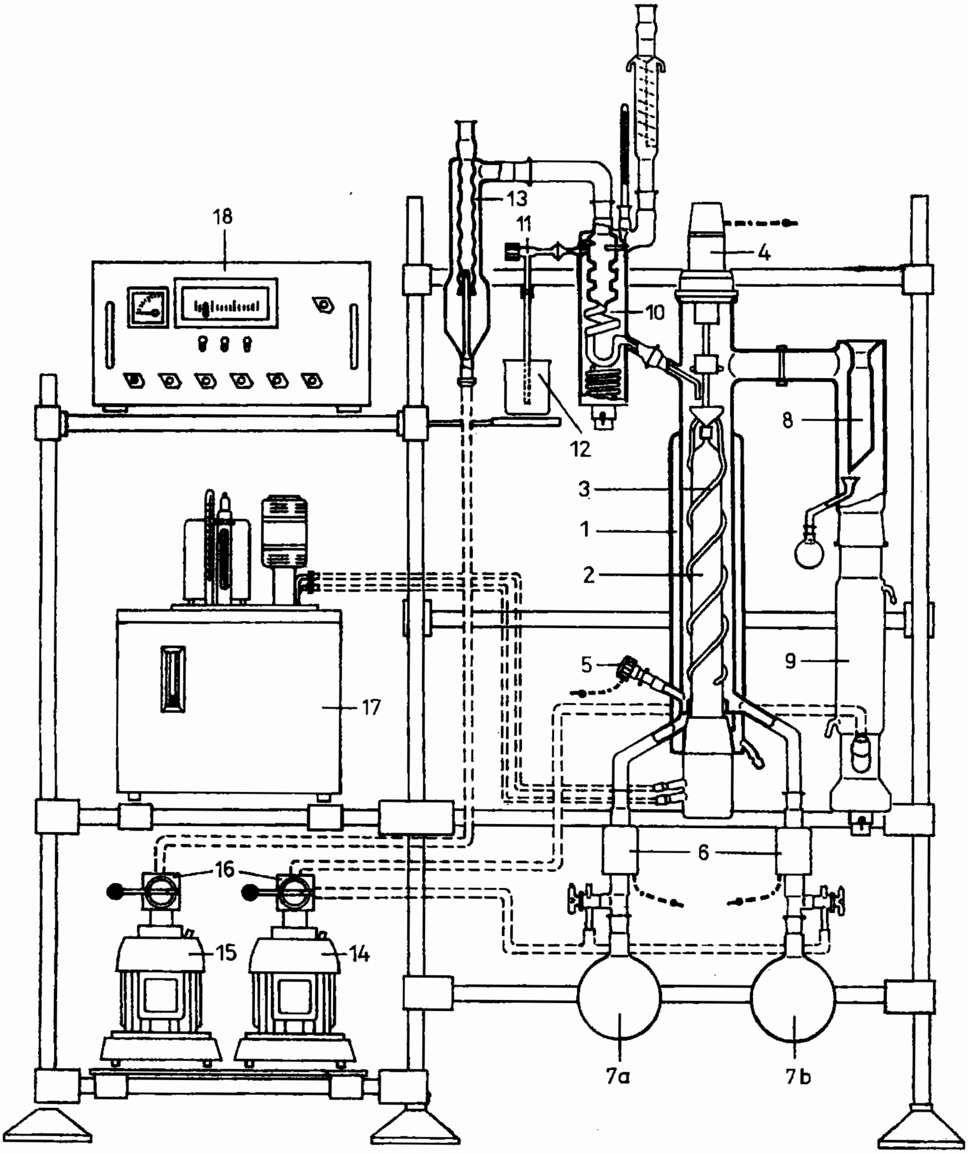


Fig. 210
Molecular distillation apparatus MDR 600

1 = still with condensing jacket, *2* = evaporator, *3* = glass spiral, *4* = motor for spiral, *5* = thermocouple, *6* = electromagnetic valve for change of receivers, *7a* = receiving flask for residue, *7b* = receiving flask for distillate, *8* = cold trap for still, *9* = high-vacuum oil diffusion pump, *10* = degasser, *11* = control valve for feed, *12* = storage vessel, *13* = degasser cold trap, *14* = two-stage rotary-valve vacuum pump, *15* = one-stage rotary-valve vacuum pump, *16* = vacuum stop valve, *17* = universal laboratory thermostat, *18* = switchboard lation of the film are obtained. The residence times are as short as a few seconds. These technical data are given by the manufacturer:

nominal throughput	1000 g/h
throughput[1])	250···2000 g/h
rate of evaporation[1])	18,000 g/h (maximum)
spiral velocity	approx. 40···90 r.p.m.
evaporating surface area	approx. 600 cm^2
distillation temperature	300 °C (maximum)
working voltage	380/220 V
power consumption	2 kW
condensing water consumption	approx. 350 l/h
cooling agent for freeze traps	liquid air (nitrogen); in some cases: CO_2-acetone mixture

The KDL 4 laboratory short-path distillation apparatus of Leybold-Heraeus GmbH & Co KG, Cologne, was designed on the assumption that in general the first step in a molecular distillation is the degassing of the product which is followed by several distilling stages at different temperatures. The wipers consisting of Teflon or Teflon-coated ceramic rollers were placed between the inner condensing cylinder and the heated outer wall. The KDL 4 is a multistage apparatus which combines a number of short-path stills made of glass or special steel. The continuous operation is illustrated by Fig. 211. Pressures of 10^{-3} torr can be reached. The minimum throughput is about 100 g/h. A more modern apparatus (KDT 6) of the same manufacturer is designed to handle extremely corrosive substances. Hence glass has been used as a constructional material almost exclusively. The throughputs lie around 10 kg/h. Constructional and operational aspects of short-path distillation equipment on a semi-technical and technical scale were discussed by Habendorff [140a].

Some of the devices based on a falling film are equipped with an arrangement for recycling, as shown in Fig. 212. The circulation is brought about by an electromagnetic pump and the liquid is generally injected onto a ring of wire gauze to produce an even distribution [152].

The main problem in designing an apparatus of the falling-film type is to prevent channelling on the evaporating surfaces. The following measures have been adopted for this purpose:

1. roughing the surface of the evaporator by sand-blasting, etching, or sintering glass powder on (Figs. 196, 205, 206);
2. the provision of a wire-gauze ring, or a closely-fitting concentric cylinder of wire gauze or glass cloth at the point where the feedstock is admitted (Figs. 196, 212);
3. the use of an evaporating surface having wave-shaped or spiral extrusions (Fig. 210);
4. the introduction of the feedstock by a rotor with or without wipers or the rotation of the whole evaporator (Figs. 200, 201, 202, 203, 211).

---

[1]) depending on the substance processed

The principle of producing very thin films by *centrifugal distribution* has been developed mainly by Hickman [153] for apparatus of various sizes up to large industrial units [151]. Fig. 213 illustrates a laboratory apparatus arranged for circulation. The mixture to be distilled is introduced by pump *a* from the storage vessel *e* onto the rotating, heated disk *b*, and is there distributed by centrifugal action into a thin film. The condensing surface *c* is a short distance from the disk. The distillate may be removed directly or returned to the storage vessel *e* according to choice. The residue is collected by the device *f* and led to the receiver *d*, from which it can also be passed back to the storage vessel for further treatment.

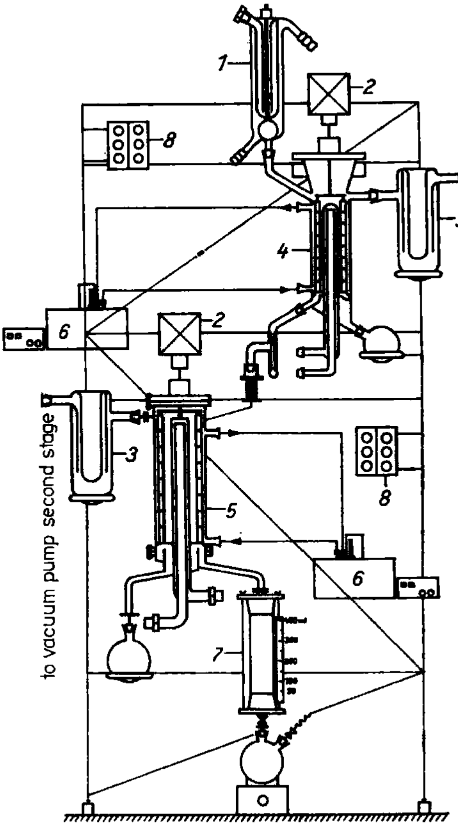


Fig. 211
Laboratory apparatus for short-path distillation KDL 4 with roller wipers

1 = metering vessel, *2* = drive for wipers, *3* = cold trap, *4* = glass-made part of still, *5* = metal part of still, *6* = circulating-type thermostat, *7* = graduated vessel (section), *8* = sockets

In their considerations on molecular distillation Hickman [152] and Embree [154] introduced the concept of the "distillability". This term is used to denote the ratio

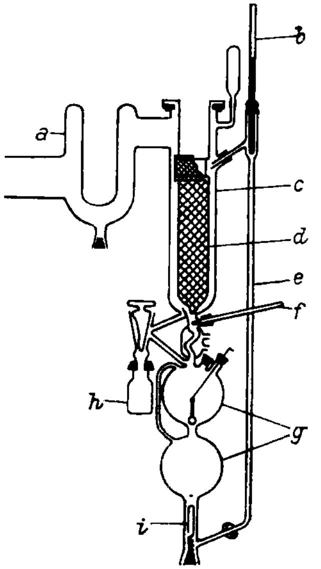


Fig. 212
Molecular distillation apparatus of Hickmann with arrangement for recycling

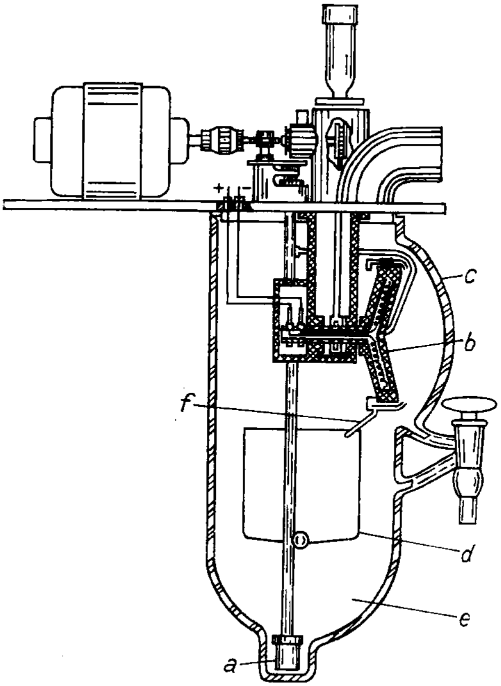


Fig. 213
Apparatus for molecular distillation with centrifugal distribution (Hickmann)

between the number of molecules of a substance *A* leaving the evaporating surface in unit time, and the number of molecules of *A* remaining in the film under identical conditions. By circulating repeatedly one can finally obtain *A* almost completely in the distillate. The time of distillation can be shortened by increasing the temperature of evaporation. An "elimination curve" may be obtained by distilling the mixture, under the same vacuum, at successively increasing temperatures (say at intervals of 10°C) and determining the composition of the distillate. Fig. 214 shows the typical shape of an elimination curve. The concentration rises to a maximum and subsequently falls back to zero. The course of the curve naturally depends on the properties of the components — especially the heat of evaporation — and on the residence time, which for purposes of comparison must also be kept constant. The maximum in the elimination curve corresponds approximately to the boiling point in normal distillation. If the residence time increases, the elimination curve shifts in such a way [159]

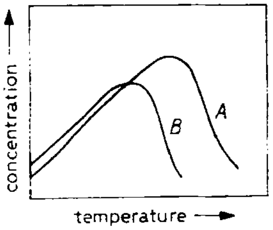


Fig. 214
Elimination curve

A = short residence time
B = long residence time

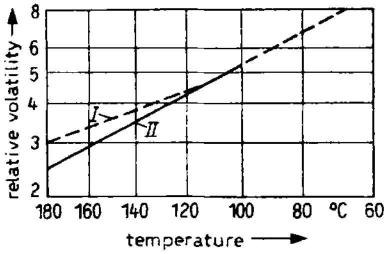


Fig. 215
Relative volatility of the test mixture EHP/EHS

EHP: *Kp*. 0.5 torr 183—184°C; EHS: *Kp*. 0.5 torr 199—202°C
I: From an equilibrium apparatus of flask type
II: from an apparatus operating on the falling-film principle

that its maximum lies at a lower temperature (curve *B* in Fig. 214). To obtain the optimum throughput in molecular distillation the influence of various parameters should be studied, the results being expressed in the form of such elimination curves. Theoretical investigations of this problem were carried out by Gorriz et al. [155].

The method has been developed further with the aid of standard substances, mostly volatile colouring matters capable of being determined colorimetrically [108]. Carriers are also frequently employed with the object of achieving a good distribution of the film when the amounts of the substances become small.

Recent investigations of Hickman and Trevoy [141] on evaporation in a high vacuum and molecular distillation have yielded noteworthy results. The evaporation coefficient of a pure substance may be changed appreciably by the presence of impurities in very small quantites. In studying a test mixture, di-2-ethylhexyl-phthalate—di-2-ethylhexyl-sebacate (EHP—EHS), the investigators found that the relative volatility is highly dependent on the operating conditions, as demonstrated in Fig. 215.

Therefore, Malyusov et al. [160], in their measurements at a pressure of 10^{-4} torr, distinguished between non-equilibrium (α_{neq}) and equilibrium separation factors (α_{eq}). As the temperature rises the $\alpha_{\mathrm{neq}}/\alpha_{\mathrm{eq}}$ ratio approaches unity, as is confirmed by Fig. 215.

The test mixture di-2-ethylhexyl phthalate-m-tricresyl phosphate (EHP—mTCP) was studied at $< 1.5 \times 10^{-3}$ torr (2×10^{-3} mbar) in the range between 130 and 160°C by Uyeha and Hagihara [163]. In the lower part of this range the mixture displayed an ideal behaviour for mole fractions of 20 to 80%.

5.4.5 Pressure distillation

Mixtures that are gaseous at room temperature and higher may be distilled at pressures above atmospheric with water as cooling medium. The expense of a low-temperature cooling agent is thereby saved; on the other hand, special apparatus capable of withstanding and maintaining the increased pressure is necessary. Pressure distillation may also be useful in cases where the relative volatility increases with rising temperature, for example in that of the mixture 2.4-dimethylpentane—2.2.3-trimethylpentane, which at atmospheric pressure exhibits a difference in boiling point of only 0.2°C, but has a value of α increasing from 1.006 at 80°C to 1.055 at 200°C (*cf.* section 4.6.2).

Relatively few descriptions of laboratory apparatus for pressure distillation have been published. Glass cannot normally be employed for pressures higher than 5 atm. Schneider has described metal equipment that can withstand up to 45 atm; it is provided with a 3-litre boiler and a column of 25 mm diameter [161]. The apparatus of Simons is made of glass and is designed for pressures up to 5 atm [162]. Its manipulation is as follows (see Fig. 216). Compressed air is admitted at *A*. An arrangement for keeping the pressure constant consists of valve *B*, which is filled with mercury and contains a float *C*, terminating in a cone *D* that can close the opening *E*. By an adjustment of the mercury level with the aid of the levelling bulb *F*, float *C* maintains the pressure at the required value. If this value is exceeded by the compressed air admitted, float *C* is forced down and air can escape through *S* to the atmosphere until equilibrium is re-established. The mixture to be separated is put in still pot *H* and heated by the electric element *J*. Column *K* may be filled with any type of packing; the vapours are liquefied in condenser *L*. The condensate flows into funnel *M*, which has a small hole through which the reflux returns to the column. The distillate passes through the capillary tube *N*, where it is evaporated by a heater. The vapour is again condensed in *P*, the condensate flows down through *R* and collects above valve *S*, which is of the same type as that previously described. This valve is opened or closed by lowering or raising the levelling bulb *T*. Part of the

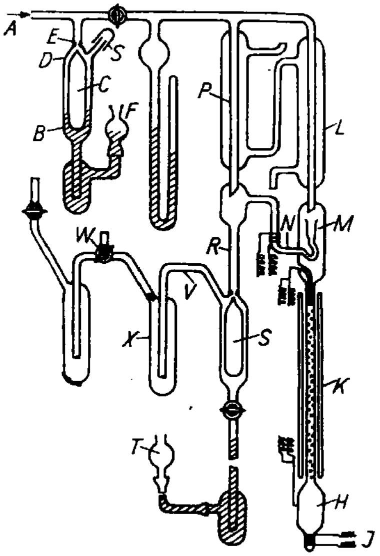


Fig. 216
Apparatus for distillations under pressures up to 5 atm (Simons)

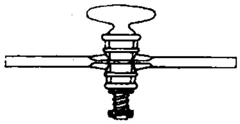


Fig. 217
Pressure tap with retaining spring

distillate remains floating on the mercury in *S*, another part flows directly to *V*. If valve *S* is closed and valve *W* opened the pressure below *S* is reduced and the fraction evaporates. It is re-condensed in receiver *X*, which is cooled by liquid air. In this way samples may be taken without any alteration of the pressure in the apparatus.

Normal glass laboratory apparatus can as a rule be used for distillation at a pressure up to 2 atm if precautions are taken. All ground joints should be secured by strong spring clips. Fig. 217 shows a pressure tap, the cone of which is kept in its seating by a strong spring.

6. Selective separating processes

By this term we denote processes in which, as the result of the addition of a substance or substances in the gaseous, liquid or solid state, a distillative separation is favourably affected (or sometimes even rendered possible). The term also includes procedures involving a reaction that gives rise to new substances, which are removed by the distillation in the same operation. Furthermore it can be taken to cover methods which by a combination with another procedure, for instance chromatography, supplement the process of distillation in specific cases.

According to Gibbs' phase rule a completely soluble binary mixture is enriched in both phases, whilst an immiscible binary mixture, with its three phases, cannot be enriched (see Fig. 29, a—d). It will be recognized, on the other hand, that three-component systems having a miscibility gap, *i.e.* showing two liquid phases and one vapour phase, are separable by countercurrent distillation [1]. A typical example is the preparation of absolute alcohol by azeotropic distillation with benzene.

6.1 Carrier vapour distillation

The most familiar example of carrier vapour distillation is the distillation of high-boiling materials *with steam*. The use of a carrier vapour has the double object of separating the volatile from the non-volatile components with a reduction in boiling point, and of thereby avoiding thermal decomposition. The process takes place under conditions comparable with those existing in vacuum distillation. The volatile substance passes over at an effective pressure p_1 that is lower than the total pressure p_{ges} of the system. The difference $p_{ges}-p_1$ is the partial pressure p_2 of the carrier vapour. In normal distillation at a reduced pressure it is necessary either to increase the temperature or to reduce the pressure during the course of the distillation. In steam distillation the same effect is obtained by an (automatic) increase in the proportion of water vapour [2].

Steam distillation is particularly valuable for purifying and separating substances partially or totally insoluble in water, such as ethereal oils, fatty acids, fatty alcohols, aniline, tallow oil, waxes, fractions of petroleum and tar etc. A further advantage of this process is that the steam displaces atmospheric oxygen and hence protects the material from oxidation. Steam distillation is much used in preparative work for dealing with gummy or alkaline reaction products.

As has been pointed out in section 4.3 and 4.5, the two components in steam distillation behave as though each of them were present alone at the existing temperature, provided they are immiscible. The total pressure acting on the boiling mixture is the sum of the partial pressures of the components, one of which is water. The partial pressures and the boiling point of the mixture may be determined, as described in section 4.5 by means of the additive formula. A more convenient procedure is to draw a diagram according to the method of Badger and McCabe [2]. In this diagram one first plots the vapour pressure curves of the substances to be distilled (Fig. 218). Next, one draws curves for the values of the total pressure minus the vapour pressure of water. For instance, water has a vapour pressure of 150 mm at 60.1 °C; thus for the curve for atmospheric pressure one plots 760 − 150 = 610 mm against 60.1 °C.

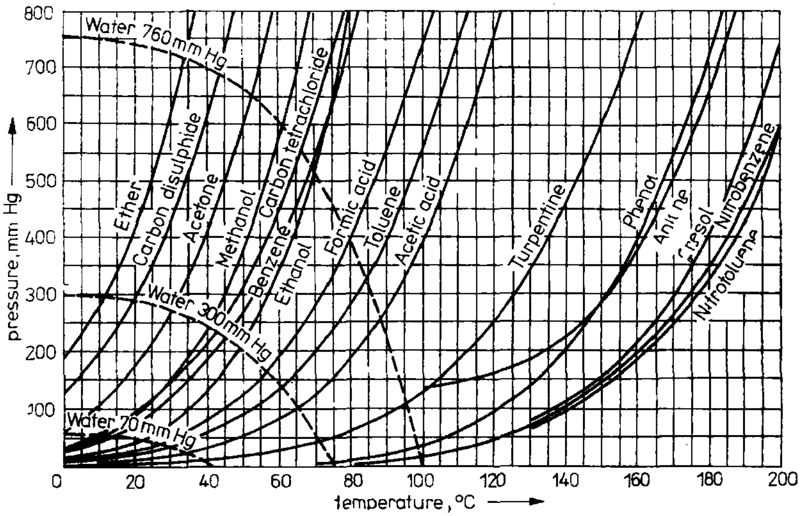


Fig. 218
Diagram for determining the boiling point and the partial pressures in steam distillation (Badger and McCabe)

The point of intersection of the latter curve with that for the vapour pressure of the substance gives the temperature of the mixed system and the partial pressures of the components. (The diagram is sometimes drawn on a logarithmic scale.)

From the partial pressures, the vapour composition can be calculated by formula (40). The proportion by weight of the component to carrier steam is determined by

$$\frac{G_1}{G_2} = \frac{p_1 M_1}{p_2 M_2}. \qquad (191)$$

For the mixture toluene-water we thus find

$$\frac{G_1}{G_2} = \frac{337 \times 92}{423 \times 18} = 4.1 \qquad (192)$$

which signifies that to distil 4.1 kg of toluene we require 1 kg of water vapour. By formula (40) we find that the toluene content of the mixture is 80.3% wt. and from Fig. 218 it is seen that the boiling point of the mixture is 84.4 °C.

Readily decomposable compounds may be distilled with steam at a reduced pressure. From Fig. 218 we see, for example, that the mixed boiling point of aniline-water, which is 98 °C at a total pressure of 760 mm, falls to 75° if this pressure is 300 mm; it is assumed, of course, that only enough steam for saturation is blown in. Steam distillation at a reduced pressure is desirable for distilling substances with low vapour pressures (such as fatty acids of high molecular weight) and for dealing with mixtures containing a component in low concentration (for instance oils containing traces of a solvent).

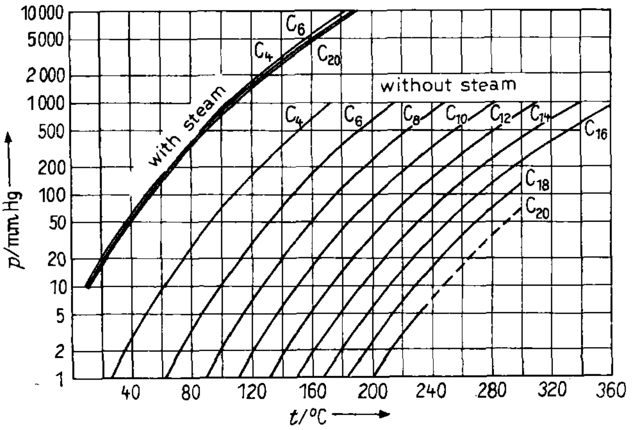


Fig. 219
Boiling points of the straight-chain, saturated, even-numbered fatty acids, with and without steam, as a function of the distillation pressure

The results of using *superheated steam* — which is widely employed in industry for the distillation of tars, mineral oils, fatty acids, glycerin etc. — have been critically discussed by Stage. Taking the saturated C_4 to C_{20} straight-chain fatty acids as an example, he showed that when using saturated steam boiling points are depressed by about 160—240 deg. C, but that at the same time the differences in boiling point, from member to member, became so small that a separation into individual compounds was then impossible (Fig. 219). If, however, the separation was performed with 10% of superheated steam at a pressure of 10 mm, the differences in boiling point remained unaffected and the inherent advantages of steam distillation (good mixing and absence of local superheating) were still present; the average reductions in the temperature, on the other hand, amounted to only 20 deg. C [3]. It may be pointed out that mixtures of fatty acids and fatty alcohols can also be separated reasonably well in stages by steam distillation coupled with partial condensation [4].

Although steam is the carrier vapour most used, on account of its low molecular weight, its high heat of evaporation and the ease with which it is condensed, other gases also find application in industry for effective pressure reduction. In the production of hard coal tar pitch, for instance, waste gases containing CO_2, N_2 and water vapour are employed as carriers [6]. The presence of inert gas does not cause any appreciable reduction in column efficiency [7]. A graphical method for calculating the condensation of steam-gas mixtures was evolved by Algermissen [8].

Apparatus for carrying out steam distillation can be put together without difficulty from ordinary laboratory components. Fig. 220 shows a set-up for distilling with saturated steam at atmospheric and reduced pressures. The flask *a* is thoroughly insulated with glass wool, or slag wool; it is advisable to heat it as well, in order to prevent the condensation of water. The steam inlet *b* is provided with a cock for drawing off condensed water and can also be employed for passing in other carrier gases. Fig. 221 illustrates the method of distilling with superheated steam in countercurrent operation. The steam is produced in a metal boiler *a*, equipped with a sight glass. Superheating takes place in the conical metal spiral tube *b*, which is connected to a water trap and a thermometer. It is advisable to include a safety valve in the steam line. An arrangement developed by Tropsch [7] has also proved suitable for superheating. For comparative experiments it is necessary to supply the steam in constant, measurable amounts. A simple method of regulating the amount is shown in Fig. 220 where water is admitted dropwise from the graduated cylinder *d* into the steam boiler, care being taken to maintain a constant level. A more accurate method is that described by Merkel [9], who regulates the amount of steam by the pressure produced in one limb of a manometer. A steam production unit has been developed by Stage et al. [10] to an arrangement in which the steam can be accurately measured.

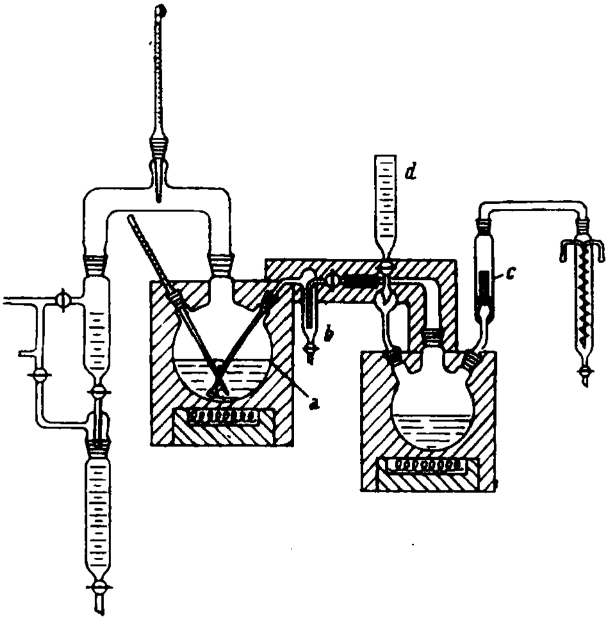


Fig. 220
Arrangement for distillation with saturated steam

Water is admitted continuously from a measuring burette into the heated apparatus, which is filled half full with sand to promote heat transfer. Alternatively the water may be evaporated in a coil immersed in a metal bath.

For the distillation of small amounts of material the apparatus of Pozzi and Escot [11] is very convenient, as the steam-boiler simultaneously serves as heater for the distillation vessel (Fig. 222). Parnass and Wagner [12] offer an arrangement for microscale work.

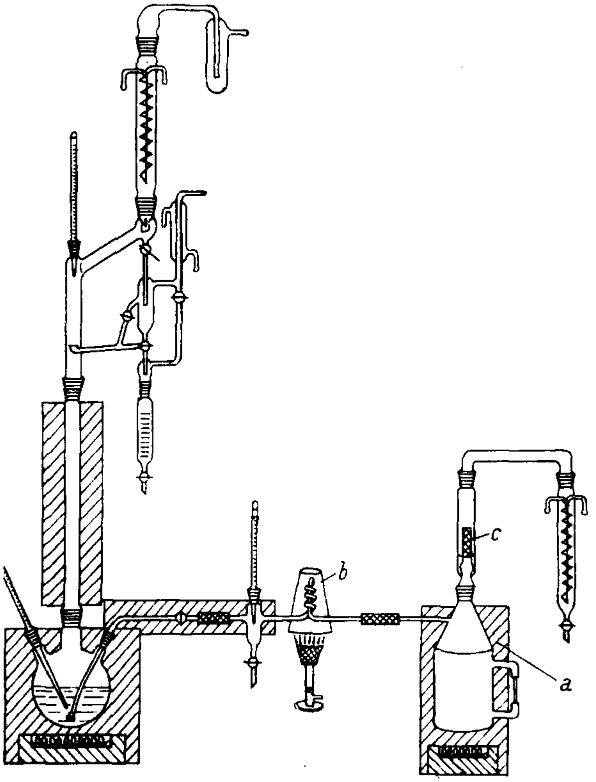


Fig. 221
Arrangement for distilling with superheated steam in countercurrent operation

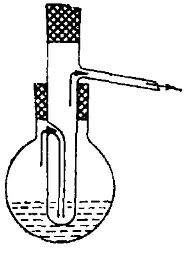


Fig. 222
Device for the distillation with steam of small amounts of material (Pozzi and Escot)

The methods of steam distillation have been summarized by Bernhauer [13] and Thormann [14]. A detailed discussion of practical and theoretical aspects of steam distillation as illustrated by the distillation of essential oils is given by von Weber [15]. Rigamonti [16] developed a nomogram which can be used to calculate the steam requirements for various enrichments. Prenosil [16a] compared theoretical and experimental steam distillation data for multicomponent mixtures. He modified the calculating method by introducing a value for evaporation efficiency. Steam distillation can also be carried out in thin-film apparatus. Berkes et al. [16b] give a description of the material transfer conditions of a steam distillation performed in such apparatus in terms of the balance equations.

6.2 Azeotropic and extractive distillation

Whilst azeotropic and extractive distillation are now employed extensively for difficult separations on an industrial scale [5], it has been usual in the laboratory to resort to other processes, such as extraction and chromatography, for separating narrow-boiling and azeotropic mixtures. It will be shown below that under unfavourable conditions selective processes, such as azeotropic and extractive distillation, offer considerable advantages. The common characteristic of the two is that the ratio of the activity coefficients of the components is influenced by adding another substance [17]. A combination of the two processes termed azeotropic-extractive rectification was proved to be feasible by Kümmerle [18]. Gerster [19] compared these selective processes with ordinary distillation from the point of view of economy.

A comparison between extraction and extractive distillation for the purpose of separating aromatic hydrocarbons from petrol produced by pyrolysis and reformate was made by Müller [19a]. He shows in which cases extraction and in which extractive distillation is advantageous, including the economical aspect. Helms and John [19b] have described the extractive distillation of aromatic hydrocarbons by the "Lurgi-Distapex" method. They used n-methyl pyrolidone (NMP). The purities obtained were 99.95, 99.7 and 99.8% for benzene, toluene and xylene, respectively. The book of Hoffmann [5] which contains numerous calculations for binary, ternary and multicomponent systems offers a thorough treatment of the problems associated with azeotropic and extractive distillation. Results of laboratory experiments on the separation of strongly non-ideal mixtures by means of azeotropic and extractive distillation as exemplified by the distillation of acryl nitrile are reported by Schober et al. [19c]. In addition, the authors have made a theoretical study of mixtures of HCN, acryl nitrile, acetonitrile, oxazole, H_2O.

In the case of *non-ideal mixtures* without a special point the equilibrium curve approaches the diagonal asymptotically at the upper or lower end (for examples see Fig. 29f and h). Even with relatively great differences in boiling point between the components a separation of such mixtures requires a considerable number of separating stages. Mixtures having a special point (azeotropes) give the following results when submitted to countercurrent distillation with sufficient separating power.

Mixtures forming an azeotrope with minimum boiling point: distillate: azeotropic mixture of the two components; bottom product: the component in excess, pure.

Mixtures forming an azeotrope with maximum boiling point: distillate: the component in excess, pure; bottom product: azeotropic mixture of the two components.

Which of the two components can be obtained pure from a binary mixture of substances A and B, forming an azeotrope, depends on the composition of the initial mixture. If this is between the azeotropic composition and 100% A, distillation can yield compound A and the azeotrope, but not the second component, in a pure state.

Azeotropes with a minimum boiling point (for examples, see Fig. 43, column 3/III) are far more numerous than those with a maximum boiling point (Fig. 43, column 5/III). According to the tables of Lecat [20], who lists 6287 azeotropes and 7003 non-azeotropes, the ratio is about 9 to 1.

The books of Horsley [51] present azeotropic data up to 1962, and the handbook on azeotropic mixtures published by Kogan et al. [21] contains 21,069 systems of which 19735 are binary, 1274 are ternary and 60 are multicomponent mixtures. The tables of the handbook are preceded by an introduction into the theoretical and experimental aspects of azeotropy written by Kogan, who edited the book. Further, he discusses the influence of temperature, the composition of azeotropic mixtures, the prediction of the azeotropic point and the study of the properties of azeotropic mixtures.

For the thermodynamic and kinetic theory of azeotropic mixtures the reader is referred to investigations by Stuke [22], Coulson and Herrington [23], Kuhn and Massini [24], Enüstün [25], Litvinov [26] and to the extensive publications of Swiętosławski [27] and Lecat [28], who also deal with ternary and quaternary azeotropes. The theory and applications of azeotropic distillation were thoroughly dealt with by Othmer [28a]. In the first volume of this fundamental book the last-named author discusses the theory of azeotropes, the problems of experimental technique and the classification of the various types of azeotropes, and considers the applications of azeotropy in industry. The second volume of the book is to deal with azeotropy from a thermodynamic point of view. An excellent introduction into the problems of azeotropic and extractive distillation in the laboratory from a theoretical as well as from a practical point of view was given by Röck [17]. In Schuberth's [29] books on the thermodynamics of mixtures the azeotropy of binary systems is discussed in Volume I.

A model concept for the description of the vapour-liquid equilibrium of azeotropic mixtures in the case of associations in the gas phase was elaborated by Serafimov et al. [29a]. Examples are the binary mixtures acetic acid-water, formic acid-water and acetic acid-formic acid and the ternary azeotrope acetic acid-formic acid-water (see Fig. 225). The real behaviour of the liquid phase is in all cases described by Wilson's equation. Svoboda et al. [19b] measured the evaporation enthalpies of 8 binary azeotropic mixtures in the temperature range from 30 to 80 °C. On simplifying assumptions the additional enthalpies of the azeotropic mixtures can be calculated from the measuring data. With this method the temperature dependence of the additional enthalpy up to the boiling point can be determined in a simple manner.

A mathematical description of phase equilibria in polyazeotropic mixtures has been given by Serafimov et al. [31a]. Tamir and Wisniak [31b] have reported the correlation and precalculation of boiling temperatures and azeotropes for multicomponent systems.

Narrow-boiling mixtures can generally be expected to be azeotropic. Azeotropy does not only occur in cases where rather specific interactions are present but also in mixtures of non-polar substances, such as benzene-cyclohexane or benzene-carbon tetrachloride. According to W. Kuhn and H.-J. Kuhn [24] the frequent occurrence of azeotropy in narrow-boiling mixtures is due to the compensation of contributions to the vapour pressure difference and the summation of contributions to the energy required for mixing. Zieborak [30] showed that the addition of hydrocarbons for the distillative dehydration of ethanol-water mixtures results in a number of quaternary heteroazeotropes and ternary homoazeotropes. (A heteroazeotrope is an azeotropic mixture which separates into two liquid phases on condensation (example: benzene-water).) The various types of polyazeotropic mixtures of liquids and the influence of these azeotropes on the course of the distillation have been investigated by Orszagh [31]. Malesinski [32] and Stecki [33] have contributed a classification of homo- and heteroazeotropic ternary systems. In a survey of possible additives for azeotropic and extractive distillation Berg [34] has dealt with the classification of liquids with regard to hydrogen bonds.

Columns having about 100 theoretical stages, suitable for dealing with numerous narrow-boiling mixtures and non-ideal mixtures without a special point, can now be constructed, since an HETP of 1 to 2 cm is attainable with modern forms of packing. If, however, 200 or 300 stages are required (for values of α equal to 1.03—1.02), it is preferable to attempt to increase the value of α. As an example we may mention the extractive distillation of the narrow-boiling mixture n-heptane-methylcyclohexane, where the difference in boiling point is only 2.7 deg. C ($\alpha = 1.075$). Normal countercurrent distillation requires 48 stages with $v = \infty$ for enriching a mixture from 15.3 mol% to 95.4 mol%. If 70% wt. of aniline is added, the same enrichment is obtained with 12.4 stages and a reflux ratio of 35. The separating factor α increases from 1.075 to 1.30 [35]. With mixtures forming an azeotrope, a selective separating process is indispensable if both compounds are to be obtained in a pure state.

The phenomenon of azeotropy can on the one hand be very troublesome, as in the distillation of dilute alcohol and similar mixtures; on the other hand it offers a means of "breaking" existing azeotropes and of separating very narrow-boiling mixtures. By the addition of a foreign compound (known as an *entrainer*) the formation of a new azeotrope, between the entrainer and one of the components of the binary mixture, is purposely brought about; as a result of the larger difference in boiling point the latter azeotrope can then be separated from the other component. An essential requirement in this method is, however, that the new azeotrope shall be readily separable into its components. Methods by which this may be achieved are:

by cooling
by salting out
by chemical removal of the entrainer
by extraction
by a second azeotropic distillation.

In *extractive distillation* a solvent boiling about 50 to 100 °C higher than the mixture to be treated is introduced; its preferential affinity for one component changes the relative volatility [17]. The solvent chosen must not form an azeotrope with any of the components to be separated, must be readily removable from the mixture and must act so as to produce an increase in the relative volatility The compounds employed are the same as, or similar to, those utilized in liquid-liquid extraction.

Examples of the apparatus used for azeotropic and extractive distillation are shown in Figs. 223 and 224.

The selectivity of distillation with an entrainer does not in general depend only on the relative volatilities but also on the diffusion rates of the components present

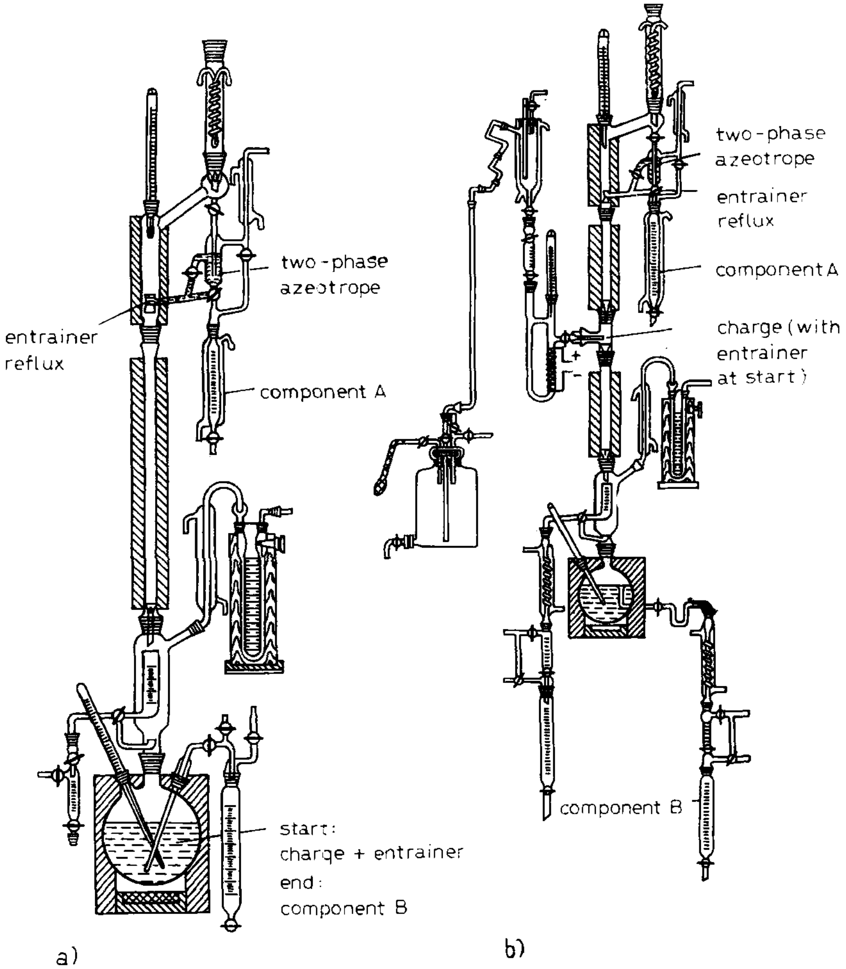


Fig. 223
Apparatus for azeotropic distillation

a) batch b) continuous

in the liquid and gaseous phases. Schlünder [35b] describes distillation with an entrainer with an excess of entrainer where an equilibrium cannot be established and selectivity is governed by diffusion. This kinetic effect could be used for the separation of azeotropic mixtures. Moreover, distillation with an additive allows the examination of the hydrodynamic and kinetic causes of incomplete equilibration.

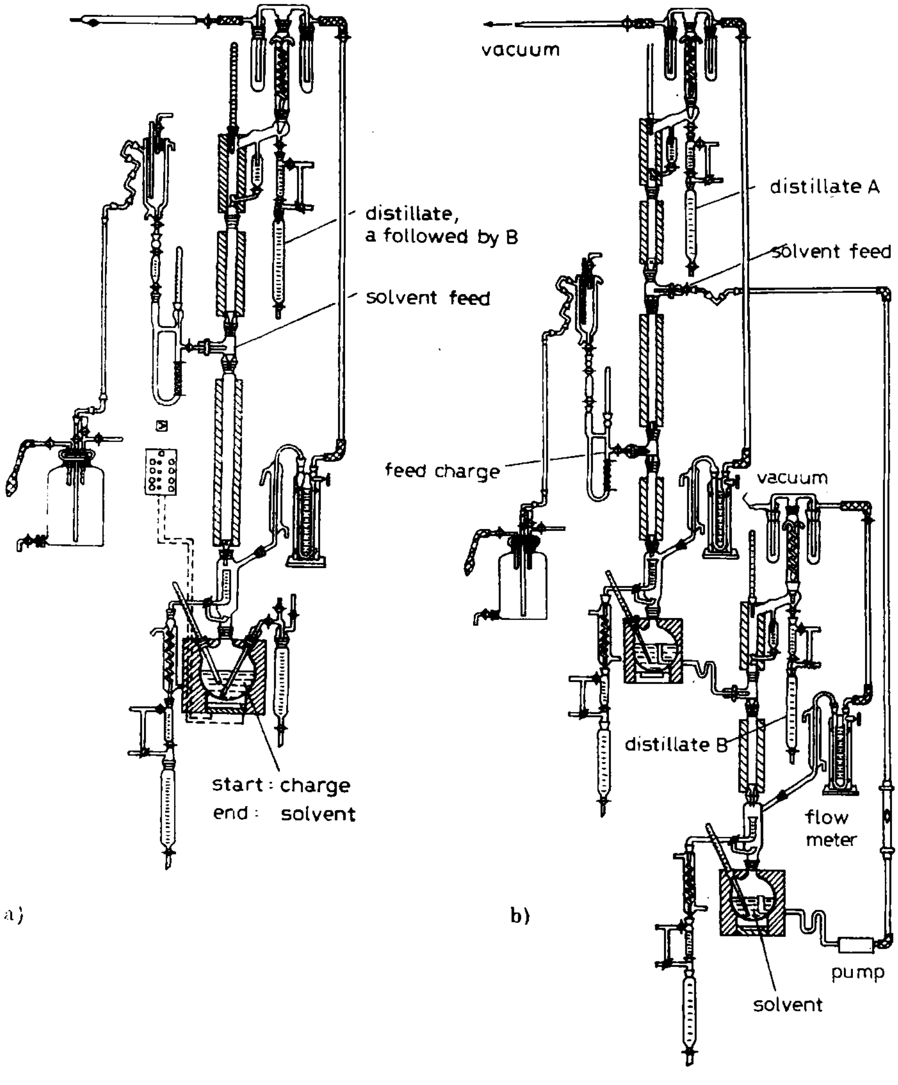


Fig. 224
Apparatus for extractive distillation

a) batch b) continuous

6.2.1 Azeotropic distillation

Azeotropic distillation is employed in the following cases:

1. For the separation of narrow-boiling mixtures, which have usually been prepared by a previous countercurrent distillation;
2. For the separation of mixtures forming an azeotrope, generally having a composition close to the azeotropic point.

As a rule the compound to be added is so chosen that it forms an azeotrope of minimum boiling point with *one* of the components. But it is also possible to select an entrainer forming a binary or ternary minimum azeotrope with both of the components to be separated; in the latter case it is necessary for the proportion of the components in the new azeotropes to be different from their initial proportions. Discussing extensive investigations of various types of phase diagrams and of the elaboration of column schemes Sharov and Serafimov [35a] have treated the problems specific to the countercurrent distillation of azeotropic multicomponent mixtures.

A particularly striking example of the treatment of narrow-boiling mixtures is the mixture indole-diphenyl, which can be separated with diethyleneglycol as entrainer. At atmospheric pressure indole and diphenyl differ by only 0.6 deg. C in boiling point; by the addition of diethyleneglycol this difference can be increased to 12.2 deg. C. The azeotropes produced: diphenyl-diethylene-glycol (boiling point 230.4 °C) and indole-diethylene-glycol (B.P. 242.6 °C), both of which contain just under 60% of diethylene-glycol, can be separated with relatively inefficient columns and low reflux ratios. As diphenyl, unlike indole, is scarcely soluble in liquid diethyleneglycol, the amount of the glycol needed is small; the azeotrope of diphenyl and diethyleneglycol, which passes over first, demixes in the receiver and the glycol can be recycled continuously to the distillation. From the azeotrope of indole and diethyleneglycol passing over at a higher temperature the indole may be precipitated with water [36].

Commercial β-picoline is a mixture of α-picoline, β-picoline and 2.6-lutidine. The difference between the boiling points of β-picoline and 2.6-lutidine is 0.15 deg. C at atmospheric pressure. By means of azeotropic distillation, using acetic or propionic acid as additive, one can separate the individual bases in a purity of 95–98% [37]. Further processes employed in industry were reported by Dummett [38].

Two processes which are of interest in industry may be mentioned here. If the ternary system water-formic acid-acetic acid is to be separated the following azeotropes are to be expected according to Hunsmann and Simmrock [39]:

B: 107.65 °C binary high-boiling azeotrope	56.7 mol% of formic acid 43.3 mol% of water
T: 107.1 °C ternary azeotrope	39.3 mol% of water 48.2 mol% of formic acid 12.5 mol% of acetic acid

Thus, the whole concentration region of the ternary system is divided into four separate distillation areas (Fig. 225). By means of azeotropic distillation with a higher ether the mixture can be dehydrated. The interdependences involved in the countercurrent distillation of ternary mixtures with special points were studied by Petlik and Avetyan [39a]. Corresponding to the azeotropic points of binary systems, ternary systems have limiting lines which cannot be exceeded in ordinary distillation. The systems acetone-chloroform-methanol and acetone-chloroform-isopropyl ethene were studied with a view to this phenomenon by Naka et al. [39b]. Kudryavtseva et al. [39d] discuss various methods of calculating multicomponent azeotropic mixtures and suggest a calculating procedure on the basis of constants obtained for binary mixtures which does not include a formulation for the concentration dependence of the activity coefficients. Results for ternary azeotropes are represented graphically' The calculation using data from binary mixtures can be carried out with a precision sufficient for practical purposes. Lino et al. [40] succeeded in reducing the proportion of water in acetone to below 1,400 ppm by azeotropic distillation using ethyl bromide as additive. Susarev and Toikka [39c] have reported a method of estimating the compositions of ternary azeotropic mixtures if the vapour pressures of these mixtures have been measured or the vapour pressure of one of the binary azeotropic mixtures is known.

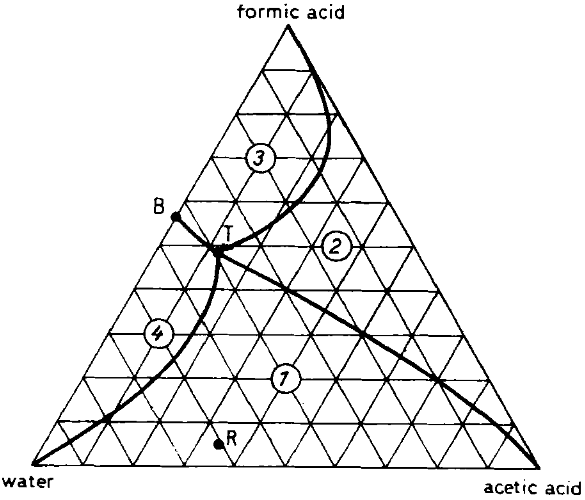


Fig. 225
Diagram of the four distillation areas of the ternary system water-formic acid-acetic acid, having a binary and a ternary azeotrope, and position of composition R [39]

It would lead us beyond the scope of this book to mention all the processes of azeotropic distillation known at the present time, since the publications and patents on this subject are numerous; the two examples selected show the wide possibilities that exist. Another field of azeotropic distillation is the dehydration of organic compounds, such as formic acid, acetic acid and pyridine. Further, mention may be made of the separation of hydrocarbons from alcohols, the purification of aromatic hydrocarbons and the separation of mono- from di-olefins. Mair, Glasgow and Rossini [41, 42] and Berg [34] have carried out a systematic investigation on the separation of hydrocarbons by azeotropic distillation. The separation of the isomers of methyl naphthalene in the presence of undecanol shows that the distillation pressure chosen is of importance also in azeotropic distillation. The optimum is 200 to 300 torr. Pure α-methyl naphthalene is obtained as residue while the distillate is a mixture with 80% of β-methyl naphthalene [43].

Since the position of an azeotropic point is not stable, besides the azeotropic and extractive distillations a change of the external thermal conditions (temperature or pressure) in the form of a vacuum or pressure distillation may be effected to make the special point disappear. Schuberth [44] has reported relations by means of which the amounts of pressure or temperature change or (in azeotropic or extractive distillation) the minimum concentration of the additive required to remove azeotropy can be approximated for homoazeotropic binary systems.

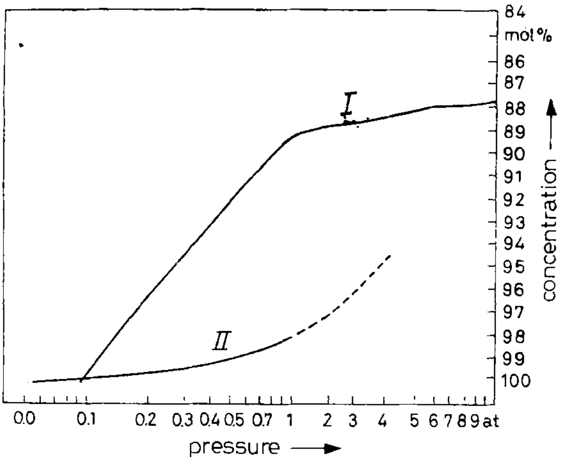


Fig. 226
Pressure dependence of the azeotropic points of the mixtures ethanol-water (I) and water-phenol (II)

The result of a diminution in pressure is frequently that the azeotropic composition becomes richer in the low-boiling constituent. A reduced pressure may thus be reached at which the special point vanishes. As examples, the mixtures ethanol-water and water-phenol may be taken (see Fig. 226). By distilling dilute alcohol at 70 mm, absolute alcohol may be prepared without the use of an entrainer. The azeotropic point water-phenol is eliminated at 32 mm. The shift in the azeotropic point has been determined by Sheinker and Peresleni [45] for two other systems:

Formic acid-water: at 50 mm Hg, 66% wt. of formic acid;
at 200 mm, 72% wt. of formic acid.

Butyl alcohol-butyl acetate: at 50 mm, 37 mol% of butyl alcohol;
at 760 mm, 79 mol% of butyl alcohol.

Ruether and Lu [46] elaborated numerical methods which were tested on the systems ethyl acetate-ethanol, ethanol-water and methanol-benzene. An azeotrope can in some cases also be made to disappear by increasing the pressure.

Nutting and Horsley [47] have indicated a simple procedure for determining the range of pressure in which an azeotrope exists. A Cox diagram, having scales for log p along the y axis and $1/(T + 230)$ along the x axis (T in °C), is plotted with the vapour pressure curves for the pure components and the azeotrope (Fig. 227). (Owing to the linearity of vapour pressure curves in a Cox diagram, only two values are needed for each line.) If the straight line for the azeotrope intersects the lines for the components, the special point cannot exist beyond the points of intersection P and P', *i.e.*

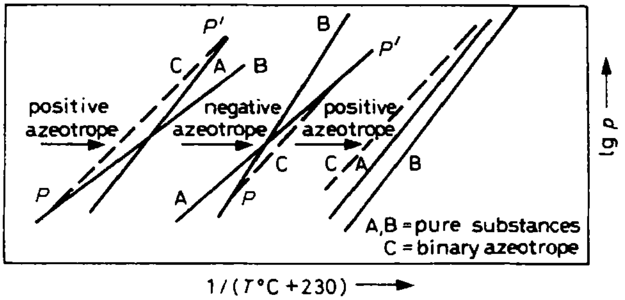


Fig. 227
Determination of the azeotropic pressure range by the method of Nutting and Horsley

when its temperature at a given pressure is between those of the components. If no intersections occur, and the azeotropic line is above or below those of both components, the azeotrope will remain present at all pressures. Joffe [48] has described a method in which it is necessary to know only the azeotropic composition at one temperature (pressure) for deriving the azeotropic compositions at other temperatures (pressures). Malesinski [49] has published formulae with which the boiling points of ternary azeotropic mixtures may be calculated.

Should it prove impossible to effect a satisfactory separation by changing the distillation pressure, the next step will be to find a suitable additive with which one of the constituents forms a heteroazeotrope, or a homoazeotrope that is easily split up [34]. An approximate method for separating heteroazeotropic mixtures based on the mathematical model for the liquid-liquid-vapour equilibrium of two multicomponent systems was elaborated by Bril et al. [49a].

To illustrate the procedure we can best take an example. The system water-pyridine gives rise to a minimum boiling azeotrope, boiling at 92 °C and containing 54% wt. of pyridine. The water is to be eliminated by the addition of an entrainer. The requirements that the latter should satisfy are the following [34, 50]:

1. It should form an azeotrope, boiling below 92 °C, with water;
2. it must not yield an azeotrope with pyridine;

3. no ternary azeotrope should be produced;
4. the proportion of water in the azeotrope should be as large as possible;
5. the mutual solubility of the entrainer and water should be low, so that separation takes place on cooling (*i.e.* they should form a heteroazeotrope).

Now minimum boiling azeotropes are formed when the forces of attraction between unlike molecules are smaller than those between identical molecules; in the converse case maximum boiling azeotropes occur. On the basis of data compiled by Lecat [20] and Horsley [51], Ewell, Harrison and Berg [52] have concluded that the forces of interaction concerned are mainly those due to hydrogen bonds, compared to which other forces such as dipolar forces and those due to induction are relatively

Table 48

Classification of liquids according to hydrogen-bonding tendency

a) The five classes according to Berg [34, 52]

Class	Kind of molecule	Examples
I.	Liquids capable of forming three-dimensional networks of strong hydrogen bonds	Water, glycol, amino alcohols, hydroxylamine, hydroxy acids, polyphenols, amides etc. Compounds such as nitromethane and acetonitrile also form three-dimensional networks of hydrogen bonds, but the bonds are much weaker than those involving OH and NH groups. Therefore, these types of compounds are placed in class II
II.	Other liquids composed of molecules containing both active hydrogen atoms and donor atoms (oxygen, nitrogen and fluorine)	Alcohols, acids, phenols, primary and secondary amines, oximes, nitro compounds with α-hydrogen atoms, nitriles with α-hydrogen atoms, ammonia, hydrazine, hydrogen fluoride, hydrogen cyanide, etc.
III.	Liquids composed of molecules containing donor atoms but no active hydrogen atoms	Ethers, ketones, aldehydes, esters, tertiary amines (including pyridine type), nitro compounds and nitriles without α-hydrogen atoms, etc.
IV.	Liquids composed of molecules containing active hydrogen atoms but no donor atoms. These are molecules having two or three chlorine atoms on the same carbon as a hydrogen atom, or one chlorine on the same carbon atom and one or more chlorine atoms on adjacent carbon atoms	$CHCl_3$, CH_2Cl_2, CH_3CHCl_2, CH_2Cl-CH_2Cl, $CH_2Cl-CHCl-CH_2Cl$, $CH_2Cl-CHCl_2$, etc.
V.	All other liquids — *i.e.* liquids having no hydrogen-bond-forming capabilities	Hydrocarbons, carbon disulphide, sulphides, mercaptans, halohydrocarbons not in class IV, non-metallic elements such as iodine, phosphorus, sulphur, etc.

Table 48 (Continued)

b) Summary of deviations from Raoult's law

Classes	Deviations	Hydrogen bonding
I + V II + V	Always + deviations; I + V, frequently limited solubility	H bonds broken only
III + IV	Always — deviations	H bonds formed only
I + IV II + IV	Always + deviations; I + IV, frequently limited solubility	H bonds both broken and formed, but dissociation of class I or II liquid is more important effect
I + I I + II I + III II + II II + III	Usually + deviations, very complicated groups, some — deviations give some maximum azeotropes	H bonds both broken and formed
III + III III + V IV + IV IV + V V + V	Quasi-ideal systems; always + deviations or ideal; azeotropes, if any, will be minima	No H bonds involved

c) Solutions giving maximum boiling azeotropes

Components	Examples
Water + strong acids	Water + HCl, HBr, HI, HNO_3
Water + certain associated liquids	Water + formic acid, hydrazine, ethylenediamine
Donor liquids (class III) + non-associated liquids containing active hydrogens (class IV)	Acetone + chloroform, cyclohexanone + bromoform, butyl acetate + 1.2.2-trichloropropane
Organic acids + amines	Acetic acid + triethylamine, propionic acid + pyridine
Phenols + amines	Phenol + aniline, o-cresol + dimethylaniline
Organic acids + donor liquids containing oxygen	Formic acid + diethylketone, butyric acid + cyclohexanone
Phenols + donor liquids containing oxygen	Phenol + methylhexylketone, o-cresol + ethyl-oxalate
Phenols + alcohols	Phenol + n-octanol, o-cresol + glycol

unimportant. On this basis liquids may be divided into five classes according to the number and strength of the hydrogen bonds between the molecules. These five classes have been collected in Table 48, part (a). By looking up the hydrogen-bond classes to which the two components belong it is possible, on referring to part (b) of the table, to estimate the departure from ideal behaviour of a mixture of other classes, and so to select a suitable entrainer [52]. In part (c) of the table the components giving maximum boiling azeotropes have been listed (see p. 156 of [29]).

Following Ewell's classification of mixtures, Eduljee and Tiwari [52a] extended the relations found by Yoshimoto. They studied various properties of the interactions of the components in the mixture and determined the temperature range within which no azeotrope was formed. The mean standard deviations in predicting the azeotropic composition and the boiling point (from the boiling points of the pure components) were found to be 0.17 and 0.03, respectively, for 14 combinations.

Table 49

Suitable additives for removing water from pyridine by azeotropic distillation [50]

Class	Additive	$Kp._{760}$ (°C)	Azeotrope with H_2O (°C)	Parts of additive reqd. for removing 1 part of H_2O	Solubility in 100 parts of H_2O
III	Isobutyl formate	98.2	80.4	11.8	1.0
	Ethyl propionate	99.0	81.2	9.0	2.4
	Methyl butyrate	102.0	82.7	7.7	1.5
	Ethyl isobutyrate	111.7	85.2	5.6	trace
	Di-isobutylether	122.2	88.6	3.4	trace
	Amyl formate	132.0	91.6	2.5	trace
IV	Ethylene chloride	83.0	72.0	11.0	0.9
	1,2-dichloropropane	96.8	78.0	7.4	0.3
V	Benzene	80.2	69.3	10.2	0.1
	Toluene	110.7	84.1	6.4	trace

In the system water-pyridine, the compounds mentioned in Table 49 can be considered as possible entrainers. Water (class I) presents large departures from Raoult's law when mixed with liquids of classes III, IV and V, whilst pyridine (class III) gives small departures, if any.

It will be seen that the boiling point of the azeotrope of water and the entrainer is lower, the lower the boiling point of the entrainer. The ideal choice will be an entrainer combining a sufficiently low azeotropic boiling point, an economically low proportion in the azeotrope and a small solubility in water.

Berg and collaborators [34, 52] investigated a number of narrow-boiling hydrocarbon mixtures. For azeotropic distillation they found the optimum additives listed in Table 50. It is obvious that the normal separation factor α can be drastically changed into α_{az} by optimum additives.

Whether or not a compound forms an azeotrope with a given component is also important in extractive distillation, where the occurrence of azeotropes is generally undesirable. Some further empirical methods, applicable both to azeotropic and extractive distillation, will therefore be mentioned.

A simple graphical procedure for predicting azeotrope formation has been de-

Table 50

Optimum additives for the azeotropic distillation of hydrocarbons

Mixture to be separated	Normal separation factor α	Optimum additive	Azeotropic separation factor α_{az}
neohexane-cyclopentane	1.006	n-propylamine	0.987
cyclohexane-2.4-dimethylmethane	1.006	acetone	1.025
methylcyclohexane-iso-octane	1.046	ethanol or 1.4-dioxane	1.084
3-methylpentane-hexene-1	1.009	methylenechloride	1.159
3-methylpentane-2-ethyl-1-butene	1.037	ethylformiate	1.156
2.2.4-trimethylpentane-2.2.4-trimethylpentene-1	1.040	isopropylacetate	1.129
n-heptane-2.2.4-trimethyl-pentene-1	1.045	isopropylacetate	1.129
ethylbenzene-p-xylene	1.035	2-methylbutanol	1.079
p-xylene-m-xylene	1.020	2-methylbutanol	1.029
m-xylene-o-xylene	1.105	methylisobutylcarbinol	1.150

scribed by Mair, Glasgow and Rossini [41]. Fig. 228 shows the boiling points of azeotropes formed between benzene and various hydrocarbons as a function of their compositions [53]. If the boiling point of the pure hydrocarbon, plotted along the y axis, is connected to the boiling point of the azeotrope on the curve, straight lines with various slopes are obtained. From the diagram it may then be predicted that hydrocarbons boiling below 68° and above 100 °C will not give azeotropes with benzene. Further, one can determine the boiling point and composition of the azeotrope formed by any hydrocarbon and benzene by drawing a line parallel to an adjacent line already on the figure, starting from the boiling point of the pure substance on

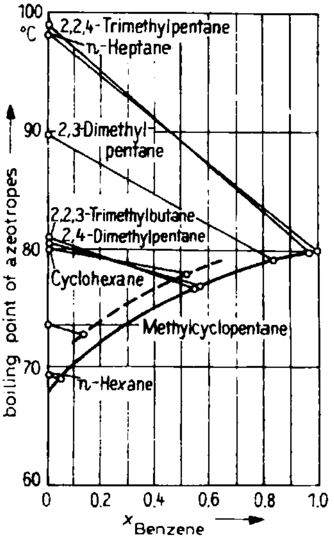


Fig. 228
Determination of azeotropic data (Mair, Glasgow and Rossini)

the y axis. (The gradients of these lines depend on the boiling points of the pure hydrocarbons in question and their degree of branching). If, for instance, we draw the line as described for the hydrocarbon 3-ethylpentane (B.P. 93.5 °C), we find on the curve that the azeotrope with benzene boils at about 80 °C and contains 96 mol% of benzene; these values agree closely with observed data. Methods reported by Horsley [54] and Meissner and Greenfeld [55] yield similar diagrams.

A graphical method proposed by Novikova and Natradze [56] is based on a three-dimensional co-ordinate system, in which the variation of the parameters is represented by a straight line. The abscissa corresponds to the azeotropic composition in mol%, the ordinate to the reciprocal of the boiling point and the applicate (third axis) to the logarithm of the pressure. If the azeotropic data are known at two pressures it is possible to determine with accuracy for binary mixtures:

1. the azeotropic data at another pressure,
2. the range of pressures over which an azeotrope exists, and
3. the concentration range of azeotropic mixtures.

Litvinov [26] evolved a graphical method for determining the probability that azeotropy occurs in ternary systems. He shows that ternary azeotropes may occur even when the system in question has no binary azeotropes. The existence of a quaternary azeotrope, however, is associated with the occurrence of binary and ternary azeotropes. Marinichev and Susarev [56a] elaborated an extensive system of equations in order to infer physical properties of quaternary azeotropes.

According to Skolnik [57] a purely arithmetical prediction is also possible. For the members of a homologous series (e.g., hydrocarbons) and a second component (e.g., benzene), these linear relations hold:

$$\log x_{\mathrm{az}} = A(273.1 + \vartheta_{\mathrm{az}}) + B, \tag{193}$$

with x_{az} = concentration of the second component in the mixture in mol%; ϑ_{az} = boiling point of the azeotrope, °C; A, B = constants; and

$$\log (D - \vartheta_{\mathrm{az}}) = E - F(273.1 + \vartheta), \tag{194}$$

where D, E and F are constants and ϑ is the boiling point of the member of the homologous series. The curves shown in Fig. 229 are derived from expressions (193) and (194). Curves I and II correspond to (193) and (194), respectively. The azeotropic data of hydrocarbons of the same homologous series can be read immediately from the curves. Thus, e.g., the boiling point of 2.2-dimethyl pentane is at 79.2 °C. Curve II gives an azeotrope composition of 50 mol% and curve I, a boiling point of the azeotrope with benzene at 75.8 °C. Curve II also serves to determine the boiling range over which an azeotrope with benzene can exist. This is the range from 65 to 98 °C, which is in good agreement with the values obtained by the graphical method of Mair, Glasgow and Rossini. The boiling range of the paraffins which form homogeneous azeotropes with benzene is called the "azeotropic effect" of benzene [57]. A diagram constructed by Nakanisi et al. [58] on the basis of infrared-spectroscopic data predicts azeotrope formation for a number of components in the temperature range from 30 to 150 °C in binary mixtures with methanol.

The use of limiting activity coefficients for the prediction of azeotropic compositions at constant temperatures and of the partial miscibilities in binary liquid mixtures has been reported by Brandani [58a].

According to Martin [58b], binary systems form azeotropes if these conditions are satisfied:

1. An azeotrope with minimum boiling point is formed if the activity coefficient of the high-boiling component is greater than the vapour pressure ratio of the pure components.
2. A heteroazeotrope exists if the limiting activity coefficient of the low-boiling component is greater than 7.4.

The validity of these relations was tested on the system water-n-propanol.

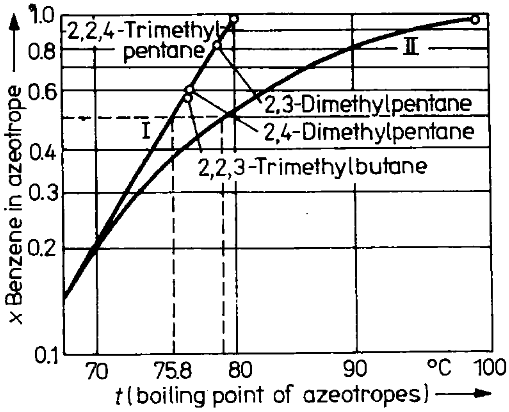


Fig. 229
Determination of azeotropic data (Skolnik)

The calculation of the conditions required for separation by distillation, such as the number of stages and the reflux ratio, is performed as described in chapter 4. For regular systems, having an azeotropic point but only a small heat of mixing, Kuhn [59] gives the following formula as a means of calculating the number of theoretical stages, corresponding to formula (114) of Fenske for batch distillation with $v = \infty$:

$$n_{\min} = \frac{1}{\delta_0} \frac{2x_{\mathrm{az}} - 1}{2(1 - x_{\mathrm{az}})} \left[\frac{1}{x_{\mathrm{az}}} \left\{ \frac{x_E}{x_E - x_{\mathrm{az}}} - \ln \frac{x_B}{x_{\mathrm{az}} - x_B} \right\} - \left\{ \ln \frac{x_E}{1 - x_E} - \ln \frac{x_B}{1 - x_B} \right\} \right] \tag{195}$$

$\delta_0 = x - 1$;

x_{az} = the concentration at the azeotropic point.

In this equation it is assumed that $x_E < x_{\mathrm{az}}$, that is to say that the desired enrichment lies below the azeotropic composition. When $x_E = x_{\mathrm{az}}$ the number of stages required, $n_{\min} = \infty$.

Szapiro [60] has derived formulae for the separation of binary mixtures containing low proportions of the heavy component and of mixtures approximating to the azeotropic composition. Calculations for the mixtures water-ethyl acetate (1.75%), benzene-toluene (4%) and ethanol-water (11%) are given as examples. Hunsmann [61a] demonstrates the procedure of calculating an azeotropic column, taking as an example the separation of 1.3-butadiene and 1-butene by azeotropic distillation with methyl amine. First, binary and ternary equilibria are measured in the technically important pressure region. The results are expressed as a set of equations, which are used to calculate plate after plate, progressing from the bottom upward. The calculations show the influence of temperature and an excess of amine. The method was checked using a small column. Agreement was quite satisfactory.

The mode of operation and the dimensioning of a heteroazeotropic distillation as exemplified by the separation of the system water-acetic acid has been described by Wolf et al. [61b]. Morozova and Platonov [61c] analyzed the structure of phase diagrams of multicomponent mixtures using a digital computer. They studied the requirements for the separation of azeotropic mixtures. In order to achieve optimum column combinations Serafimov et al. [58c] studied the ternary mixture isopropanol/benzene/water on the basis of a mathematical treatment of the separation of heteroazeotropic mixtures. In another paper [58d] a procedure was presented for the separation into its components of the water-containing mixture with acetone, ethanol, benzene and butyl acetate by means of the thermodynamic and topological analysis of the phase diagram structure.

To conclude this section an example will be given of an azeotropic distillation in which a ternary azeotrope is formed — the preparation of absolute alcohol by distillation with benzene as auxiliary substance. If 95% wt. alcohol is distilled in batch with the calculated quantity of benzene, there first passes over at 64.9 °C a ternary azeotrope, separating at 28 °C into two layers; the compositions of the azeotrope and these layers are as follows:

	azeotrope (at 28 °C)	upper layer (84.7%)	lower layer (15.3%)
benzene, % wt.	74.1	85.6	8.1
ethanol, % wt.	18.5	11.6	53.1
water, % wt.	7.4	2.8	40.6

When the water has been eliminated, there follows at 68.3 °C a binary azeotrope containing 32.4% of ethanol and 67.6% of benzene, and finally at 78.4 °C alcohol of about 99.8% purity distils over. On an industrial scale the preparation takes place continuously, but in the laboratory it is often more convenient to operate in batch and work up the two layers of the ternary azeotrope and the binary azeotrope in portions.

6.2.2 Extractive distillation

Extractive distillation, like azeotropic distillation, is employed for concentrating mixtures beyond an azeotropic point and for separating narrow-boiling or non-ideal mixtures having separation factors close to unity. The scope of extractive distillation, however, is more extensive than that of azeotropic distillation, on account of the almost unlimited number of additives that are available for use. The separating efficiency is strongly dependent on the amount of solvent added and hence the latter should be determined as exactly as possible.

The separation of n-heptane-methylcyclohexane, with aniline as auxiliary solvent, has already been cited as an example of the treatment of a *narrow-boiling mixture*. The system methylcyclohexane-toluene has an equilibrium curve which approaches the diagonal very closely, so that the relative volatility becomes very nearly equal to unity at high concentrations of methylcyclohexane. An excessively large number of stages would be needed to obtain methylcyclohexane in a pure state, but by the addition of 55 mol% of the polar solvent aniline the relative volatility is increased and the separation is consequently very greatly facilitated. Extractive distillation is also useful for separating *azeotropic mixtures*. For example, the azeotrope of cyclohexane and benzene can be dealt with, again, by the addition of aniline, to yield pure cyclohexane as overhead product. Kortüm and Bittel [61] have reported the separation of primary, secondary and tertiary aromatic amines with glycerine and paraffin oil. It is notable that they used a largely automated apparatus for both batch and continuous extractive processes. Extractive distillation has proved quite useful even for the separation of multicomponent mixtures containing components from various classes of substances. Thus, *e.g.*, aromatic hydrocarbons can be separated from mixtures with non-aromatic hydrocarbons by extractive distillation using a butane diol such as butane diol-2.3 and adding octyl alcohol as solvent [62]. A detailed report of the recovery of pure benzene by extractive distillation with dimethyl formamide from the point of view of process engineering is given by Lehmann et al. [62a].

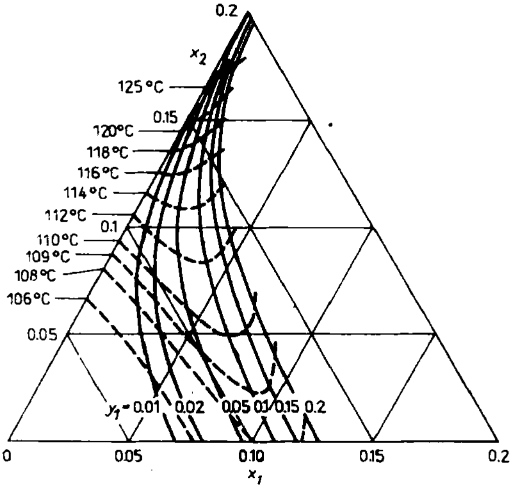


Fig. 230
Isobaric equilibrium $HCl-H_2SO_4-H_2O$ at 750 torr: x_2 molar fraction of H_2SO_4 in liquid phase
——— lines of constant vapour composition
– – – isotherms

Another interesting example of extractive distillation is the separation of HCl from azeotropic hydrochloric acid with H_2SO_4 as described by Grewer [63]. He used a graphite column. Fig. 230 shows the isobaric boiling equilibrium for his system.

Solids may also be used as additives. For the removal of small amounts of methylene chloride from acetone, Ino et al. [94] found $ZnBr_2$ to be the most suitable salt, more than 50 wt. % being soluble in acetone. The salt was removed from the reflux in a stirring kettle. A procedure for separating and purifying isoprene by extractive distillation and subsequent countercurrent distillation has been described in detail by Saraev et al. [94a].

The principle of extractive distillation consists in enhancing the individual effect Δx of the boiling equilibrium by introducing an additive. It is even conceivable to change an azeotrope with minimum boiling point into one with maximum boiling point, *i.e.*, to make a positive activity coefficient become negative [63]. The solvent to be added, which is normally a high-boiling substance, has to be chosen such that the relative volatility of the components is strongly increased. It is introduced continuously near the top of the column so that a higher concentration in the liquid phase is maintained in the whole column (see chap. 6.3).

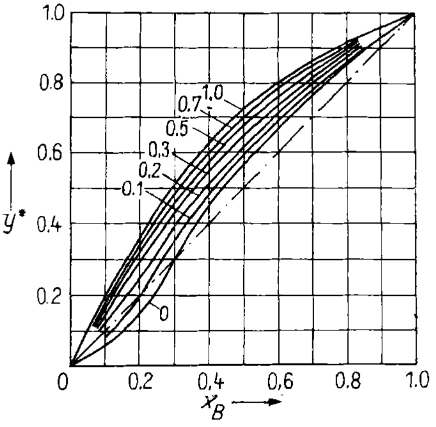


Fig. 231
Equilibrium curves of the mixture acetone-chloroform to which various quantities of methyl isobutyl ketone have been added

Fig. 231 shows the equilibrium curves of the azeotropic mixture acetone-chloroform to which have been added various amounts of the extracting agent, methylisobutylketone. (The quantities are mole fractions.) The binary system gives an azeotrope with maximum boiling point at 34.5 mol%. This disappears when 30 mol% of the additive is present; further additions cause a still larger increase in the relative volatility [50].

Pavlov et al. [63a] studied extractive distillation on the basis of C_4 and C_5 hydrocarbon cuts, using 19 auxiliary liquids. They plotted the separation factors obtained in diagrams thus showing the influence of high-boiling hydrocarbons.

An auxiliary liquid for extractive distillation should comply with the following requirements:

1. the substance should not form an azeotrope with the components of the mixture in question;
2. the additive should be easily separated from the components;

3. there should be as large a difference as possible between the degrees of departure from Raoult's law given by the additive with each of the two components so that the relative volatility of the two initial components should be increased as much as possible [64].

The conditions for azeotrope formation and their avoidance have been described above (see chap. 6.2.1). In addition, according to Scheibel [65], the separation coefficients of the mixtures to be separated are indicative in this respect. Ease of separation of the additive from the components is generally ensured because the additive is relatively high-boiling. According to Berg [34, 52], those liquids (of Table 48) are suitable additives which belong to classes I and II. These are chiefly substances capable of strong hydrogen bonding and of acting as both proton and electron donors. They include phenols, aromatic amines (aniline and derivatives), higher alcohols, glycol, etc.

Starting from the extractive distillation of allyl chloride-propyl chloride and n-butane-trans-butene-2 mixtures, Garber and Mironenko [65a] derived a universal method for selecting suitable auxiliary liquids. For the characterization of additives in extractive distillation the gas-chromatographic vapour space method was suggested by Hachenberg and Schmidt. Data are obtained in the form of peak area ratios of components 1 and 2 in the vapour spaces over the non-boiling mixtures with and without additive.

The choice of an extracting agent having the required selective action will involve a fair amount of preliminary experimental work. The most reliable method is to determine the equilibrium curve of the mixture to be separated in the presence of several quantities of the additive. Rose [35] has reported the results of such measurements on the mixture n-heptane-methyl cyclohexane upon addition of different liquids. He denoted the relative volatility with additive present by α_e. For the purpose of comparing the effect of the various additives he set the relative volatility of the components alone equal to unity and then determined the efficiency $N = \frac{\alpha_e}{\alpha}$. It is seen that the addition of aniline (92%) gave the greatest effect on the phase equilibrium. The effect of the additive on the relative volatility of the components may also be estimated from the integral heats of mixing [50].

Kogan [66] has shown that upon addition of a third component to a binary mixture that component increases in relative volatility in which the third component is less soluble. Further principles applicable to the selection of additives have been discussed by Kafarov and Gordijewski [67] and Kogan [68]. The connections between gas-liquid chromatography and extractive distillation have been elucidated by Röck [69] and Porter and Johnson [70]. They have pointed out that the latter method provides a simple means of finding suitable additives for extractive distillation.

A rapid estimate of the effect of additives can be obtained by determining differences in boiling point. To the mixture of the components is added, as a first step, an equal volume of the auxiliary liquid in question and the boiling point is observed. The boiling point of the mixture is then calculated, assuming additivity on a molar basis. If the difference between the calculated and the observed boiling points is considerable, the additive will generally prove satisfactory [35].

Additives which are required to have a selective effect on the low-boiling component may be chosen under the aspect of relative polarity. While liquids with the same polarity give an ideal solution, mixtures of components with different polarity deviate from ideal behaviour depending on the extent of this difference. Thus, *e.g.*, the highly polar mixture acetic acid-water can be influenced by the addition of a non-polar high-boiling oil in such a way that the relative volatility of the water is increased. In the case of a non-polar mixture, such as cyclohexane-benzene, a polar extracting agent, such as aniline, causes an increased volatility of the cyclohexane. Berg et al. [52] and Hildebrand [71] have developed this method further.

Extractive distillation is not limited to the separation of binary mixtures, but is also capable of removing particular classes of substances from multicomponent mixtures, as for instance benzene from mineral oil fractions. Mixtures of saturated and unsaturated hydrocarbons having closely similar boiling points can be separated by extractive distillation with ketoesters [73]. Recently, the separation of lower hydrocarbons $C_1 \cdots C_2$ has been gaining ground [74]. Garner et al. [75] studied the efficiency of packed columns in the extractive distillation of the system methyl cyclohexane-toluene with the addition of furfurol and derived equations for this process.

After the optimum additive has been chosen the liquid-vapour equilibria of the ternary or multicomponent systems have to be determined as exactly as possible in extractive as well as in azeotropic distillation. For this reason Null and Palmer [76] looked for methods allowing equilibrium values to be obtained from as few experimental data as possible.

The number of stages needed for an extractive distillation can be calculated with the Fenske formula (section 4.7.5.3) if the value of α_e in the presence of the additive is taken. One can also apply the graphical construction of McCabe-Thiele, using the equilibrium curve corresponding to α_e, but employing the proportions in the solvent-free mixture for the calculation (see chap. 4.7). Another simple way of determining the number of stages necessary for an extractive distillation has been reported by Gelbin [77] who used the pole height method after Bosnjaković.

A modified McCabe-Thiele method employed in extractive distillation has been described by Nagel and Sinn [78]. Kortüm and Faltusz [79] have dealt with a variety of problems involved in selective separating processes ranging from the design of an automatic apparatus of special steel for continuous operation to the calculation of the minimum reflux ratio and the required amount of additive.

The quantity of auxiliary liquid to be employed is dictated by the liquid reflux. If, for instance, in our example of aniline-n-heptane we assume that the selected molar proportion of aniline to n-heptane is to be 83 mol%, we find from the molecular weights and densities that the ratio by volume is 3 : 1. Now if the calculation has shown that for a load of 1100 ml/h of n-heptane a reflux ratio of 10 : 1 is required, it follows that $3 \times 1100 \times 10/(10 + 1) = 3000$ ml/h of aniline must be supplied at the column head. We then obtain 100 ml/h of pure n-heptane as distillate, while 1000 ml/h of n-heptane, together with the 3000 ml/h of aniline, return to the column as reflux. The extract may be allowed to accumulate in the still pot until the low-boiling component has been collected completely as distillate, after which the high-boiling component is removed by batch distillation so as to leave the additive as residue. Alternatively, the second component can be distilled off continuously in another column as overhead product, and the residue (the additive) drawn off at the base and returned to the first column (Fig. 224).

To conclude the more theoretical considerations, some examples of extractive distillation [64] are given in Table 51.

Table 51

Examples of the separation of ideal, non-ideal and azeotropic mixtures by extractive distillation

Additive	Mixture to be separated	$\Delta Kp._{760}$ (°C)	Remarks
Aniline	n-heptane-methylcyclohexane	2.7	Ideal mixture ($\alpha = 1.07$)
	benzene-cyclohexane	0.7	Azeotrope
	n-heptane-toluene	12.8	Non-ideal mixtures; asymptotic approach of equilibrium curve to diagonal
Phenol	n-heptane-toluene	12.8	
	iso-octane-toluene	11.4	
	methylcyclohexane-toluene	9.5	
Ethyleneglycol monobutylether	Methylethylketone-water	20.4	Azeotrope
Diethylether	Ethanol-water	21.6	Azeotrope
Higher ketones and alcohols	Acetone-methanol	8.5	Azeotrope
Higher esters and alcohols	Ethylacetate-ethanol	1.3	Azeotrope
Higher ketones and chloro compounds	Acetone-chloroform	5.0	Azeotrope

Normal laboratory apparatus may be used for azeotropic and extractive distillation, whether performed batchwise or continuously. Packed columns and plate columns are equally suitable. Only rarely are additional components necessary (see Figs. 223 and 224).

Let us consider azeotropic distillation first. If a homogeneous azeotrope is produced, no changes in the normal apparatus for countercurrent distillation are required. When a heterogeneous azeotrope results the whole azeotrope is not returned to the column as reflux, but only the phase rich in additive. For this purpose an "azeotropic column head" is employed, as shown in Fig. 232, which allows either the heavy or the light phase to be used as reflux. The reflux is preferably returned to the column at some distance below the head. In continuous operation, if a homogeneous azeotrope is formed, the additive is mixed with the feed; if the azeotrope is heterogeneous it is sufficient to supply the necessary quantity of auxiliary liquid through the "azeotropic column head" (Figs. 223 and 232). More azeotropic column heads will be described in chap. 7.5.3.

Extractive distillation needs a section of column to which the additive is continuously supplied. The additive should be admitted somewhat below the top of the column so that a few plates are available to separate distillate and additive. In continuous operation the feed is introduced at about one third of the column height from its base (Fig. 224). As we have said previously, the procedure may be made fully continuous by drawing off the bottom product and passing it into a second column; there it is separated into the high-boiling component and the auxiliary liquid, the latter being recycled to the first column.

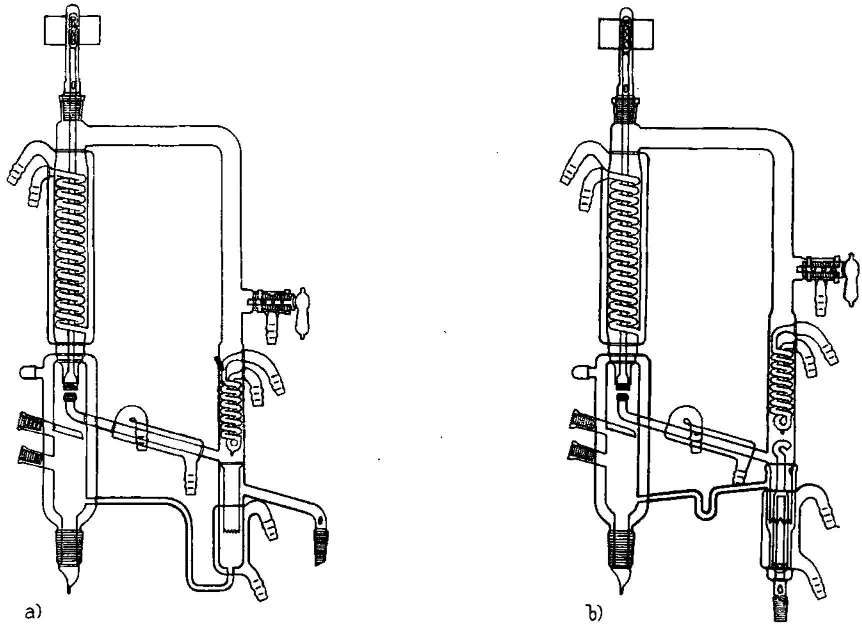


Fig. 232
Azeotropic column head with magnetic reflux division and phase separation

a) Take-off of the lighter phase
b) Take-off of the heavier phase

It should be noted that extracting agents may be employed which boil at lower temperatures than the initial mixture. In such cases the auxiliary liquid is admitted just above the still pot. This arrangement is necessary, for example, in the extractive distillation of ethanol-water with diethyl ether.

6.3 Solution distillation and special methods

In the selective processes so far described an alteration in the phase equilibrium is attained either by the use of a carrier vapour or by the addition of other liquids (azeotropic and extractive distillation).

Another possibility is to dissolve salts in the mixture to be separated, so as to bring about a change in the ratio of partial pressures of the components. This method of *solution distillation* has been employed mainly for mixtures of which one component is water. The mixture water-acetic acid, for example, at atmospheric pressure has an equilibrium curve approaching the diagonal very closely above 96% wt. acid, and it is consequently very difficult to eliminate the water entirely. From an industrial point of view this distillation also possesses the economic drawback that water (the distillate) has nearly five times the heat of evaporation of acetic acid; this becomes important in the concentration of dilute acid. It would therefore be preferable if the acetic acid could be obtained as overhead product and the water as residue. This can be realised by the addition of 8% wt. or more of calcium chloride to the mixture [80]. With a 30% wt. water-acetic acid mixture, for instance, the relative volatility α drops from a value of 1.36 at 760 mm to 0.525 in the presence of 20% wt. of $CaCl_2$; in other words the volatilities have been reversed and the acetic acid becomes the more volatile component. It is essential, however, for the salt to be evenly distributed over the whole length of the column. Daubach [81] has shown that the addition of 10 g of $CaCl_2$ to 100 ml of the azeotrope of ethanol and water causes a disappearance of the azeotropic point (Fig. 233); a distillate of high purity can thus be prepared by introducing a solution of this salt at the top of a continuous column [82]. Similar experiments were carried out by Tursi and Thompson [83] with $NaNO_3$ and K_2SO_4. Novella and Tarasso [84] used salts which are soluble in both components, such as $CuCl_2$ and $KCl_2H_3O_2$. They found that they thus prevented azeotrope formation. Schier [85] has discussed the influence of metal salts on the liquid-vapour equilibrium of aqueous nitric acid. Using the apparatus of Othmer, Olefir et al. [85a] examined the position of the azeotropic point in the system HNO_3/H_2O on adding different amounts of KNO_3. The azeotropic point was shifted from 68.2% HNO_3 (in the system HNO_3/H_2O) to 81% HNO_3 (in the system $HNO_3/KNO_3/H_2O$).

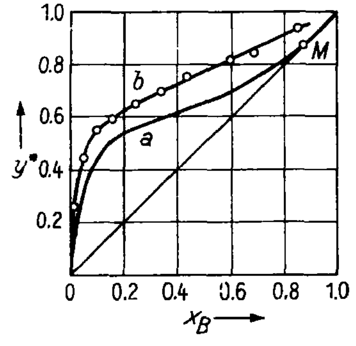
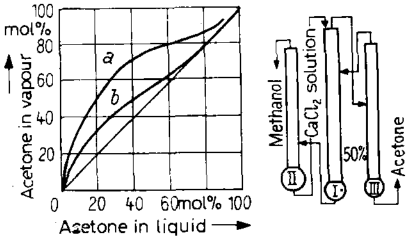


Fig. 233
Equilibrium curve of the system ethanol-water.
a = as such; b = with 10 g $CaCl_2$ in 100 ml of mixture

Similarly, the azeotropic mixture methanol-acetone can be enriched beyond the azeotropic point by the addition of 3.5 parts by volume of an aqueous calcium chloride solution of density 1.2 (a 2.3-molar solution at 20 °C) [86]. Fig. 234 shows the course of the equilibrium curve with and without the additive and also the flow diagram of the operation. For the mixture water-phenol the addition of 17% of NaCl results in a shift of the azeotropic point from 91 to 84% wt. of water, so that the heterogeneous region of the system can be utilized [87]. Ethanol-water mixtures saturated with potassium nitrate in the concentration range from 15 to 70% yielded higher enrichments than mixtures without additive [88]. Guyer et al. [89] investigated the effect of sodium chloride on the vapour-liquid equilibrium of the mixture formic acid-water. In the presence of 35.5% of salt an azeotrope no longer occurs so that a high concentration of formic acid can be obtained. Systematic investigations of the salt effect in the system ethanol-water have also been conducted by Miró et al. [90].



a) b)

Fig. 234
a) Equilibrium curves of the system methanol-acetone
a = in the presence of $CaCl_2$ solution (2.3 molar)
b = without additive
b) Flow diagram of the operation

Furter [91] has analyzed the state of the art from the point of view of employing the salt effect in industrial processes, especially in extractive distillation. In addition, he has made up a list of references covering the years 1966 to 1977 [91a]. Schubert et al. [92] investigated the effect of some metal chlorides and other salts on the isothermal ($\vartheta = 60$ °C) phase equilibrium behaviour of the systems n-propanol-water, n-butanol-water and methanol-water. Using $CH_3OH/H_2O/NaBr$ as an example, the method of predicting salt effects for vapour-liquid equilibria as developed by Schuberth has been extended to unsaturated solutions [92a].

Jaques and Furter [95] derived an equation for the salt effect on the water-vapour equilibrium in binary mixtures which correlates the temperature and the liquid concentration of the three components ethanol, water and salt. The equation has 6 constants. The theory of the salt effect has been discussed by Furter and Meranda [96]. On the basis of simplifying assumptions Sada et al. [97] have established a relation for the calculation of vapour-liquid equilibria for non-aqueous binary systems in which the salt is dissolved only in one component (*e.g.*, benzene-ethanol with lithium or calcium chloride).

The above examples indicate that selective separating methods are of particular importance for complicated separations. Systematic experimental work will undoubtedly open up further applications. The combination of the distillation process with adsorption effects led to the technique called adsorptive distillation. The influence of the nature of the packing material on the efficiency of the separation of the mixture water-acetic acid has been studied by Fuchs and Roth [93].

7. Constructional materials and apparatus

Various forms of apparatus have already been mentioned incidentally in chapters 1 to 6. A summary of the characteristic properties of glass as a constructional material together with important constants has been given by Pietzsch and Rautenberg (see chap. 5, ref. [30b]). The present chapter will deal principally with recent developments in the components and equipment needed for different kinds of distillation. A selection has purposely been made among the many types, often identical in principle, that are available and this selection will also demonstrate that further standardization is possible. Standardization benefits both the user and the producer, but it must, of course, be applied in such a way that every process likely to be employed can be performed in suitable conditions.

7.1 Constructional materials for distillation apparatus

The materials of construction for distillation equipment are metals, porcelain, silica and — most important of all — glass. Metals are chosen for distillations at high temperatures and pressures, where the resistance or strength of glass becomes insufficient. For instance 18:8 stainless steel (18% chromium, 8% nickel) can be used not only at high temperatures and pressures but also with many corrosive substances. Ceramic materials such as porcelain are not often used now that glassware suitable for pilot-plant and industrial use is available. Silica finds its main application in water stills and for operations at very high temperatures. Certain synthetic polymers, such as Teflon, have been employed for the construction of various components such as gaskets.

Glass is a material that was used 5000 years ago in ancient Egypt, not only for household utensils, but also for alchemical equipment, and it has retained its prominent position in the laboratory to the present day. Its wide use follows from its very favourable chemical and physical properties.

The transparency of glass gives it the undisputed advantage of allowing an operation to be seen. In processes that must proceed adiabatically an evacuated glass jacket can be used up to 120°C or more for heat insulation. At higher temperatures and in large apparatus a jacket of glass wool, provided with a slit for observation, forms a satisfactory insulation (*cf.* section 7.7). Glass is also very resistant to corrosion. There are, in fact, numerous separations and chemical reactions that can be performed only in glass or ceramic apparatus. The hardness and smoothness of glass, which reduce superficial deposits and allow the apparatus to be cleaned rapidly and easily, together with its low coefficient of expansion, have favoured its use in the laboratory. In the preparation of pharmaceutical materials and of distilled water glass has the valuable property of ensuring products free from odour, taste and metallic contamination.

The principal disadvantages of glass in comparison with metals are its fragility and its lower resistance to changes in temperature. By special processes of annealing it is possible to make glasses containing internal stresses of such magnitudes that they counteract breakage. The present trend is to produce special glasses, certain properties of which have been improved for particular applications. It will doubtless never be possible to evolve an ideal glass offering the same range of application and ease in machining that are presented by metal alloys, and it will therefore remain necessary to compromise by selecting among the many types of glass that are now available [1, 5].

No useful purpose would be served by including in this book a detailed list of the chemical and physical properties of glasses. The testing conditions may vary appreciably, which makes it difficult to arrive at meaningful comparisons. Besides, all the specifications required are given in the catalogues of the glassware manufacturers [1].

Extensive tables of constants can be found in the publications of Mönch [2] and Eitel et al. [3]. A paper prepared at the Central Laboratory of the VVB der Glasindustrie (Association of the Glassware Manufacturers), Ilmenau, GDR [4], contains the constants of chemical glasses as compared with those of porcelain, metals and plastics. Also, applications of glass as a constructional material and the properties of glass fibres and products made of glass fibres are exhaustively dealt with.

For the uses of semi-technical glass apparatus in the laboratory and in pilot plants the reader is referred to the papers of Rieger [5]. By using special types of glass it is possible to make apparatus capable of withstanding distillation pressures up to 4.3 kg/cm^2 [6]. The use of porcelain in the laboratory has been discussed by Kammel [7].

7.2 Standard apparatus and unit parts

Reference has already been made to standardized, conventional methods of distillation in chap. 3.1 Fig. 235 shows the device used for Engler distillations which has been improved by employing ground joints. Thus, the immersion depth of the thermometer and the position of the side tube for the distillate remain exactly fixed. Automatic apparatus based on this device will be described in detail in chap. 8.1. The use of such apparatus is to some extent justified in industrial analyses, where rapid work is essential, but it is unsuitable in more exacting applications. Furthermore, it cannot be employed for vacuum distillation. For simple unrectified distillation at reduced pressures down to 10 mm Hg it is preferable to employ the Claisen flask (Fig. 236). If the pressure is measured near the receiver, low values will often be found. In accurate work the pressure and temperature should be measured close together. If the pressure is below 10 mm it should be determined at the spot indicated by dotted lines in Fig. 236. Another disadvantage of both the Engler and the Claisen apparatus is that the bubble point cannot be defined exactly. According to the pertinent standard the temperature is measured in an Engler apparatus when the first drop of the distillate leaves the condenser. Here as in the Claisen apparatus the distillate contains also higher-boiling material which makes boiling appear to begin at a higher temperature. Due to the small amounts (about 100 g) which are commonly used in analytical work shifts of the bubble point affect the results strongly (cf. Fig. 135). Recently, test distillation apparatus (Fig. 237) for amounts of 200 to 500 ml has increasingly been used. It contains a short packed column and allows initial operation at an infinite reflux ratio in order to determine the bubble point exactly.

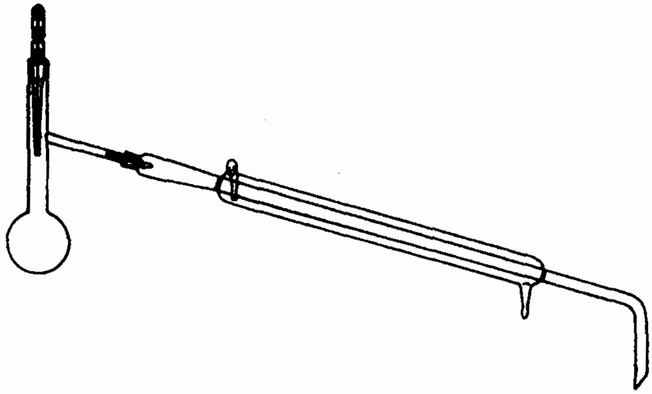


Fig. 235
Engler distillation apparatus with standard ground joint

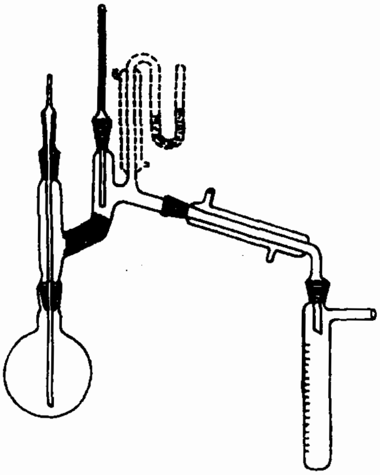


Fig. 236
Vacuum distillation apparatus with Claisen flask

By incorporating a pressure regulator such apparatus gives quite reproducible results when used at reduced pressure (*cf.* section 8.3). If an auxiliary liquid (chaser), having an initial boiling point about 50 deg. C above the final boiling point of the mixture, is added it is possible to collect the whole of the feed as distillate. Towards the end of the distillation the auxiliary liquid then constitutes the hold-up of the apparatus [8]. This technique is common in many forms of analytical distillation.

Simple unrectified distillation is used in the laboratory chiefly for the recovery of solvents and other contaminated liquids, and for performing initial separations on large amounts of mixtures. The only apparatus needed for this purpose is a flask, a still head with a ground-in thermometer and components for condensation, vacuum connection and collecting the distillate. It is frequently advisable to include a spray trap consisting of a short section — say 5 to 10 cm — of column. Fig. 238 demonstrates the wide range of possibilities offered by the use of readily available parts [9].

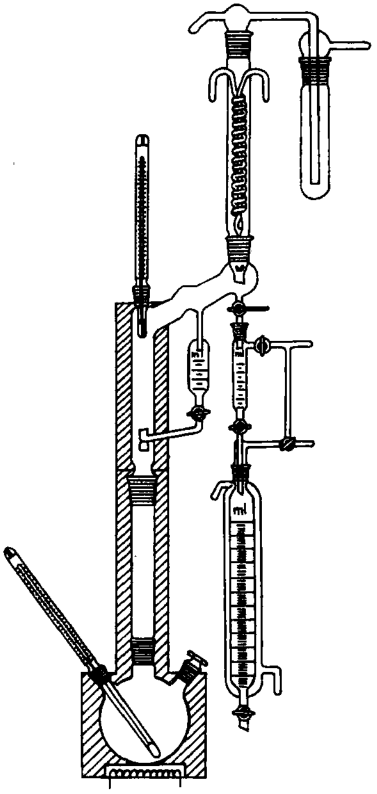


Fig. 237
Apparatus with column for analytical work made from Destinorm components

The still head *1* is suitable both for low- and high-boiling substances, whilst the "bridge" *13* is intended for high-boiling, solidifying materials. Air-cooling usually suffices for condensing substances of high boiling point and is obtained with component *3* or the reflux condenser *16*. If fractions solidify in an air condenser they may easily be melted with the aid of a Bunsen burner or an electric heater. A safer course in such a case is to use component *14* or *15* as condenser, since they have jackets that may be kept warm and can be cleaned after use. In this respect the screw-type condenser *14* is convenient, as in some versions the screw portion may be removed by means of a ground joint for cleaning. When low-boiling substances are distilled, cooling must be thorough and a normal Liebig condenser *5* may prove to be insuffi-

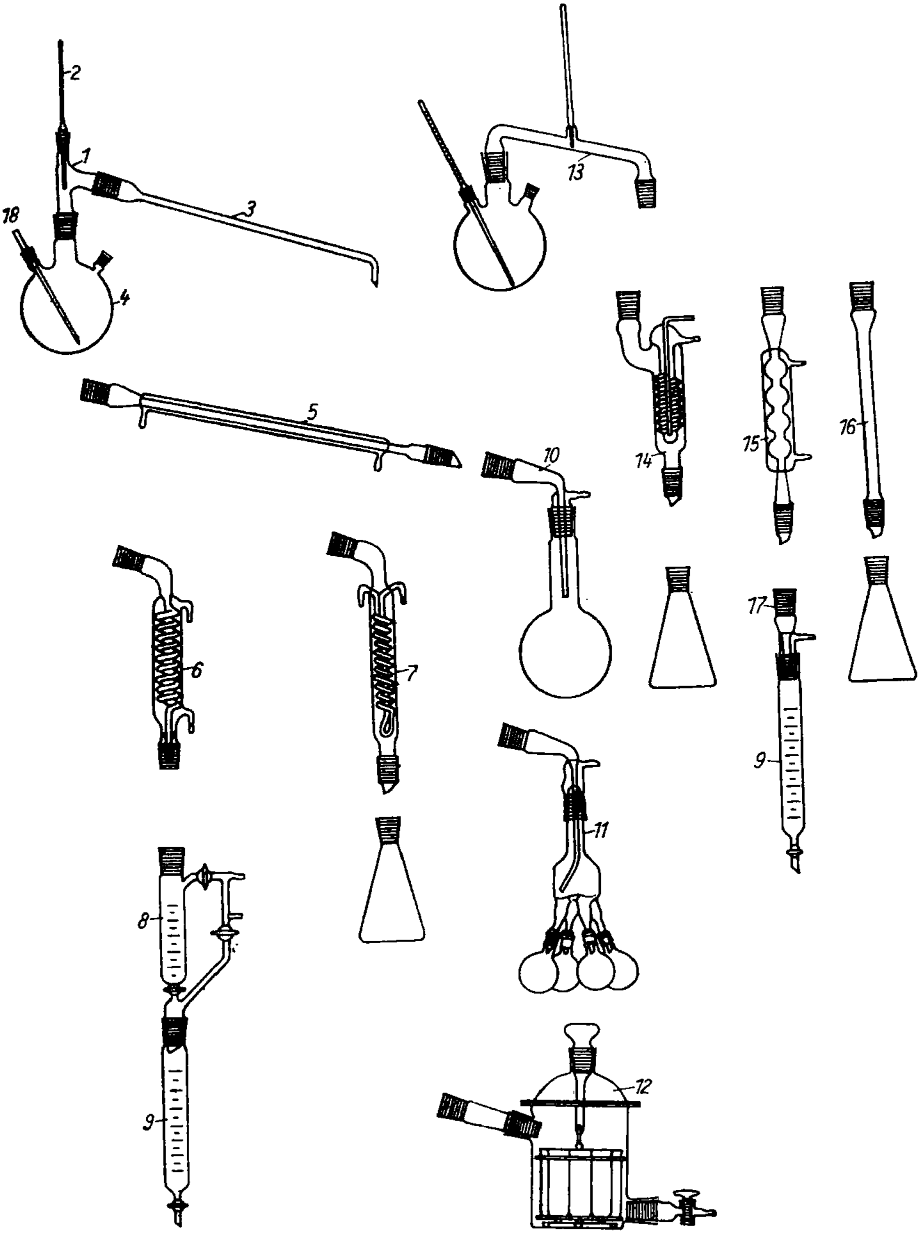


Fig. 238
Components for simple distillation

cient; the spiral condenser *6* and the Dimroth condenser *7* provide more efficient cooling and also allow a more compact, vertical arrangement. For vacuum work the Anschütz-Thiele receiver *8* is most usual, since it permits any number of fractions to be taken without interruption of the distillation. It is also useful for operations at atmospheric pressure in which gases are evolved. The distillate may be collected in graduated cylindrical vessels *9* which allow the volume to be read off at any instant.

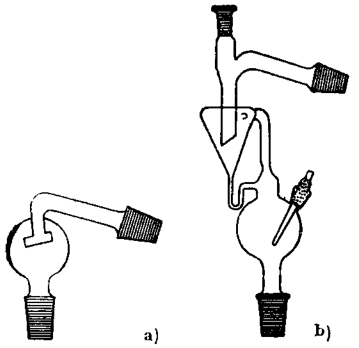


Fig. 239
Still heads for the distillation of foaming liquids

a) Reitmeir b) Friedrichs

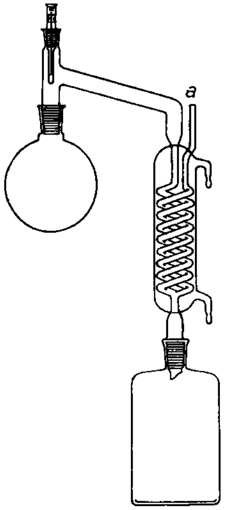


Fig. 240
Arrangement of Friedrichs for the distillation of inflammable substances

The adapters *10* and *17* can be employed in cases where the distillate is not separated into fractions. Sketch *11* shows a receiver with which three fractions may be collected, while version *12* can take 7 fractions. If it is necessary to use a boiling capillary, the Claisen still head (Fig. 236) may be chosen, or else a three-necked flask with a capillary *18* inserted into one of the ground joints.

For foaming liquids special still heads are available, such as the pear-shaped type for mild foaming (Fig. 239a), and the Friedrichs cyclone (Fig. 239b).

Very low-boiling or inflammable substances can be more safely distilled with an arrangement due to Friedrichs (Fig. 240). The vent *a* is connected to a pipe leading to the open air.

Apparatus for countercurrent distillation can be assembled from the components to be described in the next paragraphs. Even complicated arrangements simulating industrial installations, having more than one column and numerous auxiliaries, as shown in Figs. 134 and 162 present little difficulty [10, 11]. With the parts of the Destinorm series designed by the author a large variety of apparatus, from the simplest equipment for straight distillation, vapour pressure measurement and equilibrium curve determination to extensive apparatus for continuous distillation at normal and reduced pressures (Fig. 223 and 224), may be set up. A similar series (Labodest) was developed by Stage (manufactured by Fischer Labor- und Verfahrenstechnik, Bonn-Bad Godesberg), and the components manufactured by the Normag, of Hofheim, and by the Normschliff-Glasgeräte GmbH, Wertheim, can be assembled for use in the various separations.

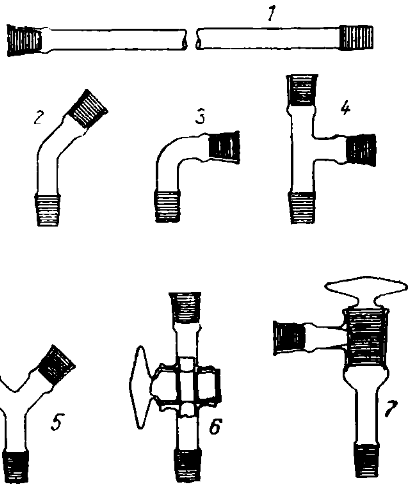


Fig. 241
Pipe components

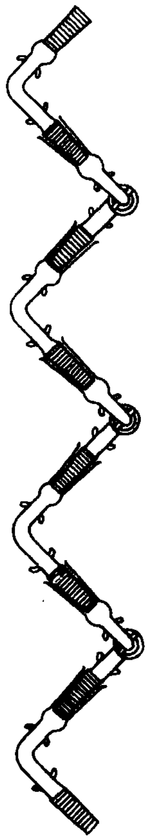


Fig. 242
Chain of joints (Friedrichs)

Long lengths of piping may conveniently be built up of 1 — $1^1/_2$ m sections (Fig. 241/*1*). 135° and 90° bends (Fig. 241/*2* and *3*), T- and Y-pieces (Fig. 241/*4* and *5*) are available for constructing any assembly of pipe, in which stopcocks (Fig. 241/*6* and *7*) may be included. To increase the flexibility of lines, ball-joints may be used, or a chain of joints (Friedrichs: Fig. 242), which gives flexibility in all directions, is a possibility.

Connections between one size of ground joint and another can be made by means of adapters (Fig. 243), which are obtainable commercially in almost any practical combination of sizes (*cf.* Table 52).

Table 52

Commercially available adapters for various joint sizes

Socket	NS	12.5	14.5	14.5	24	29	29	29	29	29	29	29	29	29
Cone	NS	14.5	14.5	29	29	24	29	34.5	45	55	60	70	85	100

Joints may also be connected with vacuum tubing by the use of parts such as that illustrated in Fig. 243/7.

As can be seen from Table 53 some of the components mentioned above have been standardized.

Piping systems can be set up in a similar manner using plane and ball joints. Maximum lengths of the straight sections for semi-technical purposes are of the order of 3 m. A great variety of components similar to those shown in Fig. 241 are

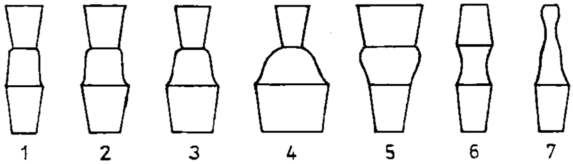


Fig. 243
Adapters for various joint sizes

1–4 = cone ≧ socket
5 = cone < socket
6 = cone to cone
7 = NS 14.5 cone to rubber tubing

Table 53

Standardized components

Standard	Component
TGL 13828	connecting pieces, straight
13831	connecting pieces, bent (90°)
13834	connecting pieces, S-shaped
13835	connecting piece with one-way tap
13836	connecting piece with steam pipe
13837	connecting piece with drop-counter
13838	connecting piece with tap funnel
9966	adapters with ground joints
9973	U-pieces with two joint sockets
9978	boiling capillary
	All the above components are provided with standard ground glass joints
DIN 12404/63	boiling capillary with standard ground joint
12565/70	dropping funnel

commercially available for semi-technical and pilot plants. For details the reader is referred to Refs. [1, 5, 7]. By now, a number of standards have been issued (TGL 10192—10200, 11641—11644, 12023—12032, 20277 and drafts for DIN 28800—28808).

7.2.1 Taps and valves

As can be seen from Table 54, a number of glass taps and stop-cocks have been standardized.

Figs. 189 and 190 show taps for vacuum work. Kinza has devised a three-way tap [12] having the unusual feature that if the plug is always turned in the same direction no mistakes in position can be made in vacuum work (Fig. 244). Wolf [13] has published an excellent review of standardized and special-purpose taps. The latter include the "Vestale" rotary disk shown in Fig. 245. Straight-way taps, drain cocks, three-way and four-way taps are supplied for semi-technical purposes.

While ordinary glass taps require grease, those having exchangeable Teflon plugs can do without it. The Otto Fritz GmbH Normag, Hofheim/Taunus, make various taps of Duran glass with safety rings. The miniature taps of the French firm Gaflon are entirely made of Teflon. To connect them with the glass tubes Teflon gaskets and screwings are used.

Even with ordinary taps the plug should be protected against coming off (Fig. 217). As there is always a danger that the valve plug may be withdrawn accidentally when it is turned, it is advisable to provide the valve with a rubber disc or ring, or better still with a safety clip of steel wire (Fig. 246).

Glass taps with greased ground surfaces, in particular with dimensions > 40 cm, are unsuitable for semi-technical or pilot plants. In these cases valves are used instead of taps, especially since the combination of glass and Teflon has made possible many

Table 54
Standardized glass taps for distillation apparatus

Standard		Component
TGL 21734	Sheet 1	taps, survey
	Sheets 2—7	special taps
13843	Sheet 1	high-vacuum taps
	2	one-way taps, dimensions
	3	two-way taps, dimensions
DIN 12541/67	Sheet 1	preliminary standard one-way tap cocks, masses
/70	Sheet 1	preliminary standard one-way tap cocks, tests for tightness
12551/67	Sheet 1	preliminary standard one-way tap cocks, provided with non-interchangeable, massive cocks
12553/61		two-way taps with non-interchangeable cocks
12554/67		three-way tap cocks with non-interchangeable cocks
12563/67		three-way tap cocks with angular bore (120°), provided with non-interchangeable, massive cocks

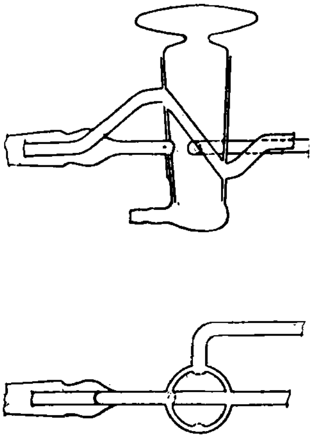


Fig. 244
Kinza's three-way tap

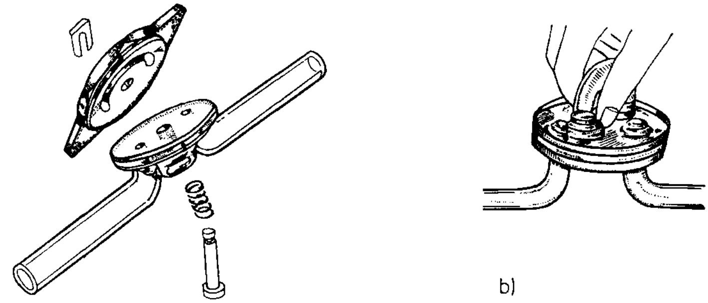


Fig. 245

a) The parts of the rotary disk "Vestale"
b) The rotary disk "Vestale" (DBP 1, 112, 846)

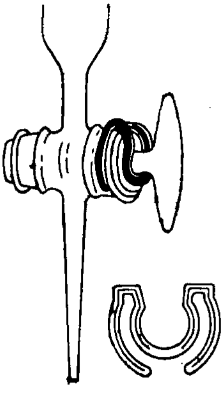


Fig. 246
Steel wire safety clip for tap

new valve designs [1]. The tap plugs are replaced by Teflon spindles in the valves for laboratory work as shown schematically in Fig. 247. Messrs. Sovirel offer precision valves of the "Torion" series for a range of diameters from 2.5 to 10 mm. The valves are said to be vacuum-tight down to 10^{-4} torr. In the valves of semi-technical plants

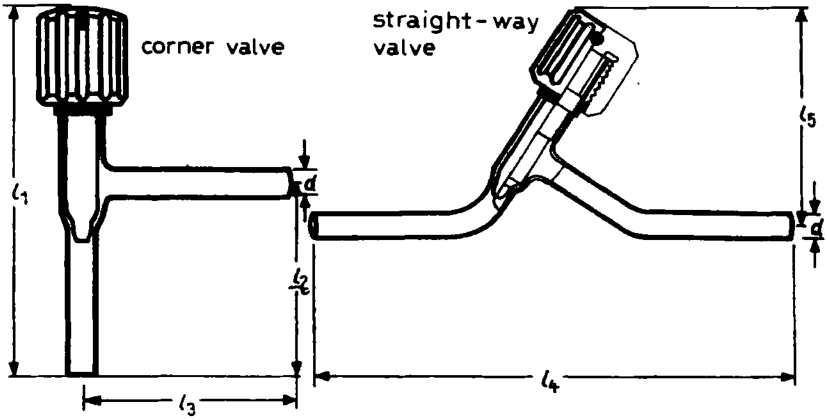


Fig. 247
Precision valve of glass with PTF spindle for the control of liquid and gas flow (face and tube diameter $d = 4$ and 7 mm)

Fig. 248
Pneumatically controlled valve with nominal widths 25, 32, 40 and 50 mm

closure is achieved by Teflon bellows provided with a Teflon plate or cone (Fig. 248). The valves may be operated manually by means of electromagnets, electromotors or pneumatic drive. This enables distillation plants to be controlled automatically to a large extent. The glassware manufacturers provide a variety of valves with plane or ball joints having nominal widths up to about 150 mm. These may be classified (*cf.* chap. 5.1.3.2) as:

straight-way valves, drain valves, corner valves,
throttle valves, non-return valves with flaps or balls,
safety valves for overpressures up to 5 atm.

7.3 Columns

It was pointed out in section 4.1 that the exchange of material and heat in a column are processes taking place at the boundary between the liquid and vapour phases. A column should therefore present as large a surface as possible for this exchange, but this surface should not be associated with a large hold-up (section 4.10.5). The best column is one having both a small HETP and a low hold-up.

In an attempt to classify columns systematically, selection criteria were established by Heckmann [14]. The number of column constructions that have been described is large, so that only the characteristics of the fundamental types, listed below, will be described.

Empty columns,
Packed columns,
Plate columns,
Columns with stationary elements,
Columns with rotating elements.

Reichelt [14a] has reported a combination of packed and plate column. The countercurrent motion of the phases sets the packing (mostly light spheres) which is supported by grids (= plates) whirling. Thus, relatively high throughputs are obtained. Data on the lower and upper limits of operation of a packed column apparatus with moving packing are given by Handl [14b].

7.3.1 Empty columns

Favourable features of empty columns are that they give a low hold-up and a small pressure drop, so that their main applications are in the fields of micro-distillation (section 5.1.1), high-temperature distillation (5.3.2) and vacuum distillation (5.4.1). In such columns the exchange takes place between the vapour and the film of liquid falling down the walls. The possibilities and problems involved in the use of falling films have been studies in detail by Malewski [15].

Empty columns may be divided into the following types:

a) straight or spiral smooth tubes,
b) tubes with an increased surface area,
c) concentric-tube columns.

Owing to their low resistance to flow empty columns may be heavily loaded, but as a result of the small surface for exchange the efficiency is as a rule low (with the exception of group 3), particularly at high loads.

Smooth vertical tubes, with diameters of 20—50 mm, are now rarely used for separations, except as spray traps in simple distillations. Their HETP will not be lower than about 10 cm unless the load is small, say less than 30 ml/h. Attempts have therefore been made to improve their efficiency by *increasing their surface area*. The Wurtz (*cf.* Fig. 15) and Young columns, consisting, respectively, of series of simple and pear-shaped bulbs, produce a better separation, but have a larger hold-up. Data for unfilled columns are given in Table 55.

Table 55

Data for empty columns

Type	Diameter (mm)	Length (mm)	Load (ml/h)	HETP (cm)	Hold-up per theoretical stage (ml)	References Chap. 7
Empty vertical tube	30	1000		25		[16]
Tube with sintered glass on walls	7	500		12.5		[16]
Vigreux	12	460	54	5.4		[18]
			96	7.1	0.46	
			294	7.7	0.62	
			540	7.7	0.68	
	24	460	120	10.2	1.3	
			240	12.1		
			510	11.5	1.8	
Vigreux, modification of Ray	6	1200	60	2.0	<0.02	[17]
Jantzen	4—6		50—200	4—6	0.2—0.6	[19]

Other means for increasing the area are the application of an inner layer of sintered glass [16] and the provision of vertical and inclined indentations, as in the well-known Vigreux column. Slanting indentations also have the advantage of promoting the redistribution of liquid from the walls to the centre (Fig. 249). A modification of the Vigreux column by Ray [17] has the indentations at right angles to the walls. Its separating efficiency is better than that of an empty tube (see Table 55). The Vigreux column is useful for relatively simple separations, where it is important to keep the hold-up low, as in micro-distillations or high-temperature distillations of tars and other high-boiling materials that have to be evaporated to a small residue [18]. Similar purposes are served by the Jantzen *spiral column* (Fig. 250), which is made commercially with inner tubes of 3 and 6 m (straight) length and gives a hold-up of 0.2 to 0.6 ml per theoretical stage. In a test run with the mixture carbon tetrachloride-benzene, performed with a Jantzen column of 6 m straight length, 6 mm tube diameter, 50 mm spiral diameter and 12 mm pitch, the following data were determined:

Flooding load	900 ml/h;
Hold-up per theoretical stage	0.4 ml at 50 ml/h load;
HETP	4.3 cm (load 50 ml/h); 5.4 cm (load 90 ml/h); 5.6 cm (load 190 ml/h).

For insulation, the Vigreux column is usually provided with a sheath, while the Jantzen column has a vacuum jacket.

Fig. 249
Vigreux column with air-insulating jacket

In the use of all empty columns it is important for the wall temperature to be lower than the temperature of the reflux, since the maintenance of a uniform film is otherwise impossible.

All empty columns have a satisfactory efficiency only if the load is kept relatively low. However, if a number of tubes are combined in parallel, the total load may be raised to any required value. Such a column was patented in 1936 by Fenske [20].

If a narrow, vertical tube, say, 0.6 cm in diameter is used at a load of 10 ml/h, an HETP of 1.73 cm may be found [21]. Such a tube, having a length of 1 m, would produce a pressure drop of 2.7 mm Hg and would have a hold-up of only 0.4 ml. Starting from such data, Kuhn [22] developed the so-called *hairpin countercurrent principle* (Fig. 251). The basic idea is that a small separating effect, occurring under stationary conditions in a direction at right angles to the axis of the tube (vector a), is multiplied by means of a flow along the length of the apparatus, changing its direction at the ends (indicated by arrows u_1 and u_2). In order that a high efficiency may be attained, the vapour velocities must be kept as small as possible and the reflux ratio must be very high. For a reasonable throughput it is then necessary, as already stated, to combine a large number of tubes in parallel (Fig. 252). The reflux is produced for all elements collectively by means of a thermostat *c* and the distillate

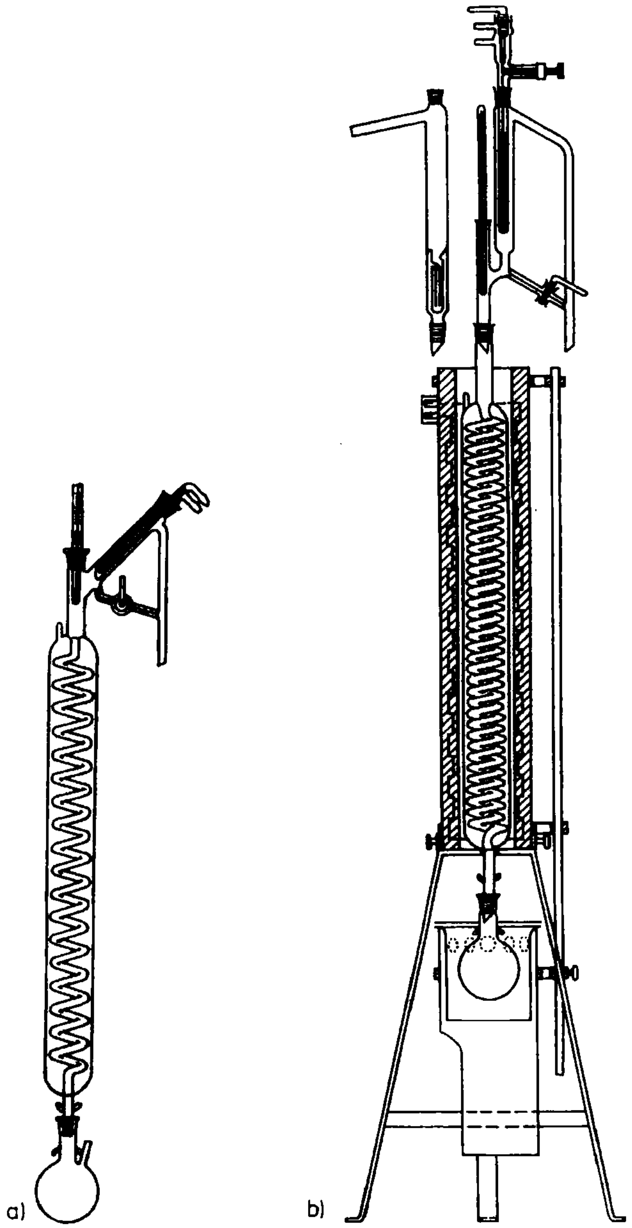


Fig. 250
Jantzen spiral-tube column with vacuum jacket

a) Straight length 3 m
b) Straight length 6 m

Table 56

Throughputs (grams per 24 h) of Kuhn's multiple-tube column, having 100 tubes, diam 0.2 cm, length 2 m

Initial to final concentrations, $x_B \rightarrow x_E$ (mol %)		40 → 60	10 → 90	10 → 99	50 → 90	1 → 99
Difference in boiling point (°C)	0.1	30	—	—	—	—
	0.31	300	5	2.9	22	0.2
	1.0	3,000	50	29	220	2
	3.1	30,000	500	290	2,200	20
	10.0	300,000	5,000	2,900	22,000	200

is taken from the ends of the tubes through superheated capillary tubes *d* (cf. also Fig. 157).

Table 56 shows the throughputs, with various initial and final concentrations and various differences in boiling point, for a multiple-tube column containing 100 parallel tubes (diameter 0.4 cm, length 2 m). The values were calculated [22] for a molecular weight of 100 and a boiling point of approximately 90 °C.

Another multiple-tube column, containing 61 tubes of 0.2 cm diameter and 1.5 m length, was employed for the separation of the isotopes ^{12}C—^{13}C, where the difference in boiling point was only 0.03 deg. C. The number of stages was determined by analysis of the products in the mass spectrometer. The hold-up of a tube 2 m long

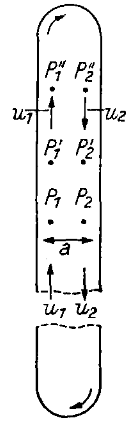


Fig. 251
Diagram of the multiplication of separating effects by the hairpin countercurrent principle of Kuhn

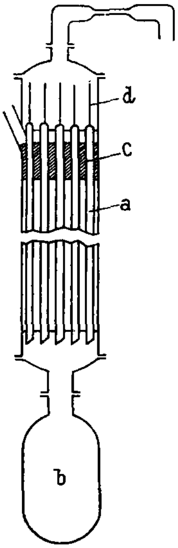


Fig. 252
Multiple-tube column (Kuhn)

and of 0.2 cm diameter amounts to about 0.5 g [22]. The method has also been used successfully for the separation of close-boiling isomers, such as the xylenes (Fig. 253) and the isomeric amyl alcohols. This type of column would appear to be promising for many problems of separation requiring more than 100 stages, since its HETP is extremely small.

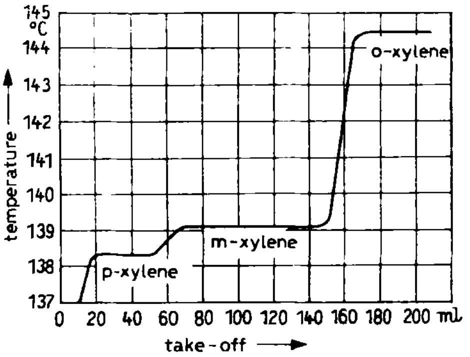


Fig. 253
Separation of the isomeric xylenes with Kuhn's multiple-tube column, length 0.8 m

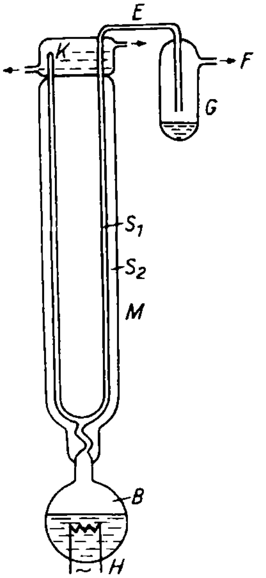


Fig. 254
Concentric-tube column (Kuhn)

B = still pot, H = electric heater, M = vacuum jacket, S_1 and S_2 = concentric tubes, K = condenser, G = cold trap, F = vacuum connection

The calculating methods were discussed in chap. 5.1.4.2 for ideal mixtures. Craig [23] has described a concentric tube column with narrow gap which is suitable for micro-scale work, its capacity being 0.25 ml. The annular space for distillation is provided by a thin rod being placed in a capillary.

Kuhn's starting point for the calculations on the multiplication of the separating effect [24, 25] was a column having an annular cross section, formed by two concentric cylinders (Fig. 254). Such columns are known as concentric-tube columns (compare

Fig. 257). They have also been studied extensively by Westhaver [26], Donnell and Kennedy [27] and recently by Jantzen and Wieckhorst [28], who compared them with columns containing Stedman packing and wire spirals. As shown by Fig. 255, the concentric-tube column is superior to the last-named types at loads below 100 ml/h. The loss in pressure in a concentric-tube column can be calculated [21] by

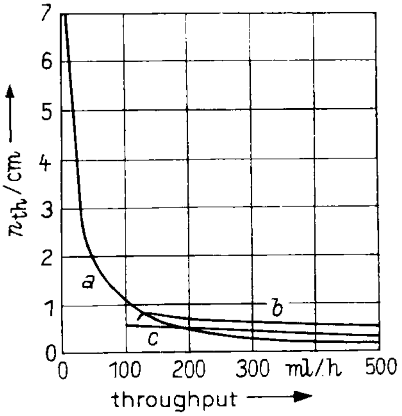


Fig. 255
Number of theoretical plates as a function of the throughput [28]

a = concentric-tube column, diam. 2.5 cm (gap, 0.4 cm), *b* = Stedman column, diam. 2.5 cm, *c* = packed column with helices 4 × 4 mm, diam. 2.4 cm

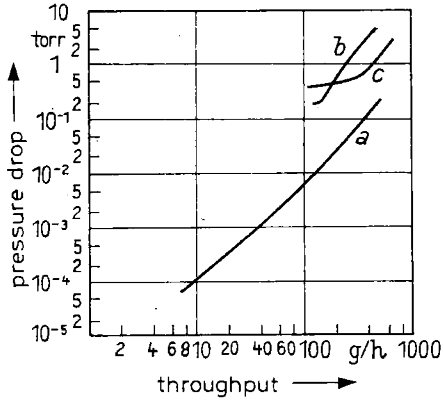


Fig. 256
Pressure drop as a function of the throughput at atmospheric pressure, referred to 50 theoretical plates [28]

a = concentric-tube column, *b* = Stedman column, *c* = packed column with helices 4 × 4 mm means of the formula:

$$p_1 - p_2 = \frac{3\eta_1 l Q}{2ba^2}$$

in which $p_1 - p_2$ = the pressure drop in dynes/cm^2,

η_1 = the viscosity of the vapour in poises,
l = the length in cm,
Q = the volume of vapour per unit time (cm^3/sec) at the average pressure $\frac{1}{2}(P_1 + P_2)$,
b = the average circumference of the gap in cm,
a = half width of gap in cm.

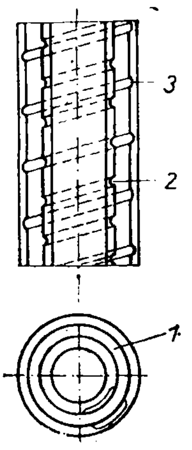


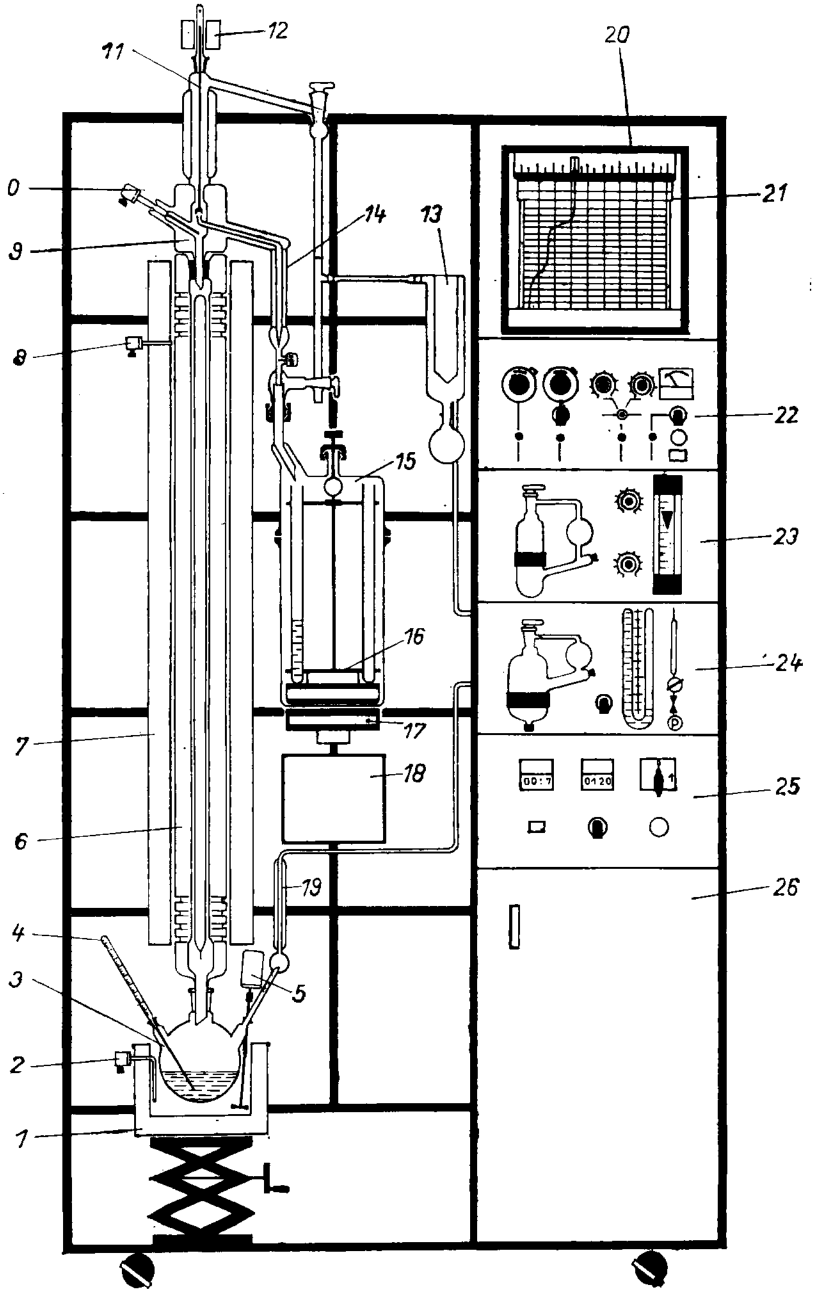
Fig. 257a)
Section of a concentric-tube column (Fischer)

1 = gap for vapour flow, *2* = inner tube with profile for spiralling reflux of liquid, *3* = outer tube with inverted profile for reflux of liquid

Fig. 257 b)
Fully automatic concentric-tube column for semi-micro operation

Control system: electronic control for oil bath according to temperature or differential column pressure — electronic control or follow-up control for heating jacket — reflux control with vapour division — vacuum control — fraction collector control — recording of all data — protection against superheating and interruption of cooling water supply

1 = oil bath with variable height support, *2* = resistance thermometer oil bath, *3* = still pot, *4* = thermometer residue, *5* = motor for stirrer, *6* = concentric-tube column, *7* = compensating heating jacket, *8* = resistance thermometer heating jacket, *9* = column head with condenser, *10* = resistance thermometer for head, *11* = valve armature, *12* = magnet coil, *13* = vacuum receiver, *14* = distillate condenser, *15* = fraction collector, *16* = support for receivers, *17* = magnetic coupling, *18* = automatic drive, *19* = condenser for differential pressure measurement, *20* = switch cupboard, *21* = 6-colour compensating recorder, *22* = Minitron 5, control device for still pot, heating jacket and column head, *23* = differential pressure controller and cooling water safety device, *24* = vacuum controller, *25* = fraction collector control, *26* = cupboard for accessories


12
11
20
0
14
13
21
9
8
22
15
23
16
24
7
17
18
25
00:7
0120
6
19
26
4
3
5
2
1

In comparison to the two other types of column mentioned, the concentric-tube column, in the region examined, caused a pressure drop lower by a factor of about 10 (Fig. 256). Koch and Feind [29] determined the pressure drops of concentric-tube columns with gap widths from 4.05 to 19.68 mm, the diameter of the outer tube being 49.96 mm in all cases. The measurements were carried out under isothermal conditions. Other studies concerned the heat transfer with the gap heated via the outer tube. Beck [30] investigated the heat transfer and pressure drop in vertical concentric and excentric gaps with forced flow and free convection.

Donnell and Kennedy [27] had previously demonstrated that with concentric-tube columns an HETP of 0.5 to 0.6 cm can be attained if certain requirements are fulfilled:

1. a uniform gap must be present throughout the whole length of the column; this may be attained by the use of precision bore tubes:
2. the walls must be uniformly wetted, for example by etching out a spiral;
3. adiabatic operation (obtainable by proper insulation or thermostatic jacket heating) is essential;
4. the column must be uniformly loaded (*e.g.* by automatic control of the rate of evaporation).

In a number of papers Fischer [31] has reported his work on concentric-tube columns and the experimental results obtained. He developed all-glass apparatus which is particularly suited for a mild countercurrent distillation of high-boiling substances, the pressure drop being of the order of 10^{-1} to 10^{-3} torr and the operating hold-up lying between 0.1 and 1.5 ml. The apparatus is highly automated and can be used for pressures from atmospheric down to 10^{-3} torr so that still pot pressures below 0.1 torr are reached. Intense exchange of material is secured by an optimum hydrodynamic design of the tubes as shown in Fig. 257a. The optimum vapour velocity is given by

$$w_{\text{opt}} = \frac{\sqrt{2} \times D}{0.5 \times a}, \tag{196}$$

where D = diffusion coefficient of the vapour product under operating conditions and a = gap width.

Fig. 257b shows the schematic diagram of a fully automatic concentric tube column for work on a semi-micro scale as developed by Fischer. It is manufactured in 7 versions with 10 to 80 theoretical stages for still pot capacities from 0.5 to 4,000 ml. A controlled oil bath provides a constant temperature of about 0.1 °C. Further details can be gathered from the legend (see also chap. 8.1.2).

7.3.2 Packed columns

This type of column consists of a tube filled with packing in a random manner (*cf.* section 4.10.2). The packing is supported by some form of grid (Fig. 258) or by a perforated funnel fused into the column; the latter arrangement is employed in the columns of Stage's Labodest series and the author's Destinorm series of components

(Fig. 259). The support should have at least the same free cross-sectional area as the packing resting on it. It is the usual practice to place a few larger-sized packing units on the grid before introducing the actual packing in order to minimize flooding. As a general rule the size of the packing should be about 1/10th of the column diameter.

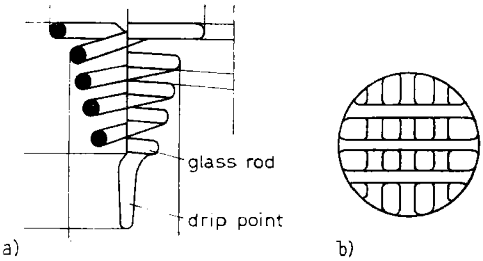


Fig. 258
Grids for supporting packing
a) spiral b) flat

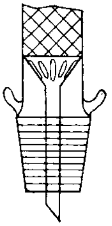


Fig. 259
Perforated funnel as packing support

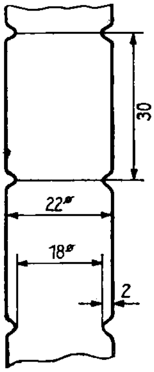


Fig. 260
Column with restrictions (Grosse-Oetringhaus)

In order to prevent the reflux from running down the walls of the column (section 4.2) it is desirable to collect it and lead it back to the centre at short intervals. Grosse-Oetringhaus [32] attempted to do this by providing the column with restrictions, 2 mm deep, at distances of 30 mm, as shown in Fig. 260. A better method is to divide the column into sections, the reflux from each section being collected and redistributed (section 4.10.2). Alternatively, discs of wire gauze with conical depressions may be employed. They have the advantage of causing almost no dead volume [33].

The diameter of the column should be chosen according to the required throughput (section 4.11). Columns for normal laboratory use have diameters of 10—50 mm ($\frac{3}{8}$—2 inches); if the diameter is larger, the operation is generally classed as semi-technical. In pilot plants, column diameters range from about 150 to 400 mm.

The effective lengths of these columns were purposely restricted to 500 and 1000 mm so as to ensure that tests with various kinds of packing would be comparable. If a larger number of separating stages are required several column sections can be connected in series. Should this number of stages have to be fairly exact, as for comparisons with an industrial installation, it may prove necessary to employ a section of non-standard length; in analytical work, however, this will seldom occur.

7.3.3 Plate columns

In the laboratory and on a semi-technical scale, plate columns are used mainly for special purposes, for instance in constantly-occurring separations where a distillate of high purity has to be prepared. Distillations carried out for comparison with industrial plate columns may similarly require the use of laboratory plate columns. In analytical work at atmospheric pressure the sieve-plate column has proved reliable.

In industrial continuous distillations plate columns are preferably used [34]. Recent developments of laboratory and semi-technical apparatus have been thoroughly discussed by Stage who has also dealt with the question of systematic tests for efficiency [35]. The advantages of bubble-cap columns in continuous operation have already been mentioned (cf. chap. 5.2.2.3; Fig. 167). Cyclic operation (Fig. 164) yields efficiencies >150%.

From a constructional aspect plate column may be subdivided into *bubble-plate*, *bubble-cap* and *sieve-plate* columns. All of these are employed mostly at atmospheric pressure, as their relatively high resistance to vapour flow gives rise to an appreciable pressure drop.

The action of a plate column is based on the fact that a certain amount of liquid is present on each plate and that the ascending vapour is forced to pass through this liquid. The reflux flows down from each plate to the next through tubes (downcomers), which may be situated either inside or outside the column (cf. chap. 4.2 and 4.7).

It should be noted that valve-plate columns with nominal widths of 50, 100, 200 and 300 mm have recently been employed for laboratory and pilot plant distillations [35a]. They are made in Czechoslovakia, the constructional material being Simax glass. They can be used at reduced pressures for distillate boiling temperatures up to 115 °C.

A *bubble-plate column* due to Keesom [36] is shown in Fig. 261. A layer of liquid is formed in trough *a*; the reflux is conducted downwards by tube *b*. As in all bubble-plate and bubble-cap columns the vapour, in traversing the liquid, undergoes a change in direction; it here passes under the rim of each section and bubbles up through the liquid layer. Owing to its relatively low stage efficiency Keesom's column is now seldom used. Bubble-cap columns, on the other hand, have been increasingly used for various purposes, especially for the determination of data for scaling-up. According to Stage [35], they are best suited for continuous operation on the laboratory and semi-technical scales because they have a wide range of loading and their efficiency is largely independent of the load and the liquid-to-vapour ratio as well as of short-time fluctuations in the control. The Bruun *bubble-cap* column

[37] has found wide application in the laboratory (Fig. 262). It resembles industrial bubble-cap columns in construction, but has the disadvantage that the downcomers are outside the column. There is thus a tendency for the reflux to lose heat. In order to counteract this tendency to some extent the column is provided with an air or vacuum insulating jacket (Fig. 263). The reflux tubes *a* and *b* are so constructed as to maintain a liquid layer of about 10 mm on the plates. The vapour passes up through

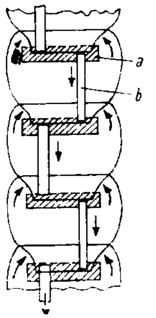


Fig. 261
Bubble-plate column (Keesom)

a = weir for liquid level,
b = downcomer

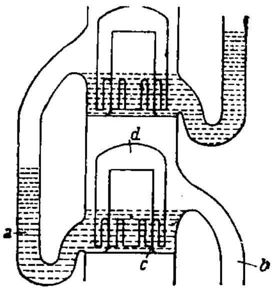


Fig. 262
Bruun's bubble-cap column

a = reflux tube (in), *b* = reflux tube (out), *c* = vapour tube (riser), *d* = serrated cap

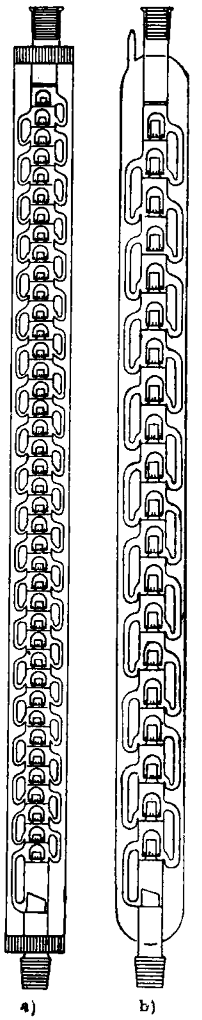


Fig. 263
Bruun's bubble-cap columns

a) with 40 actual plates and removable air jacket
b) with 20 actual plates and vacuum jacket

risers *c*, which are covered by loose caps *d*; the latter are serrated along their lower rims, so as to break up the vapour into small bubbles.

A column accurately duplicating industrial columns is Krell's bubble-cap column (Fig. 139), which has internal downcomers. It is made in diameters of 50 to 70 mm and has proved particularly useful for carrying out investigations designed to parallel

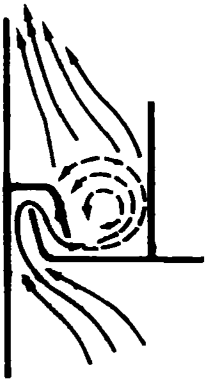


Fig. 264a)
Vapour path through collision plates

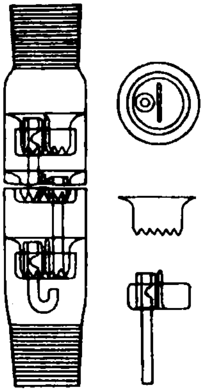


Fig. 264b)
Vapour collision plate (Stage)

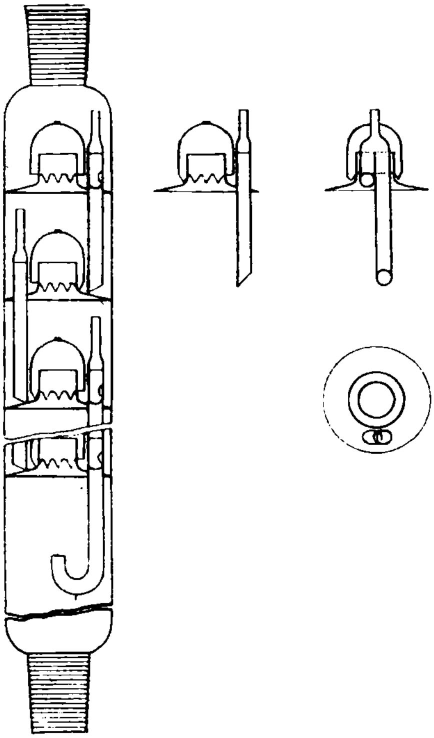


Fig. 265
Stage's bubble-cap column, with shielded reflux tubes

large scale distillations. This column can also be equipped with sampling taps and thermometer wells. Heated, hinged column jackets are available for insulation.

The multi-chamber column of Klein, Stage and Schultze [38] also has internal downcomers. The vapour is distributed on each plate by a number of holes arranged in a circle, the intention being to produce small bubbles giving a thorough mixing of the liquid. Stage has also developed a bubble-cap column provided with so-called

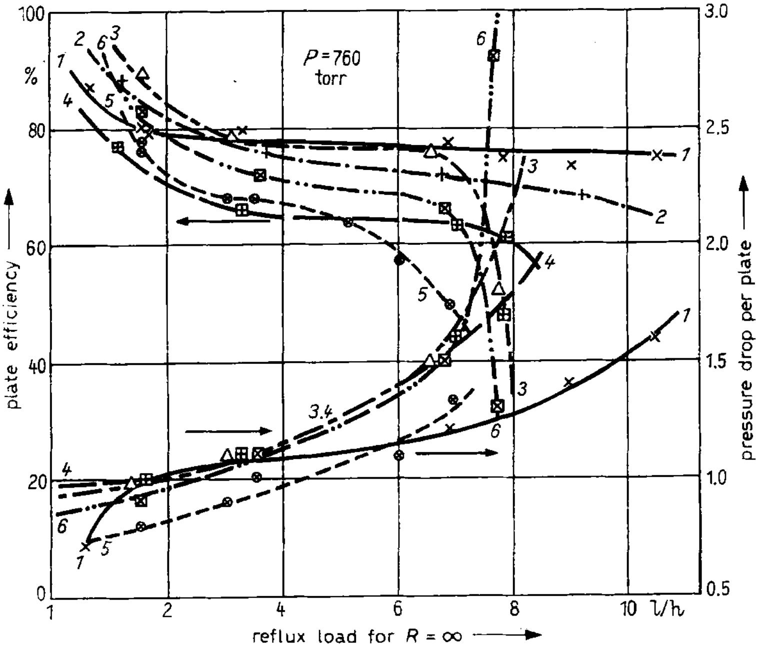


Fig. 266

Efficiency and pressure drop as functions of the reflux load (l/h) at 760 torr for various bubble-cap columns with dimensions as given in Table 57

1 = Labodest bubble-cap column with vapour collision plates, *2* = Labodest vapour collision plate column, *3* = Labodest bubble-cap column with shielded reflux tubes, *4* = bubble-cap column (Schmückler-Fritz), *5* = Brand bubble-cap column, *6* = Normschliff bubble-cap column

"vapour collision plates", in diameters of 40 to 130 mm. The vapour enters at the circumference of a rotating layer of liquid on the plate (Fig. 264a) and then impinges on the opposite wall. The vortices produced in this way favour mass transfer, and this is further promoted by the long path covered by the liquid from its entry to exit (Figs. 264b and 167). The plate efficiency varies little with the load and lies between 80 and 90%. Another type of bubble-cap column due to Stage (Fig. 265) has shielded downcomers and permits high liquid loads to be applied. Fig. 266 provides a comparison of pressure drops and plate efficiencies for the mentioned columns. Table 57 contains data for various bubble-cap columns and Fig. 267 displays their constructional differences.

Table 57

Cross-sectional areas for vapour and liquid flows in 6 plate columns as compared by Stage [35] (for the meaning of numbers 1–6 cf. Fig. 266)

No.	Dimension	Column No.					
1		1	2	3	4	5	6
2	Outer diameter (mm)	55	55	55	55	62	58
3	Inner diameter (mm)	51.5	51.5	51.5	51.5	57.5	54
4	Column cross-section (cm^2)	21	21	21	21	26	23
5	Outer vapour riser cross-section (cm^2)	3.51	7.8	2.58	3.31	7.9	3.29
6	% of 4	16.7	37	12.3	15.7	30.3	14.4
7	Inner vapour riser cross-section (cm^2)	2.44	5.2	2.12	1.13	3.5	1.76
8	% of 4	11.6	24.7	10.1	5.4	13.7	7.7
9	Area of openings produced by serration (cm^2)	5.58	3.1	3.1	2.25	1.82	2.1
10	% of 4	26.65	14.7	14.7	10.7	7.0	9.2
11	Area covered by cap (cm^2)	5.58	1.83	1.83	0.85	4.33	1.0
12	% of 4	26.65	8.7	8.7	4.05	16.6	4.36
13	Total cross-sectional area for vapour flow (cm^2)	11.16	4.93	4.93	3.10	6.15	3.10
14	% of 4	53.3	23.4	23.4	14.8	23.6	13.6
15	Cross-sectional area for vapour flow outside cap (cm^2)	9.7	4.15	13.45	10.0	8.83	16.3
16	% of 4	46.3	20.0	64.0	47.5	33.9	72.5
17	Area for vapour flow within the cap (cm^2)	9.74	7.17	6.38	6.6	7.22	6.4
18	% of 4	46.2	34.1	30.4	31.5	27.8	28.0
19	Cross-sectional area for liquid flow (cm^2)	1.04	0.67	0.29	0.6	0.39	0.5
20	% of 4	4.93	3.15	1.38	2.38	1.5	2.19

Sieve-plate columns have perforated plates on which a small amount of liquid is maintained by the pressure of the ascending vapour. They therefore require a minimum load, as the liquid otherwise falls through the perforations. This type of column has proved excellent for analytical distillations of low-boiling hydrocarbons. In the sieve-plate column of Oldershaw, as modified by Groll [41], the holes (diam. 0.75 to 1 mm) are arranged in circles and pass vertically through the plates (Fig. 268). The reflux flows down through a central tube to the next plate. (For the pressure losses in these columns see Table 33, section 4.11.) The sieve-plate column of Sigwart, on the other hand, has external downcomers and cup-shaped plates with horizontal holes (Fig. 269).

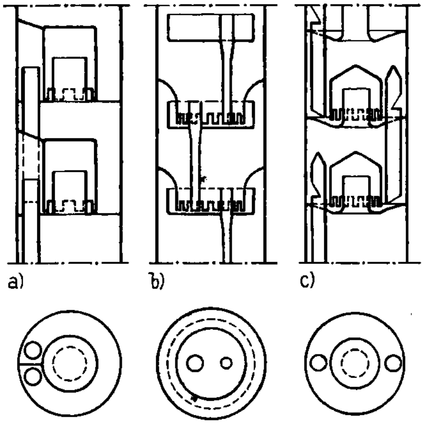


Fig. 267
Recent bubble-cap columns

a) column due to Schmückler and Fritz [40]
b) Brand column [35]
c) Normschliff column [35]

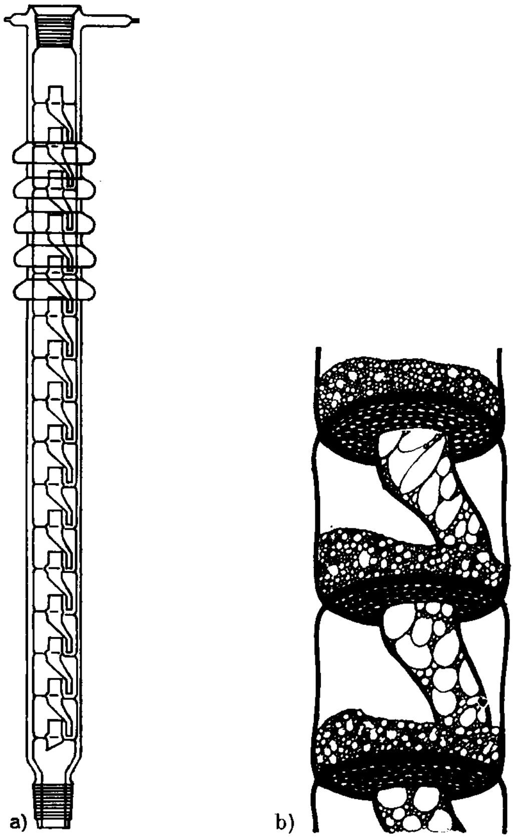


Fig. 268
Sieve-plate column (Oldershaw-Groll)

a) with vacuum jacket and expansion bellows
b) in operation

The plate efficiencies of sieve-plate columns have been determined by a number of investigators under various conditions. Van Wijk and Thijssen [43] tested a column of this type with an I.D. of 38 mm (1.5 in.), having 8 actual plates spaced at distances of 120 mm (5 in.). With the test mixture n-heptane-methylcyclohexane it was found that the plate efficiency fell off markedly when the concentration of one of the components was reduced to about 0.1 mol%. Depending on the vapour velocity (10—27 cm/sec), the plate efficiency had a value between 86 and 75%. At a constant vapour velocity (17 cm/sec) and a concentration in the still pot of $x_B = 50$ mol% the plate efficiency varied with the reflux ratio (0.54 to 1.0) from 65 to 85%.

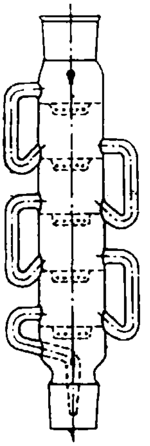


Fig. 269
Sieve-plate column of Sigwart

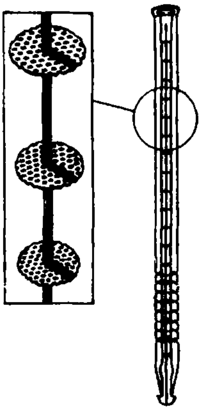


Fig. 270
Perfo-drip sieve-plate column [46]

Umholtz and van Winkle [44] carried out investigations on a sieve-plate column of 25 mm (1 inch) diameter and 50 mm plate spacing. The free cross-section was 16.2%. The highest efficiency was obtained when the diameter of the holes in the plates was 1.9 mm. Tests with an o-xylene-p-xylene mixture showed that the efficiency dropped from 90 to 65% on reduction of the pressure from 750 to 50 mm Hg. When the load was increased the efficiency first rose, but from 200—250 g/cm² h onwards it remained nearly constant. In a later investigation [45] the influence of the plate thickness and of the properties of the mixture (surface tension, density of vapour and liquid) were examined.

A recent form of perforated plate column, the "Perfo-drip" column [46], consists of a tube of very uniform inside diameter into which are inserted a number of perforated plates of stainless steel, fitting onto a central rod so that the plate spacing can be varied at will (Fig. 270). The insert can also be made in Teflon. The column is stated to have a higher efficiency than the Oldershaw one and is easy to clean.

By making the vapour pulsate McGure and Maddox [47] could increase the efficiency of an Oldershaw sieve-plate column of 32 mm diameter and 30 mm plate spacing (each plate having 82 holes of 0.85 mm diameter). For a given system the efficiency depended on the amplitude and frequency of pulsation.

A basic requirement for all plate columns is that the distance between the plates should be sufficient to prevent mechanical entrainment of liquid. Liquid carried upward by the vapour flow would markedly decrease the efficiency. Wagner et al. [48] made experiments with radioactive tracers in a vacuum distillation apparatus to determine non-volatile impurities in the distillate. In connection with mechanical entrainment Newitt et al. [49] made theoretical and experimental studies of the mechanism of droplet formation and of droplet size distribution.

The hydrodynamic conditions prevailing in sieve-plate and bubble-cap columns have been discussed by Melikyan [50].

The properties of the plate columns dealt with above are summarized in Table 31 [35, 38]. Since the plate efficiencies of the various columns have not been determined under uniform conditions, the figures given are not directly comparable; they serve only as an indication of the magnitudes that can be attained.

7.3.4 Columns with stationary elements

In distinction to plate columns, in which the various parts are permanently built in, and packed columns, which contain packing in a random arrangement, the columns to be described now are provided with some loose, regularly-arranged form of solid or perforated contact element.

On a technical scale those inserts are now called packings. On the packing surfaces a thin film is formed by the falling liquid which, in the case of perforated material, gives high degrees of wetting (cf. chap. 4.2). These, in turn, result in the relatively high efficiency of these "wetting columns".

They may be divided into the following types:

a) Columns with continuous glass spirals;
b) Columns containing wire-gauze spirals;
c) Columns containing wire helices;
d) Columns containing Stedman packing and inclined-film packing.

The *glass-spiral column* of Widmer [51] (Fig. 271) was evolved from a column having a syphon closure and concentric tubes described by Golodetz [52]. A basic shortcoming is that it does not operate on the countercurrent principle, and it is not to be recommended. A column designed by Dufton, containing a glass spiral with a pitch diminishing towards its upper end (Fig. 272), has a small hold-up but a relatively low efficiency. Its HETP is generally more than 10 cm.

An appreciably higher efficiency is attained in a column due to Lecky and Ewell [53], which is packed with a *wire-gauze spiral* formed by shaping a strip of gauze in a screw form around a glass centre (Fig. 273). Its HETP is of the order of 1–5 cm, and the hold-up approximately 0.5 ml per theoretical plate. The construction of the spiral, which is not easy, has been described by Stallcup et al. [54]. An insert more easily made is that of Bower and Cooke [55], which is constructed to fit a diameter of about 5 mm. A Monel gauze strip (approximately 120 mesh) is so bent that vertical surfaces stand above each other at an angle of 90°, whilst the horizontal surfaces form two 90° sectors (Fig. 274). A convenient way of inserting the spiral is to moisten it with oil, attach a copper wire to its end and pull it into the column, which should preferably be made of precision bore tube. The oil is removed with a solvent and the copper wire may be dissolved in concentrated nitric acid. Data for this column are given in Table 58.

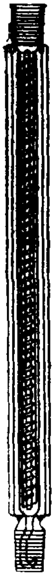


Fig. 271
Widmer's column with concentric tubes and glass spiral

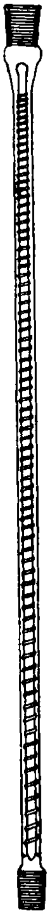


Fig. 272
Dufton column with glass spiral

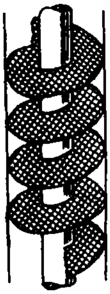


Fig. 273
Wire-gauze spiral column of Lecky and Ewell

The surprisingly small hold-up should be particularly noted. The pressure drop is also relatively low, so that this column is especially valuable for vacuum distillation at pressures down to 1 mm with small charges (6—15 ml).

An insert that is more difficult to construct, but has a higher efficiency, is the wire-wound type of Podbielniak [56], known as "*Heli-grid*" *packing*. It consists of a helix of wire laid as a screw around a central core (Fig. 275), here again it is essential for the packing to make good contact with the wall, so that the reflux does not flow

Table 58

Data for column with wire-gauze insert (Bower and Cooke) (Fig. 274)

Load (ml/h)	HETP (cm)	Hold-up per theoretical plate (ml)
38.5	1.88	0.045
63.0	2.28	
84.0	2.54	
110.0	2.79	0.066

down the outside tube. Heli-grid packing is made for column diameters of 8—30 mm; the wire is 0.25 mm thick and is wound with a spacing of 0.25 mm between the turns. Data for columns with this packing are collected in Table 59. Another form of packing due to Brezina consists of a central pin coated with a glass fabric around which a tube of glass fabric is wound as a spiral. The HETP values lie between 1.60 and 2.37 cm. The high efficiency of Heli-grid packing is due to a film of liquid retained by capillary action between the turns of wire [57].

On account of their extremely low HETP's, even at high loads, Heli-grid columns are of value for analytical distillations. Together with the concentric-tube and multiple-tube columns they constitute the most efficient group of columns at present known.

Another type of element, known as Stedman packing [58], consists of wire-gauze pieces of double-conical shape (Fig. 276a). It also is characterized by a high efficiency coupled with a low hold-up, and it can operate with large loads. The difficulty,

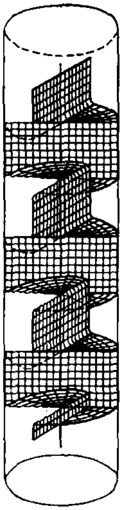


Fig. 274
Wire-gauze insert (Bower and Cooke)

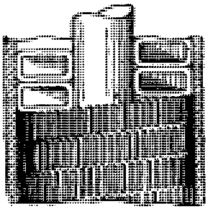


Fig. 275
Podbielniak's Heli-grid packing

Table 59

Data for columns with "heli-grid" packing

Diameter (mm)	Load (ml/h)	HETP (cm)	Hold-up per theoretical plate (ml)
11.0	200	0.9	0.07
	245	1.14	
	315	1.4	
	375	1.64	flooding point
25.0	500	1.0	0.33
	1000	1.25	0.53
	1500	1.58	0.76
	2000	1.90	1.07

again, is to pack it in such a way that the reflux cannot flow down the walls. The use of precision-bore tubing is hence almost essential. The holes a, through which the vapour passes, are on opposite sides of the column. Koch and van Raay [59] constructed a modified form of this packing, consisting of spherical segments and hence possessing some elasticity (Fig. 276b). The rolled edge, on account of its springiness, fits closely to the column wall. It is consequently possible to employ tubes varying as much as 0.5—1 mm in diameter. The original and modified forms, nevertheless, yielded about the same HETP when tested with n-heptane-methylcyclohexane mixture, as will be seen from the figures listed in Table 60.

According to Bragg [60] the theoretical plate number of columns containing Stedman packing of 10—3300 mm diameter can be calculated by the following formula:

$$n_s = 2.8 + \frac{6.5}{L^{0.27}} + \frac{0.5}{L^{0.9}} \qquad (197)$$

in which n_s = specific number of theoretical plates per foot of effective column length; L = amount of reflux (gals/h) at the operating temperature.

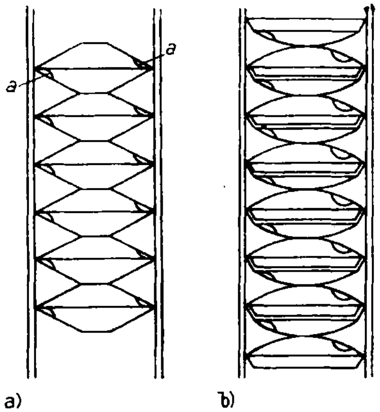


Fig. 276
Stedman packing

a) Original form
b) as modified by Koch and van Raay

Table 60

Data for a column with original Stedman packing and Stedman packing as modified by Koch and van Raay (Column diameter: 25 mm; column length: 1 m)

Packing	Load ($ml/cm^2 \cdot h$)	Reflux ratio	HETP (cm)
Original Stedman	30	∞	1.25
	100		1.96
	200		2.42
	220		2.54
Koch and van Raay	25	40:1	1.43
	50	100:1	1.59
	120	100:1	2.35

A simple form of element is the *inclined-film* packing [61]. Elliptical leaves of stainless steel gauze are arranged as a zig-zag in the column. Here again the vapour holes are diametrically opposite to each other (Fig. 277). The packing is made for column diameters of 15, 30 and 50 mm and has the following characteristics (Table 61).

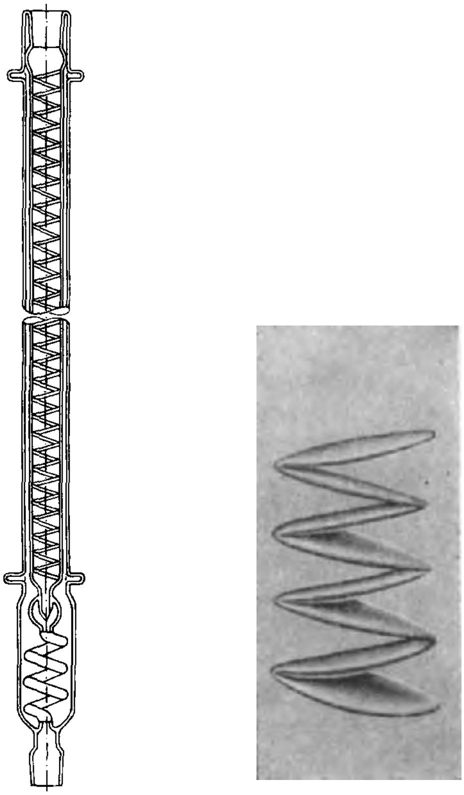


Fig. 277
Column with inclined-film packing

Table 61

Data for a column with inclined-film packing

Diameter	Number of leaves	Reflux (ml/h)	HETP (cm)	Hold-up per theoretical plate (ml)
15	230	250	1.82	0.4
30	115	400	2.40	0.83

Packings are increasingly used in vacuum distillations down to 1 torr on a semitechnical scale. Their chief advantage is high efficiency with low pressure drop. If the packing can be shaped such that the aero- and hydrodynamic conditions remain constant throughout the column operation (*cf.* chap. 4.2) the separating efficiency will be independent of column diameter over a wide range. Following the principle of the Stedman packing inserts structured as fabrics began to be developed [62]. In a newly developed distillation apparatus the Multifil packing was tested by Juchheim [63]. This is a special-steel wire netting with excellent capillary action for the liquid and a free cross section of about 95% for the gas (Fig. 278). The packing is available in standard lengths of 100 mm with diameters from 25 to 87 mm. The number of sections used depends on the required separating length. With electrical heating of a 1 m column 60 theoretical stages (HETP = 1.66 cm) were measured using o-xylene-m-xylene as test mixture. For semitechnical plants Hyperfil packings are supplied in sections of 100 mm length and diameters from 100 to 375 (as a maximum, 900) mm. Their distributing power for the liquid phase is quite satisfactory up to 300 mm diameter. With greater diameters the distribution of the liquid should be enhanced by special arrangements (Fig. 279). For use on a technical scale Huber et al. [64] developed the Sulzer packing which also consists of wire netting or glass-fibre fabric sections. It has regularly arranged flow channels (*cf.* chap. 4.2) which are at an angle to the column axis. Packings consisting of thin perforated metal or ceramic plates are

Fig. 278
"Multifil" wire-netting packing

based on the same principle [64a]. Sulzer packing made of plastic is available in the form of cylindrical synthetic-fibre (polypropylene and polyacryl nitrile) fabric sections of 200 mm length [64b].

A survey of the present state of the various types of Sulzer packing given by Meier [64c] includes a comparison of performances. Besides, the use of heat pumps and the activities of a special laboratory for process engineering are reported. The applications mentioned show the versatility of Sulzer packings, particularly in vacuum distillation.

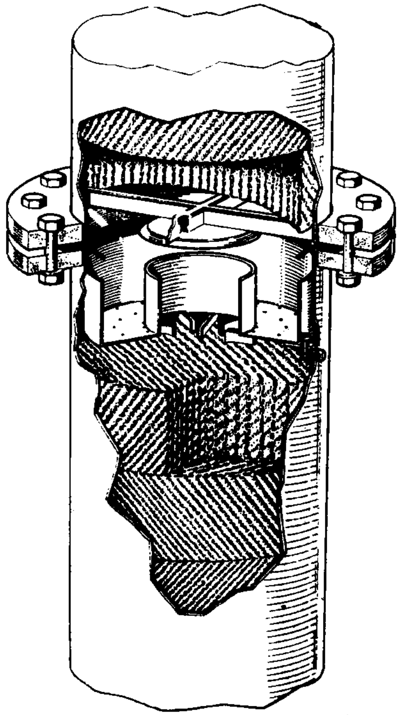


Fig. 279
"Hyperfil" packing

Systematic tests of wire netting inserts with diameters of 28 and 150 mm were made by Timofeev and Aerov [65] for vapour velocities from 0.07 to 0.47 m/s. They varied, above all, the angle of inclination, the flow channel depth and the specific surface.

Besides these wire netting elements which are mostly quite expensive a number of other packings have been developed all of which required that the liquid be evenly distributed over the walls of the packing (Fig. 280). They may be made of expanded metal, glass or some ceramic material. According to Stage (in a prospectus of the ACV) packings with meshes of sizes 6 × 6 and 10 × 10 mm having diameters from 25 to 150 mm are available in short and standard sections of 200 and 1000 mm, respectively. Fig. 281 shows an ACV packing of 200 mm diameter. In Fig. 280 the schematic diagram of the distributing head of a laboratory column is represented.

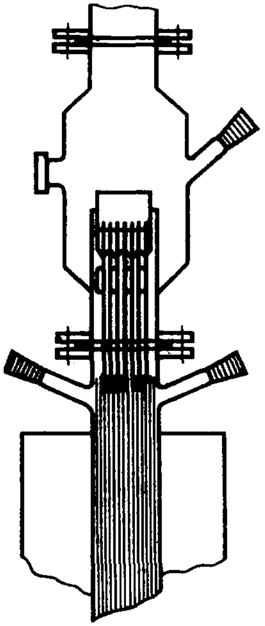


Fig. 280
Diagram of the distributing head of a laboratory column for falling film operation

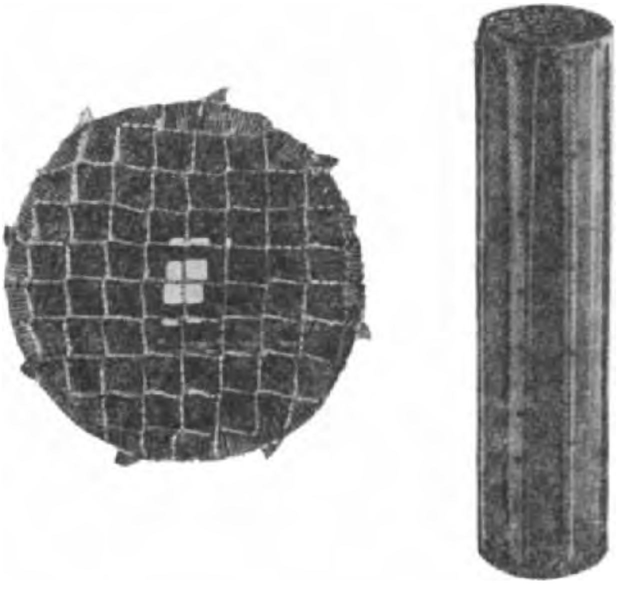


Fig. 281
Wire-mesh packings with diameter 200 mm (ACV)

The packing developed by Kwasniak [65a] consists of zigzag strips of metal which are oriented differently. Endřst et al. [65b] examined a packing made of expanded metal with a mesh width of 10.5 mm. They used a glass column of 50 mm diameter and 1.5 m separating length which was operated at various pressures and loads with chlorobenzene-ethyl benzene as test mixture. At 50 torr they found HETP values of 43 cm and pressure drops of 5 to 15 mm column of water per separating stage. Packings consisting of glass-fibre fabric and metal foils with quartz sand displaying a so-called capillary-hydrodynamic effect were studied by Timofeev et al. [65c] for liquid flow rates of 14 to 600 cm^3/min.

Columns operating on the principle of simple distillation were developed by Shavoronkov and Malyusov [66]. Exchange takes place in packings containing

- vertical channels of circular or rectangular cross section in which the liquid is carried upward by the vapour;
- channels or other guiding structures in which turbulent flow and spraying result in the two phases penetrating each other in their upward flow.

Experimental results and calculating methods are reported. Further it is pointed out that it is particularly difficult to separate a sufficient amount of liquid after each stage. Recent developments are directed at providing uniform channels by introducing the packing into the columns as regularly ordered structures. Thus, using 25 mm Pall rings Billet et al. [66a] obtained considerably smaller pressure drops and twice as high gas velocities at flooding onset as compared to irregular packing.

7.3.5 Columns with rotating elements

Columns provided with built-in, rotating elements were first proposed in 1925. In view of the results of Jost et al. [73] the question has arisen whether this type of column really offers so great advantages over plate and packed columns as well as over columns with stationary elements that further development would seem promising.

Their evolution was prompted by the need to improve the separating effect without increasing the hold-up and the pressure drop. At that time an efficient column was lacking for certain classes of work, particularly for charges of 1—5 g.

The columns belonging to this group can be subdivided into the following types (cf. chap. 5.1.1):

1. Spinning band columns, containing a flat, spiral or cross-shaped rotating metal strip (Fig. 282);
2. Rotating concentric-tube columns, having a stationary and a rotating cylinder separated by a gap of 1—2 mm (Fig. 286);
3. Rotating condenser columns, of which the column wall is heated and in which a cylindrical condenser revolves (Fig. 283);
4. Conical segment columns, provided with rotor and stator elements (Fig. 284);
5. Columns containing rotating wire spirals (Fig. 285).

The first column with a rotating element, constructed by Myers and Jones, was intended for laboratory use and contained conical segments. Urey and Huffmann built a column operating on the same principle for the enrichment of the oxygen isotope ^{18}O; it had a diameter of 15 cm, a height of 10.7 metres and an efficiency corresponding to 500 theoretical stages. Lesesne and Lochte introduced a narrow rotating strip into a tube and thus created the basic model of the spinning band column, which was modified and improved by several constructors.

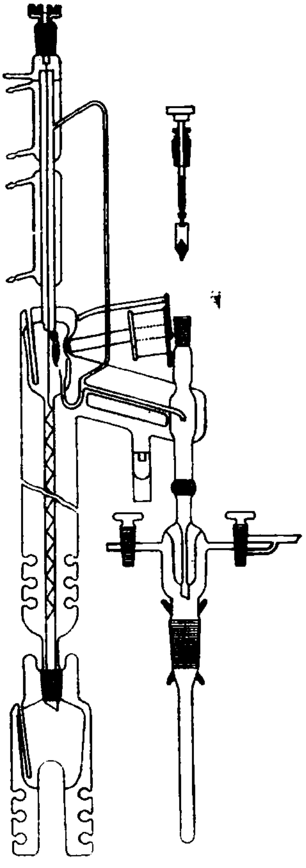


Fig. 282a)
Principle of Abegg's spinning band column

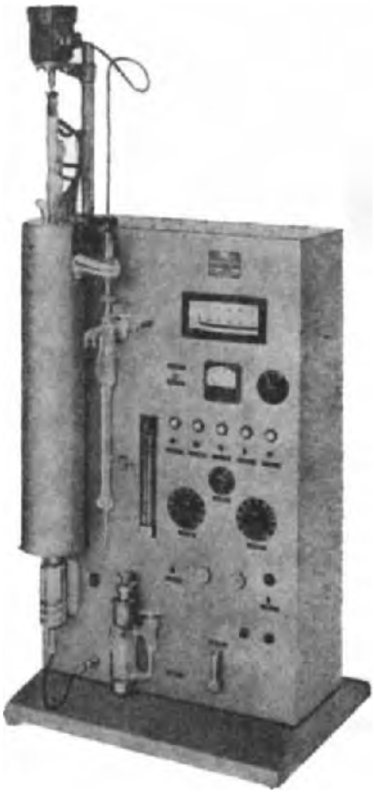


Fig. 282b)
Spinning band column (Abegg)

Fig. 282a gives a schematic diagram of the spinning band column of Abegg. The liquid moves counter to the vapour in the form of a fine spray. This yields HETP values of 2.5 to 3 cm. The band rotates with between 1000 and 3500 r.p.m. The total hold-up of a spinning band column of 375 mm length and 6 mm inner diameter is only 0.2 ml and the pressure drop for 1 m of column height is of the order of 0.5 torr. This makes this type of column very useful for the countercurrent distillation of extremely high-boiling substances since under these conditions decomposition is avoided to a large extent. Spinning band column data are listed in Tables 37, 62, 63

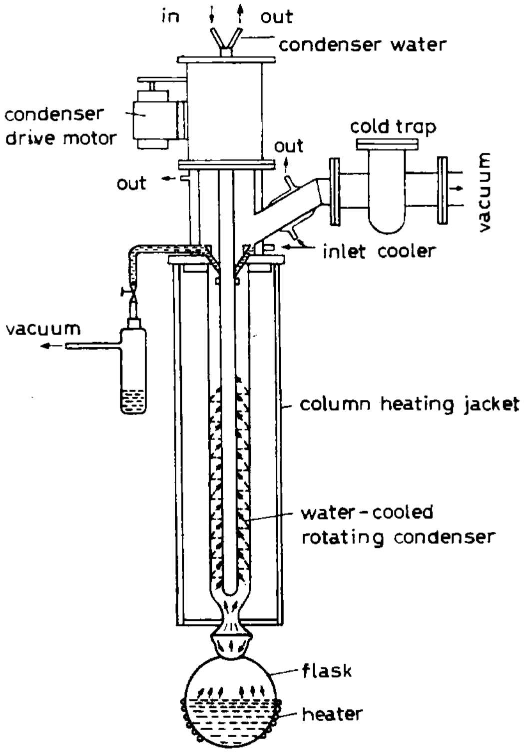


Fig. 283
Rotating condenser column (Byron, Bowman and Coull)

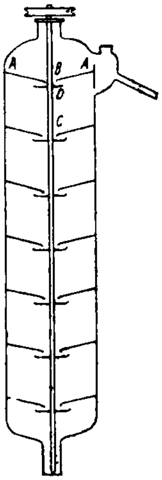


Fig. 284
Conical segment column of Myers and Jones

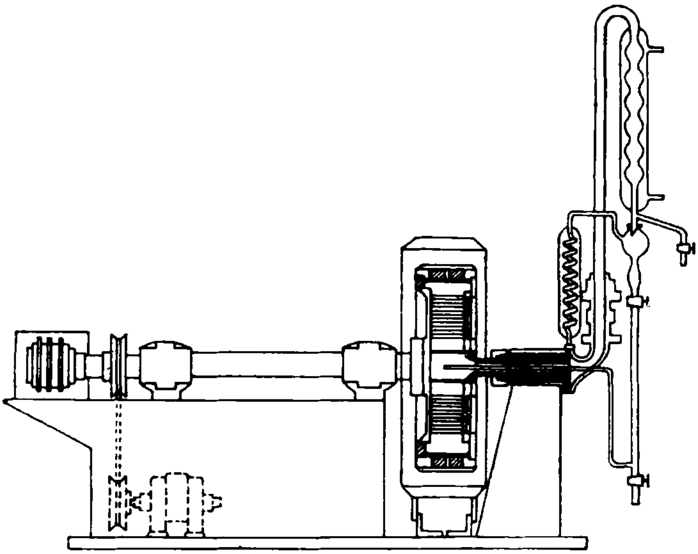


Fig. 285
Wire-spiral centrifugal column of Podbielniak

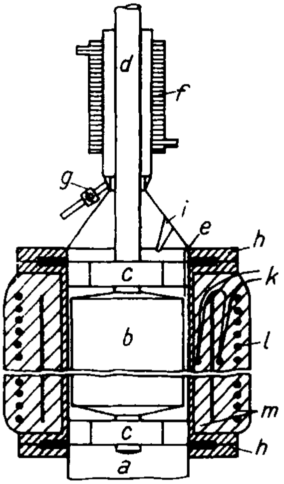


Fig. 286
Rotating-cylinder column (Jost)

a = Flask, b = Rotor, c = Ball bearing, d = Drive shaft, e = Gap, f = Condenser, g = Take-off, h = Flange, i = Thermowell, k = Differential thermocouple, l = Heating jacket, m = Insulation and 64. One disadvantage is that the efficiency decreases strongly with diminishing pressure. Thus, from an operating pressure of 760 torr to 10 torr the drop amounts to 70% [67].

A largely automated apparatus after Abegg (Fig. 282b) with a column of 6.5 mm diameter and 550 mm length has a spiral-shaped springy band of stainless steel or Teflon which rotates with 1400 r.p.m. The reflux is regulated by means of a swinging rod. The total hold-up is about 1.2 ml, the efficiency corresponds to 30 theoretical stages for loads up to 70 ml/h.

The automatic micro-vacuum spinning band column of Messrs. Ernst Haage, of Mülheim/Ruhr, is designed for capacities from 2 to 100 ml. It is made of quartz and has a length of 400 mm (25 theoretical stages) or 1000 mm (50 theoretical stages).

The "centrifugal superfractionator" of Podbielniak [68] contains a rotating spiral and allows higher throughputs to be obtained than with the other columns of this group (Fig. 285).

In the columns mentioned above the purpose of the rotating element is to fling the liquid reflux against the column wall by centrifugal action, to stir the vapour in a horizontal sense, and in some designs to scrape the liquid on the wall; all these factors increase the rate of transfer of matter and heat but they tend to produce a relatively high pressure drop. A different principle was aimed at by Benner et al. [69]. They heated the outer column and placed a cylindrical, rotating condenser inside it. The resulting separating effect is then produced by a continuous process of partial condensation and evaporation along the length of the column. Shortly afterwards, Byron et al. [70] described a similar column (Fig. 283) and developed the theory of "thermal rectification" on which it is based (*cf.* the brush still, section 5.4.3).

Rotating concentric-tube columns were evolved from stationary concentric-tube apparatus (section 7.3.1). Like the latter they consist of two cylinders separated by a gap of 1—2 mm. After Willingham et al [71] had published preliminary work, it was principally Jost [72] who worked on the further development of these columns (Fig. 286). He formulated the hypothesis that the separating effect is not so much determined by the turbulence of the vapour as by the regularity with which the film of liquid flows down. He therefore evolved rotors to which brushes were attached, with the object of obtaining a better distribution of the liquid ([73], Fig. 201). Kuhn [24] and Jost [73] showed that the highest separating effect is produced

1. by homogeneous wetting and a uniform descending film;
2. by a narrow gap, causing a short time of exchange with the vapour.

Further requirements for the proper functioning of all columns with rotating elements are a completely adiabatic operation and a constant speed of revolution of the rotor. There are, however, wide differences in the values that have been reported for the optimum speed of rotation and in the dependence of the efficiency on this speed. As will be seen from Table 62 the speeds of revolution employed vary between 250 and 6000 per minute. According to Jost [73] the number of theoretical stages is dependent on the throughput, on the shape of the rotor and on its rate of revolution. In Table 63 the optimum speeds of rotation at various throughputs have been tabulated. Figs. 287 to 289 show the same data diagrammatically.

Table 62

Data of columns with rotating elements (cf. also Table 37)

Ref. chap. 7	Type	Column height (cm)	Column diameter (mm)	Theor. stages	HETP (cm)	At a load of	ν	r.p.m.	Hold-up, pressure drop	Notes
[73]	cylinder			43	1.2	690 ml/h		2600	0.17 ml/theor. stage, pressure drop: 0.5 torr for 43 theor. stages	gap width 1 mm
[25]	cylinder		12 50		1.7 0.9	100 ml/h 300 ml/h	∞ ∞	800 6000		gap width 1–2 mm gap width 1 mm
[71]	cylinder	58.4	74.4	62	0.935	3000 ml/h		4000	17.5 ml, pressure drop: 2.0 torr	gap width 1.09 mm
[69]	rotating condenser	80		18	4.45				pressure drop: 0.2–0.5 torr	
[70]	rotating condenser	100	75	38.9	2.56	210 ml/h	5			rotor length 1 m, diameter 25 mm heat ratio 20:1
	conical segments	1070		500	2			250/1500		621 rotating elements
[25]	conical segments				1.28	60 ml/h reflux		700/1700		125 rotor elements 124 stator elements
[25]	conical segments				0.93	280 ml/h reflux				
[74]	conical segments	451	200 to 240					320		175 pairs of conical segments

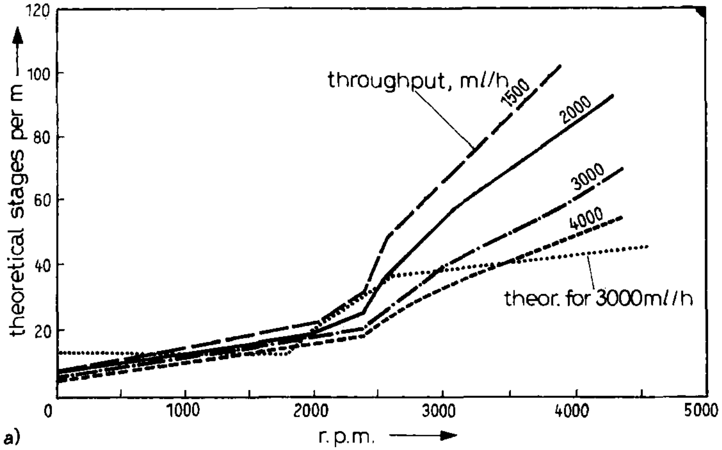


Fig. 287 a)
Relation between the specific stage number n_s and the speed of rotation, with the load as parameter, for rotating cylinder columns [71]

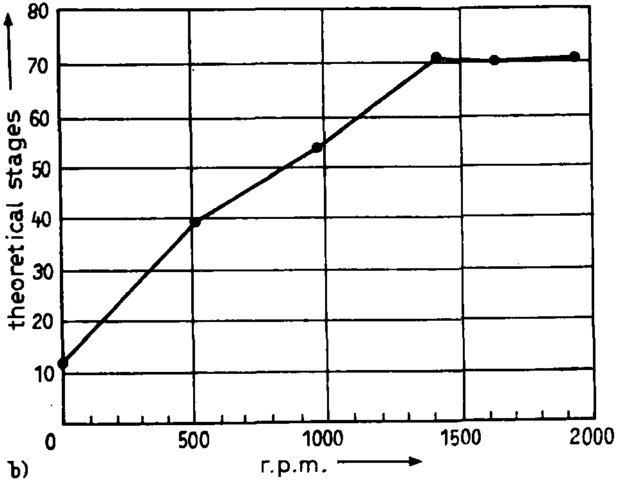


Fig. 287 b)
Relation between the number of stages and the speed of revolution for columns with a star-shaped spinning band [75]

In the case of Jost's rotating-cylinder column the number of stages drops sharply if the speed of rotation is increased beyond the optimum value (Figs. 288 and 289). On the other hand Willingham et al. [71] found a continuous increase in the stage number with the speed of revolution (Fig. 282a). In the USA a rotating cylinder

Table 63

Optimum speeds of revolution for columns with rotating elements

Column type	Type of rotor	Throughput (ml/h)	Range examined (r.p.m.)	Optimum speed (r.p.m.)	References (chapter 7)
Cylinder	with brushes 3b	690	400–2600	2000	
	3b	1330	400–2600	2000	
	4c	690	800–3200	2600	[73]*
	4c	950	400–3000	2600	
	4c	1170	400–2400	?	
	4c	1330	400–1600	?	
Cylinder	smooth gap 1.09 mm	1500	0–4000	2600	[71]**
		2000	0–4000	2600	
		3000	0–4000	2600	
		4000	0–4000	2600	
Spinning band	star-shaped	150	0–2000	1400	[75]***

* Efficiency drops rapidly above optimum speed of revolution.

** Efficiency remains constant from 1400 to 2000 r.p.m.

*** Above 2600 r.p.m. efficiency continues to increase, but the curve does not rise as steeply as between 2200 and 2600 r.p.m.

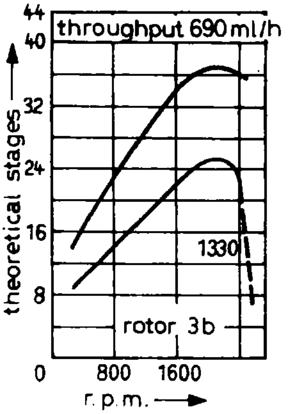


Fig. 288
Dependence of the number of stages on the load and the speed of revolution for Jost's rotating-cylinder column with rotor 3b

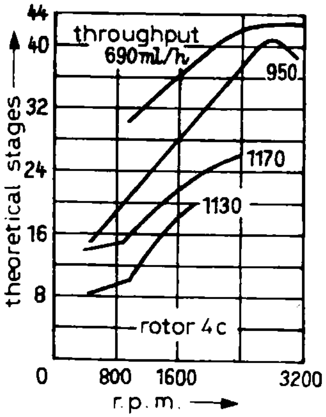


Fig. 289
Dependence of the number of stages on the load and the speed of rotation for Jost's rotating-cylinder column with rotor 4c

column having 500 theoretical stages at 8000 r.p.m. and a throughput of 4 l/h is said to have been constructed. The optimum speed of revolution is thus dependent on the size and construction of the column and especially on that of the rotor (Table 63). Gelperin and Khatsenko [74], for instance, found that in a column having conical segments the stage number remained unchanged above a speed of 320 r.p.m. This seems, indeed, to be about the optimum speed for many designs, since Huffmann and Urey state the speed had little or no influence on the efficiency in the range of 250—1500 r.p.m.

Table 64

Pressure drop in columns with rotating elements

Column			Operating pressure	Pressure drop per cm of column length	Pressure drop per theoretic. stage	References (chapter 7)
Type	Length (cm)	Diameter (mm)	(mm Hg)	(mm Hg)	(mm Hg)	
Spinning band	545	6.7	1	1.3×10^{-3}		
	82	20.0	1	2.0×10^{-3}	$34-710 \times 10^{-3}$	
	145	15.0	0.5	2.0×10^{-3}	4.3×10^{-3}	[75]
Rotating cylinder					11.5×10^{-3}	
Rotating condenser	80		0.005—1.5	4.4×10^{-3}	20×10^{-3}	[69]

The optimum speeds reported for spinning band columns vary between 1000 and 3500 r.p.m.; the shape of the strip here seems to exert an appreciable influence as well as the width. Murray [75], for example, found an optimum speed of 1400 r.p.m. with a star shaped band at a load of 150 ml/h; the efficiency remained constant if the speed was increased beyond this figure (Fig. 287b).

The time to establish equilibrium when starting up a spinning band column is approximately $^1/_2$—1 h; for a rotating-cylinder column Jost [73] also found about 1 hour. Irlin and Bruns [76] go so far as to state that one of these columns, with an HETP of 1 cm, requires an equilibration time of only 6 min. The pressure drops caused by columns with rotating elements are listed in Table 64. For comparison it can be mentioned that a packed column will give a pressure drop in the range of 0.03—1.3 mm Hg per theoretical stage, or 0.005—0.2 mm per cm of column length, depending on the size and shape of the packing, the load and the pressure.

This table shows that columns with rotating elements are clearly superior as regards pressure drop, since the values for packed columns (and even more those for plate columns) may lie several orders of magnitude higher.

The other characteristics of rotating columns are comparable to those of concentric-tube and multiple-tube columns, and of columns with wire-gauze or wire helix elements (sections 7.3.1 and 7.3.4).

From these figures it is seen that the rotating-cylinder column has the most favourable properties for laboratory use, though the high speeds of rotation that are necessary constitute a disadvantage (see Fig. 287a). In operations at reduced pressures the additional difficulty of constructing a satisfactory stuffing-box for the rapidly rotating journal also arises. Attempts have therefore been made to employ an electromagnetic drive.

Höher [77] investigated the dependence of the efficiency and the hold-up on the speed and direction of rotation for a column with a rotating spiral.

The applicability of a rotating column of the Kirschbaum-Stora type with 500 mm diameter which has 8 interchangeable components to semi-technical work was examined by Neumann [78].

Mamin et al. [78a] have reported work on a column for large-scale operation at reduced pressures.

7.4 Condensers and dephlegmators

In laboratory and pilot plant distillation cooling is practised for the following purposes:

1. the total condensation of vapours (condensers);
2. the partial condensation of vapours (dephlegmators);
3. the cooling of liquids (coolers).

In these operations the cooling agent — usually water — takes up and removes heat. The apparatus in all such cases can therefore be regarded as a heat exchanger, since it can obviously also be used to heat the liquid. In accordance with industrial practice this method is sometimes adopted in continuous laboratory distillations for heating the feedstock. If the freezing point of the distillate is higher than the temperature of the cooling water it is necessary to regulate the coolant temperature thermostatically so that no solidification occurs in the condenser. The term dephlegmator is used when the apparatus, with a limited supply of water, condenses only a portion of the vapour; this part is generally returned as reflux to the column, whilst the remaining vapour is liquefied in a subsequent condenser (*cf.* section 5.2.3).

The more important types of condensers have been fixed as to their designs and dimensions by standardization, as is shown in Table 65.

A distinction can be made between inclined and vertical condensers (Figs. 238—*5* and 238—*7*, respectively); in the latter the vapour can be made to enter either at the upper or at the lower end. If vapour enters at the upper end, cooling is very thorough, since the substance passes over the whole surface, and in certain cases the intensity of cooling may even be too great. This arrangement is, however, advantageous in the separation of water from organic liquids. The drops of water do not then remain in the condenser, as often occurs when the vapour enters at the lower end, but are washed down by the distillate. Vertical condensers with entry at the bottom have the advantage that subcooling is prevented and that uncondensable gases can escape without dissolving in the distillate. The cooling water should be made to flow in countercurrent to the vapour if the construction of the condenser allows it.

According to the form of the cooling surface we can distinguish between condensers with a smooth tube, augmented surface, or coils.

1. Condensers with a smooth tube

a) Air condensers (Fig. 238—*16* and *3*) for distillates having high boiling and/or setting points.
b) Condensers with a wide cooling jacket (Liebig; Fig. 238—*5*).
c) Condensers with a narrow cooling jacket (West; Fig. 291).

Table 65
Standardized condensers for distillation apparatus

Standard		Component
TGL 40-344	Sheet 7	condensers, compound consensers
8339	Sheet 1	condensers, technological terms of delivery
	Sheet 2	Liebig condenser
	Sheet 3	spherical condenser
	Sheet 4	Dimroth condenser
		All the above condensers are available with or without standard ground joints
DIN 12575/53		Liebig condenser, tube and cooling jacket fused together
12576/56		Liebig condenser with standard ground joint
12580/53		spherical condenser
12581/56		spherical condenser with standard ground joint
12585/57		coiled condenser
12586/55		coiled condenser with standard ground joints
12591/54		Dimroth condenser with standard ground joints

An efficient air condenser suited to the distillation of substances boiling at least 25 deg. C above room temperature has been described by Toeldte [79] (Fig. 290). The vapour ascends in tube *e* and is cooled by the surfaces *a* and *b*. As the result of being heated the air flows up the central tube *b* by convection and constantly draws in cold air. The liquid seal at the top is filled one-fifth full with a high-boiling liquid; the pressure is equalized through the holes *g*. In all condensers having the cooling surface and the jacket in the form of parallel tubes the greatest rate of heat transfer is obtained if the annular space between the two is kept as small as possible, as is done in West's condenser (Fig. 291), since the degree of turbulence is then greatest for a given flow of coolant. This type of condenser is also available with cooled socket joint (Fig. 291).

2. Condensers with augmented parallel cooling surfaces

In these condensers the cooling surface is enlarged by the provision of indentations, undulations, bulbs or a screw structure.

Examples are:

a) West's condenser with indentations (Fig. 291);

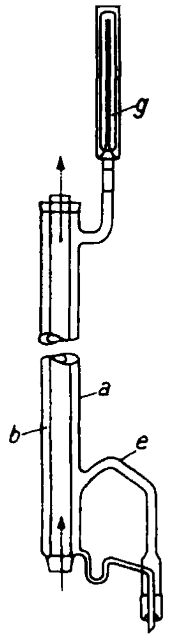


Fig. 290
Air condenser (Toeldte)

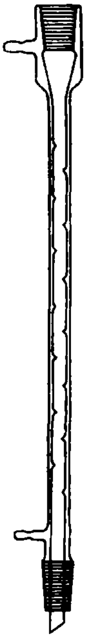


Fig. 291
West's condenser provided with indentations, narrow jacket and cooled ground joint (socket)

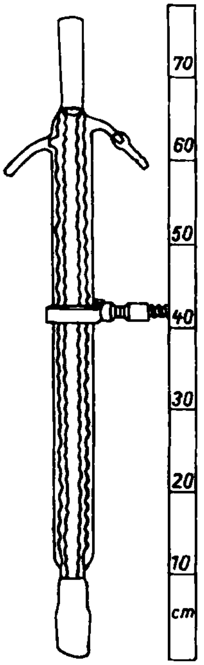


Fig. 292
Condenser with undulating cooling surface

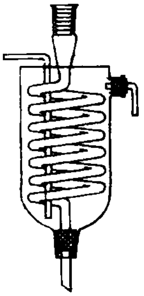


Fig. 293
Staedeler's condenser with vessel for solid cooling agent

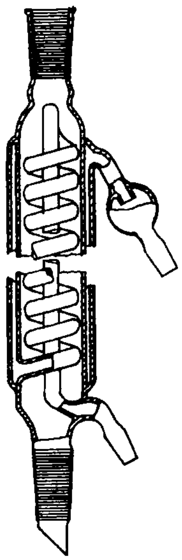


Fig. 294
Compound condenser: Liebig and Dimroth condenser combined

b) Schott's condenser with undulating cooling surface (Fig. 292);
c) Allihn's condenser with cooling surface formed by a series of bulbs (Fig. 238—*15*);
d) Friedrichs' screw-type condenser (Fig. 238—*14*).

3. *Condensers with coils*

a) Condenser with coiled distillate tube (Fig. 238—*6*);
b) Dimroth condenser with coil for cooling medium (Fig. 238—*7*);
c) Staedeler's condenser, provided with a vessel for a cooling agent (Fig. 293);
d) Compound condensers with multiple cooling surfaces.

A coil-shaped condenser is particularly suitable for dealing with vapour at atmospheric pressure. In vacuum distillation this type causes an appreciable pressure drop owing to its narrow cross-section; it is then better to employ the Dimroth form, which furthermore has a high coefficient of heat transfer. The Staedeler condenser, which can be filled with ice or CO_2 snow, is used for condensing very low-boiling substances. For the same purpose one may employ the various forms of compound condensers with multiple cooling surfaces. These condensers consist of several cooling elements placed inside one another, for instance straight tubes inside undulating tubes (Fig. 292), or a coil inside a Liebig condenser (Fig. 294).

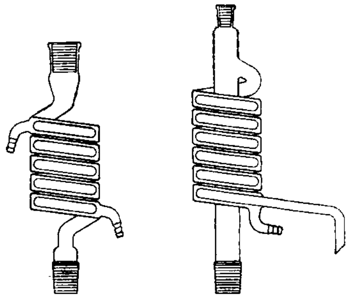


Fig. 295
Henkel condenser and still head with condenser

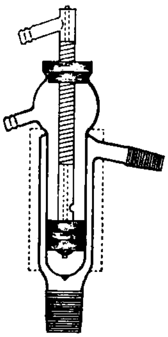


Fig. 296
Dephlegmator with variable cooling surface [80]

The condenser of Henkel [81] has a remarkably large cooling surface as related to its height. It consists of a Liebig or West condenser wound into a coil (Fig. 295) and is a typical compound condenser with a design suitable from the point of view of fluid dynamics and for vacuum work. Having a height of 20 cm it provides 500 cm^2 of cooling surface (cf. Table 66).

When a condenser with a cooled distillate tube is used as dephlegmator the problem is to exactly set the desired reflux ratio. The cooling surface of the dephlegmator shown in Fig. 296 can be adjusted as desired by operating the knurled nut, thus varying the position of the still pot [80].

With condensers made of glass one can count on a minimum heat transfer coeffi-

Table 66

Characteristics of condensers (Eichhorn [86])

Type of condenser	Length (cm)	Condensing area (cm^2)	Length of jacket (cm)	External diameter of jacket (cm)	Internal diameter of tube (cm)	Wall thickness of tube (mm)	Heat transfer coefficient k (cal · cm^2 × min^{-1} · deg. C^{-1})	Rate of heat transfer ε (cal · min^{-1} × deg. C^{-1})
Liebig	20	80	19.5	2.5	1.3	0.9	1.08	86.4
	40	159	39	2.5	1.3	0.9	0.99	157
	70	285	70	3.4	1.3	1.2	0.698	199
	100	425	100	3.4	1.35	1.2	0.652	277
Spherical	20	124.5	21	3.6	1.3	1.2	1.05	131
	30	227	32	3.95	1.25	1.2	1.02	232
	40	288	40	4.0	1.3	1.2	0.725	209
Coiled	20	120	20	3.9	0.75	0.9	1.24	149
	30	200	30	3.9	0.75	0.9	0.87	174
Dimroth coil	20	180	24	3.5	0.7	0.8	1.5	270
	30	310	35	3.5	0.7	0.8	1.42	440
Staedeler		295	25	9	0.75	1.0	0.945	278
Compound	20	220	20	4.05	2.8/1.8	1.0	0.995	199
Soxhlet spherical		200	12	12	7/3.5	1.0	0.87	174
Schott undulating		1137	41	5.1		1.2	0.575	654
Friedrichs screw		205	17	4.5			1.25	256
Bachmann double coil		435	25	4.5	0.35	0.7	0.533	232

cient k of 0.5 cal/cm^2 min. °C, and the required cooling surface area may be estimated by the use of the formula

$$F = \frac{Q}{k \cdot \Delta\vartheta_m}, \tag{198}$$

in which Q = the heat transferred in unit time (cal/min);

F = the area of the cooling surface (cm^2);

$\Delta\vartheta_m$ = the average difference in temperature between vapour and cooling medium.

Strictly, $\Delta\vartheta_m$ should be calculated by the following formula for the logarithmic mean if the condensation is isothermal:

$$\Delta\vartheta_m = \vartheta_2 - \vartheta_1/\ln\frac{\vartheta - \vartheta_1}{\vartheta - \vartheta_2} \tag{199}$$

where ϑ = the saturation temperature of the vapour (°C);

ϑ_1 = the temperature of the cooling water on entering;

ϑ_2 = the final temperature of the cooling water.

Extensive measurements on the efficiency of condensers have been performed by Friedrichs [83], Friedrichs and v. Kruska [84] and Mach and Herrmann [85]. According to recent investigations of Eichhorn [86] the heat transfer coefficients of glass condensers with a length of 200—1000 mm are from 0.5 to 1.5 cal/cm² min. °C. It is obvious that the heat transfer coefficient decreases as the condenser length increases so that it seems reasonable to have two small condensers instead of a large one. These should be supplied with cooling water separately since the drop of the heat transfer coefficient is due to the cooling water being more strongly heated with longer condensers.

The Dimroth condenser and the Friedrichs screw condenser, which give *k* values of 1.5 and 1.25 respectively, can be considered to have a good efficiency. The effectiveness of the Jena condenser with undulating tubes is a result of its very large cooling area (1 136 cm²); its heat transfer coefficient, 0.575 cal/cm² min. °C, is only moderate.

Table 67

Heat transfer coefficients for industrial glasses

Heat exchange	k (kcal $\cdot$ m^{-2} $\cdot$ h^{-1} $\cdot$ deg $\cdot$ C^{-1})
Condensation of vapours in condensers	250—300
Cooling of liquids	150
Cooling of gases	50

Brezina [82] dealt thoroughly with Liebig condenser designs and efficiencies. He derived a new mathematical relation for the examination of the efficiency of this type of condenser and suggested a measuring device for condenser tests.

By using formula (198) and the values of *k* listed in Table 66 the reader can carry out calculations for individual types of condenser; it is, however, always advisable to allow a margin of 50% above the area so found. Purchased condensers as a rule have very liberal dimensions.

However, heat exchangers for semi-technical and pilot plants have to be calculated exactly, the more so because the cooling surfaces are assembled from standardized components. For this purpose, the manufacturers of glass components give the heat transfer coefficients *k* as listed in Table 67.

For the assembly of larger cooling surfaces a variety of components, mostly in the form of coils with nominal widths from 40 to 450 mm, are commercially available.

7.5 Adapters; still and column heads

The vapours evolved in a boiler are led away, their temperature is measured and they are finally condensed. In simple distillation the auxiliary components used for this purpose are adapters and still heads. In countercurrent distillation it is also necessary to return reflux to the column and to measure the reflux ratio. Special column heads have been designed to perform these tasks. Of the numerous forms in which these components exist only a restricted number can be mentioned, so chosen as to illustrate the main differences.

7.5.1 Adapters

Adapters form the connection between the condenser and the receiver, and are usually provided with a vacuum connection (Figs. 238—*17* and *10*). The vacuum adapter of Anschütz-Thiele (Fig. 238—*8*) has given satisfaction and has been proposed for standardization in Germany. This adapter is also very useful for work at atmospheric pressure, as it allows any number of fractions to be taken (*cf.* chap. 7.1).

7.5.2 Still heads

In simple distillation still heads form the connecting link between the still pot and the condenser. As a rule they have provision for a thermometer. Fig. 238—*1* and *13* show common types. Those having a ground joint for the thermometer are to be preferred, as they ensure that the thermometer bulb will always be in the same position in the vapour tube, a fact of importance in comparative distillations.

A number of still heads have been standardized. Table 68 lists the respective specification sheets. Some examples are shown in Fig. 297.

The Claisen still head has two tubes with B 14 sockets, of which that on the right is used for the thermometer, that on the left for a boiling capillary, a stirrer or a dropping funnel (Fig. 236). This head has proved satisfactory for distillations both at normal and reduced pressures. The right-hand tube is sometimes lengthened so as to form a Vigreux column or a short column that may be packed with rings or spirals (Fig. 298). The column functions principally as a spray trap, as does the pear-shaped head (Fig. 239a) and a bulb-shaped head filled with rings (Fig. 299). Special still heads have been developed for dealing with foaming liquids (Fig. 239b). For steam distillation Prahl's still head, which has a steam injection tube (Fig. 300), may be

Table 68

Standardized still heads

Standard	Component
TGL 9974	still head with one lateral tube
9975	still head with one parallel tube
9977	bridge-type head with ground joint for thermometer
9979	Claisen still head with lateral ground joint
9980	still head with fused-on Liebig condenser
9981	still head with fused-on Dimroth condenser
13840	still head after Prahl
40-353	still head for steam distillation
DIN 12594/54	still heads with standard ground joints

used. Some still heads having fused-on vertical or inclined condensers (Figs. 240 and 301, respectively) are still manufactured. Those having inclined condensers require a good deal of lateral space, so that vertical condensers are frequently preferred. With a bridge as still head (Fig. 238—13 and 297c) and a coil or screw-type condenser the apparatus becomes appreciably shorter and more convenient.

The still head of Henkel (Fig. 295) takes up only little space. It is manufactured in several versions [81]. Further possibilities have been described in detail by Gemmeker and Stage [87].

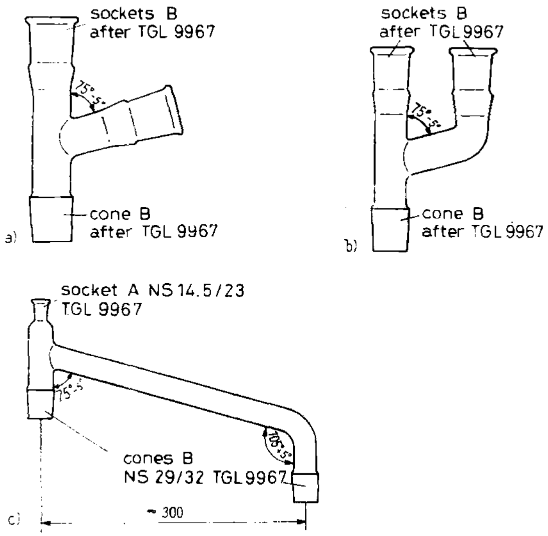


Fig. 297
Still heads

a) with one lateral tube
b) with one parallel tube
c) bridge-type head with ground joint for thermometer

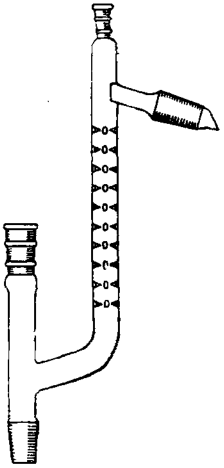


Fig. 298
Claisen still head with short Vigreux column

Fig. 299
Bulb head filled with Raschig rings

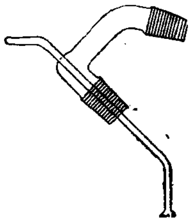


Fig. 300
Still head for steam distillation (Prahl)

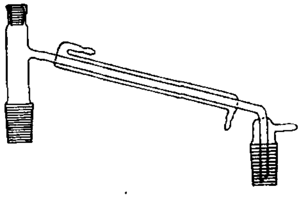


Fig. 301
Still head with fused-on condenser, vacuum connection and joint for receiver

For semi-technical and pilot plants the still heads are usually made up of the same components as those required for the assembly of lengths of piping (*cf.* chap. 7.2). Gases and liquids are introduced into the columns by means of feed lines or tubes provided with an annular rose (Figs. 138 and 142).

7.5.3 Column heads

Column heads form the link between the column and the condenser. They are used in countercurrent distillation and are therefore provided with devices for regulating and measuring the reflux ratio.

According to the way in which the reflux is produced we can distinguish between column heads for *partial* and *total* condensation [88]. A column head for partial condensation has been described in a previous part of the book (Fig. 171). In low-temperature distillation dephlegmators are commonly used since the product is often withdrawn in the gaseous state. The column heads are designed to meet this requirement (*cf.* chap. 5.3.1). As was stated in section 5.2.3, total condensation is the soundest method and it is the one most used in laboratory distillation, especially if large reflux ratios have to be maintained.

According to Thormann [19], Gemmeker and Stage [87] and Schneider and Schmidt [89] the requirements that a column head should satisfy may be summarized as follows:

1. The reflux ratio should be easily adjusted and measured.
2. The hold-up of the column head should be small.
3. The construction should be simple and sturdy; the device for distributing the reflux should not be subject to leakage or obstruction.
4. It must be possible to measure the vapour temperature with accuracy.
5. The reflux should flow back into the column at (or only slightly below) its boiling point.
6. The column head should be suitable for use both at atmospheric and at a reduced pressure.

It should be possible to measure the column load at any moment. The measurements should still be reliable at loads above 500 ml/h, when the liquid as a rule no longer flows in drops but as a continuous stream. A particularly important point is the accuracy of the temperature readings; to ensure this, the head should be so constructed that liquid from the condenser cannot reach the thermometer bulb and that the pressure at the point of temperature measurement is the same as that at which the pressure is read. A flowmeter may be used to check the rate of the cooling water (section 8.6), as excessive sub-cooling leads to a "false" reflux.

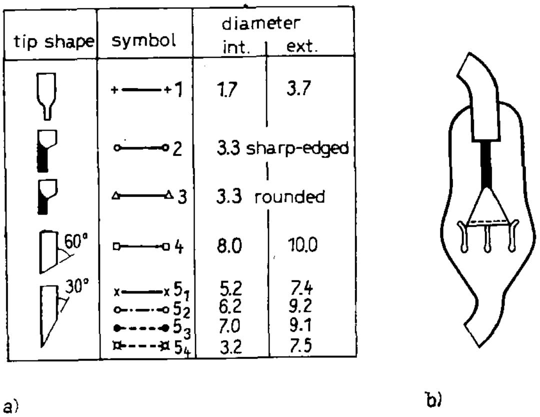
Fundamental considerations concerning the distribution of small amounts of liquid in columns for the transfer of matter have been put forward by Kloss [89a].

The methods adopted by designers of column heads in attempting to attain accurate proportioning and measurement of the reflux are the following.

1. The production (and counting) of drops falling from points, from tubes having having oblique ends or from capillary tubes.

2. The separate production of liquid reflux and distillate by condensation on two condenser surfaces in parallel.
3. Regulation of the amounts of the reflux and the distillate in the required ratio by causing these two portions to flow through capillary tubes of different lengths or diameters.
4. Automatic reflux control by mechanical means or by electronic time switches.

The *drop-production method* is that which has been most used for column heads. Schneider and Schmid [89] have systematically investigated drop-counters of various shapes (Fig. 302), and (using gasoline as liquid) have arrived at the results shown in Fig. 303. The latter figure clearly indicates that some forms of drop-counters give a considerable variation of the drop size with the load.



tip shape	symbol	diameter int.	diameter ext.
	+——+ 1	1.7	3.7
	○——○ 2	3.3 sharp-edged	
	△——△ 3	3.3 rounded	
60°	□——□ 4	8.0	10.0
30°	×——× 5_1	5.2	7.4
	○-·-○ 5_2	6.2	9.2
	●----● 5_3	7.0	9.1
	☒----☒ 5_4	3.2	7.5

a)

b)

Fig. 302

a) Shapes of drop counters examined by Schneider and Schmid

b) multiple tip for loads greater than 500 ml/h

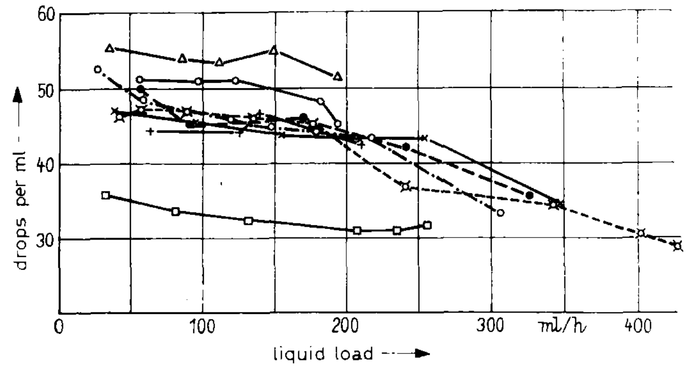


Fig. 303

Relation between the number of drops and the liquid load for drop counters of various shapes (liquid: gasoline)

In the author's Destinorm column head (WP DDR Nr. 8234, DB-Patent-Nr. 1011177) capillary tubes are used as drop-counters, whilst the distillate and reflux can also be measured volumetrically. The use of a capillary tube that has been ground flat and polished is in accordance with accepted stalagmometric practice and the short length of the capillary ensures that the hydrostatic pressure remains small (Figs. 128, 162).

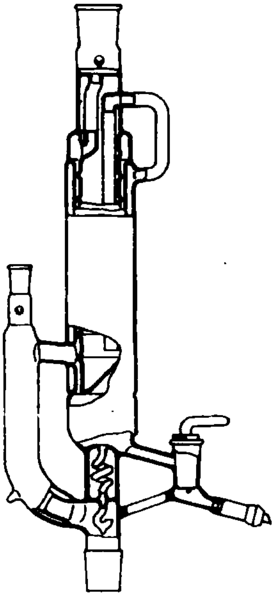


Fig. 304
Column head for apparatus working at atmospheric and reduced pressures

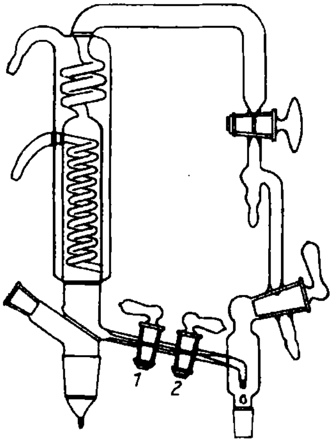


Fig. 305
Column head of Rehn and Theilig
1 = regulating tap, 2 = stopcock

Since most organic liquids of technical importance have a surface tension in air of 20—40 dynes/cm at a temperature just below the boiling point, these capillary drop-counters will give drops of about 4—5 × 10^{-2} ml, *i.e.* there will be 20 to 25 drops per ml. The higher the surface tension, the larger the drops formed.

Other examples of devices employing the drop-counting method are the Jena column head and the Normag head [91]. In the redesigned Jena head (Fig. 304) the vapour enters the condenser in the lower part, which may be coupled with additional condenser units. The tap for distillate take-off has a PTFE plug which is provided with a conical slit. The plug is graduated and the rim of the tap bears a mark so that a reproducible and precise setting of the reflux ratio is ensured. The Normag column head due to Rehn-Theilig (Fig. (305) is based on a well-known form of construction — the collecting collar or weir. A useful feature of this head is the provision of two taps in the distillate tube. The one on the left serves to control the reflux, the one on the right is for complete closure. The regulating tap is usually of the fine-adjusting type, being provided for this purpose with conical slits or multiple channels [92]. For a more accurate control, Schneider and Schmid [89] in their column head (Fig. 306) employ a ground-in glass needle valve. The column head shown in Fig. 305 may also be provided with needle valves the development of which has been described by Kramer [90]. Further variants are Teflon spindles (Fig. 247) and bellow-type valves (Fig. 248). The measurement of the reflux ratio is carried out with drop-counters ground off to an angle of 60° (Fig. 302, 303).

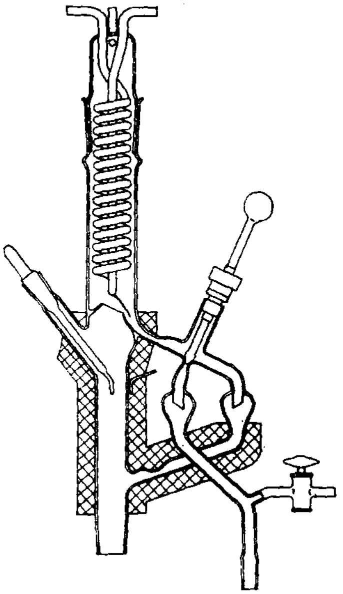


Fig. 306
Column head of Schneider and Schmid with glass valve

A column head due to Hübner [93] incorporates an ingenious combination o, condenser and distillate cooler. Sliding the condenser in the valve cone (Fig. 307) which is cooled simultaneously, controls the amount drawn off. The slope of the condenser results in a small total height of the apparatus and a low dead volume. The device used for changing the receiver also appears to be somewhat better than that of Anschütz-Thiele.

The principle of the "Corad" (constant ratio) head [94] (Fig. 308) is as follows. The reflux condenser has at its lower end a number of drop-forming tips a of various widths and can be rotated as a whole in its ground joint, so as to bring any one of these tips above the small collecting funnel b. In this manner different amounts of distillate, corresponding to certain reflux ratios, can be taken off, though accurate control of reflux ratio depends on the absence of channelling on the condenser surface. The removal of distillate can be interrupted by turning the condenser to a position in which the liquid misses the funnel.

The *automatic column heads* are based on a time cycle; by electronic or mechanical means (*cf.* section 8.4) the device is alternately switched for a definite period into each of two positions; the periods in question determine the reflux ratio. This requires that the evaporation rate is also kept constant by appropriate means (*cf.* chap. 8.4). Two types of automatic column head can be distinguished. In the first, the vapour is divided into two parts, which are separately condensed as reflux and distillate. In the second, the vapour is first completely condensed and the liquid is then divided in the proper proportion.

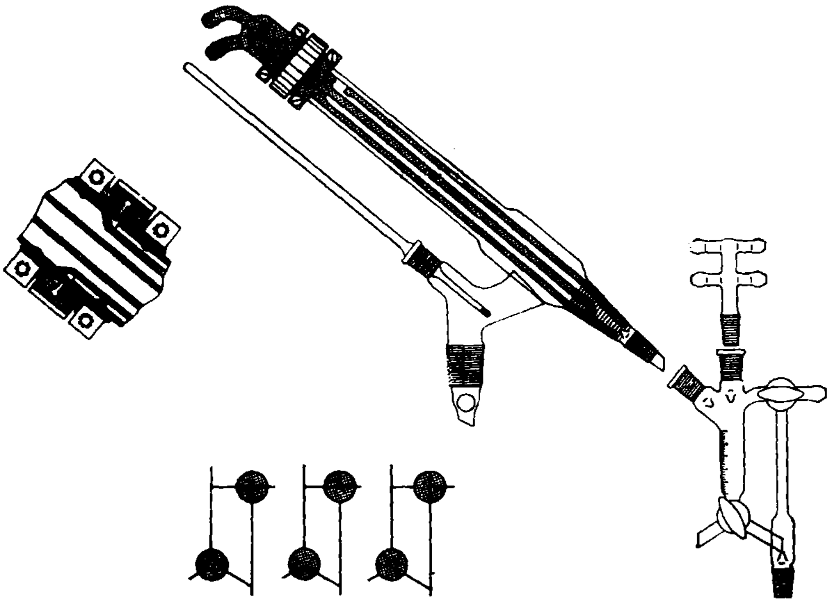


Fig. 307
Hübner's column head with combined condenser, distillate cooler and valve cone

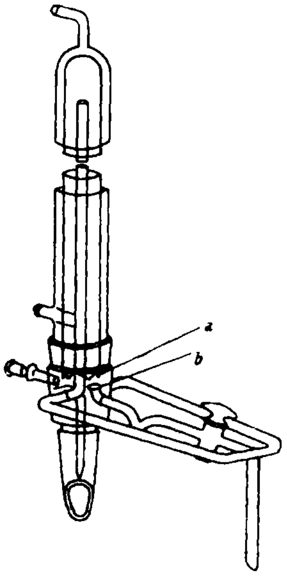


Fig. 308
"Corad" head of Lloyd and Hornbacher with separate cooling surfaces for reflux and distillate
a drop-forming tip, *b* = collecting funnel

As opposed to all other column heads the automatic forms have the advantage that they do not usually contain taps, so that there can be no contamination with grease. Furthermore they allow the reflux ratio to be set rapidly and reliably at any desired value. The hold-up is very small. Large reflux ratios, from about 30:1 up to 100:1, may be adjusted accurately, whilst with valves (even of the fine control type) the adjustment becomes extremely difficult above a ratio of 30:1.

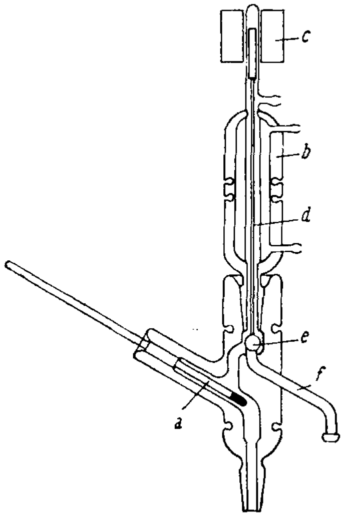


Fig. 309
Automatic vapour dividing head (Collins and Lantz)

a = ground-in thermometer, *b* = reflux condenser, *c* = solenoid, *d* = valve tube, *e* = valve, *f* = connection to distillate condenser

Fig. 309 (cf. also Fig. 257b) shows the vapour dividing head of Collins and Lantz [95]. The ascending vapour flows past the thermometer *a* to the reflux condenser *b*. A solenoid *c*, actuated by a time relay, at definite intervals pulls up the rod *d* connected to the small ball valve *e*, which is ground into seats at the top and bottom, so that a certain fraction of the vapour flows through tube *f* into the distillate condenser. This method is useful for azeotropes demixing in the liquid state. By dividing the homogeneous vapour phase the compositions of the azeotropic mixture remain unchanged. The principle of vapour division is employed in the two Normag azeotropic column heads (Fig. 232a and b).

Experiments performed by Collins and Lantz have shown that vapour division gives a smaller reflux ratio than liquid division when the time ratios are the same. The former method requires that no "false" reflux shall be formed in the column head; with this object it is carefully insulated by means of a vacuum jacket. On this account it is desirable in very accurate work to perform preliminary experiments to determine the corrections that must be applied to the calculated reflux ratio.

In Stage's [97] column head for vapour division which is provided with two magnetic valves the reflux ratio corresponds exactly to the pre-set times the valves are alternately open and closed (Fig. 310).

The method of liquid division is most usually followed. Automatic equipment utilizing this principle has been designed to operate with cone-and ball-valves, with swinging rods or with swinging funnels, all actuated electromagnetically. Fig. 311 gives an example of a system employing valves [96]. The ascending vapour is liquefied in condenser *a*. When ball-valve *b* is closed the condensate returns to the column. A solenoid *c* raises the valve-rod *d* at intervals in accordance with the reflux ratio and the liquid then flows past valve *b* to the receiver. The two valves *e* serve instead of cocks to close the receiver and are stated to function properly at pressures down to 10 mm Hg. Stage [97] uses single and double valves as well as sliding disks.

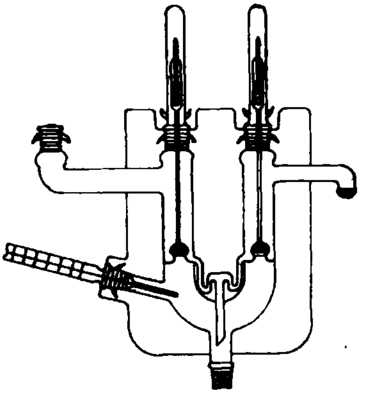


Fig. 310
Stage's column head [97] for vapour division with two magnetic valves and siphon

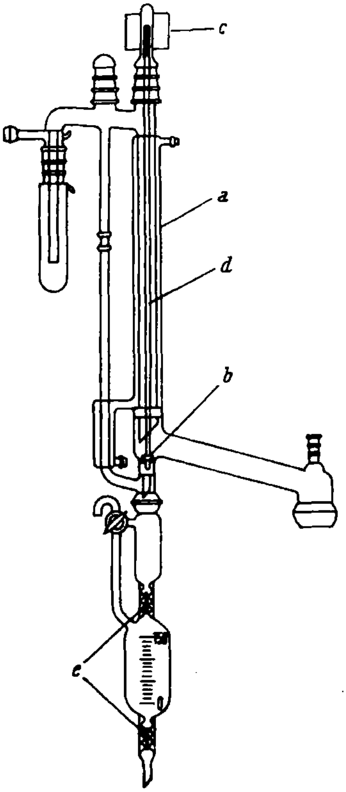


Fig. 311
Column head of Kieselbach for liquid division

a = condenser, b = ball-valve, c = solenoid, d = valve-rod, e = valve

The spinning band column of Abegg (Fig. 282) employs the principle of the swinging rod. The condensate produced on the surface of the vertical condenser flows down from its end along a short rod, which is pivoted from it and contains a soft iron core. Normally the liquid flows back into the column, but when attracted by an electromagnet the rod is deflected and the condensate falls into a funnel leading to the receiver. A more satisfactory system, capable of dealing with higher loads, is obtained by the use of a *swinging funnel;* the author's automatic column head (Fig. 312) is of this type. It was designed in such a way that the vapour flow by-passes the control mechanism; the condenser is mounted at a low level so that space *a* can contain no vapour that might interfere with the mechanism. The swinging funnel *c* can be detached from a short ground joint (not shown in the figure), whilst the connecting rod and iron core can be removed through joint *e*. Any defects can thus be rectified easily. The jacket *g* connected to funnel *f* allows low-boiling substances to be cooled and distillates of high melting point to be warmed. The column head regulates the reflux ratio with an accuracy of ±2%.

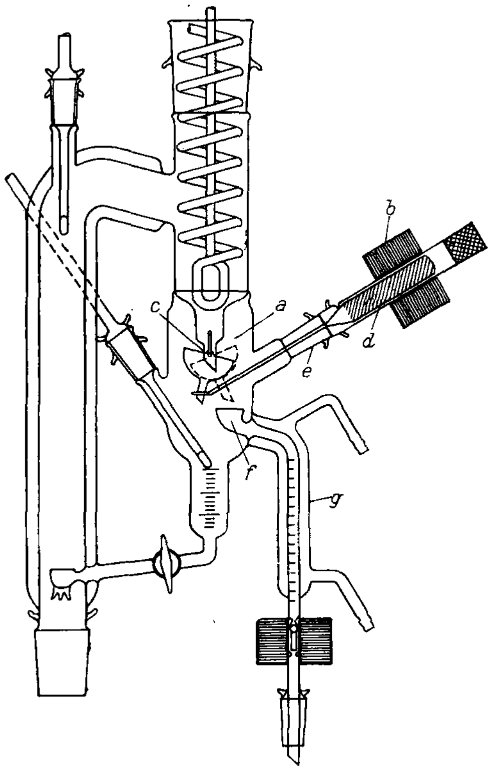


Fig. 312
Krell's automatic Destinorm column head with swinging funnel

Another column head makes use of mechanical regulation by means of a slowly moving shaft. The pivoted rod which is moved to and fro by a periodically screened jet of air delivers the distillate alternately to the column and the take-off [98].

Column heads of semi-technical plants are made up of separate condenser and reflux units. The valves are operated mechanically and, more commonly, electromagnetically. Their operation is similar to that in laboratory column heads (Figs. 306, 247). The valves are controlled automatically by means of electromagnets, electromotors or pneumatic drives (Fig. 248). For the automatic division of liquid, however, the swinging funnel is chiefly used (Fig. 142) which is actuated by an electromagnet placed outside the column wall. With the magnet switched on the distillate is taken off laterally.

7.6 Still pots, receivers and fraction collectors

The components to be described next are the first and last links in the chain of distillation apparatus. The still pot contains the substance to be distilled and the receiver and the fraction collector take up the purified and fractionated distillate, respectively.

7.6.1 Still pots

For laboratory distillation ordinary standardized, round-bottomed flasks provided with ground joints are used. They may have short or long necks and nominal capacities up to 500 ml. The Engler (Fig. 235) and Saybolt flasks (TGL 0-12363) are examples of special devices designed for standardized distillation techniques. In addition, a distilling flask with capacities from 25 to 1000 ml (TGL 0-12364) has been standardized (Fig. 313).

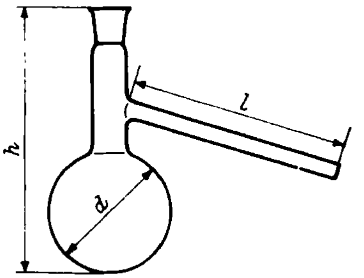


Fig. 313
Distilling flask, TGL 0-12364

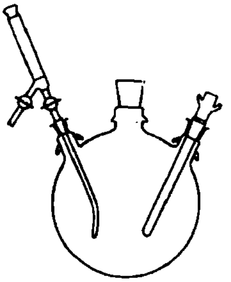


Fig. 314
Three-necked flask with thermometer well and sampling device

Long-necked flasks are used mainly for simple distillation (Fig. 313); in the absence of a column the long neck acts as a spray trap. Flat bottomed flasks should not be used for vacuum distillation because of the danger of collapse. For countercurrent distillation short, round-bottomed flasks with three necks are the most suitable. The two side-necks, provided with B 14 ground joints, are required for the thermometer, for filling and emptying, for a boiling capillary, for a gas or vapour inlet tube and for the removal of samples. The axes of the side-necks meet the axis of the centre neck at the bottom of the flask, so that there is space for these components if the column is surrounded by an insulating jacket. The necks should preferably be provided with hooks for holding the ends of retaining springs over the joints, to avoid loosening owing to sudden pressure. If it is necessary to change the thermometer during a distillation, or to avoid the use of thermometers with ground joints, a thermometer well may be employed (Fig. 314). A little oil should be put in the well to promote heat transfer.

The charge should be at most two-thirds of the volume of the flask in distillation at atmospheric pressure and not more than half in vacuum distillation.

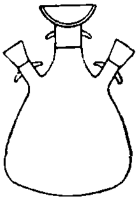


Fig. 315
Flat-bottomed flask with ball joint

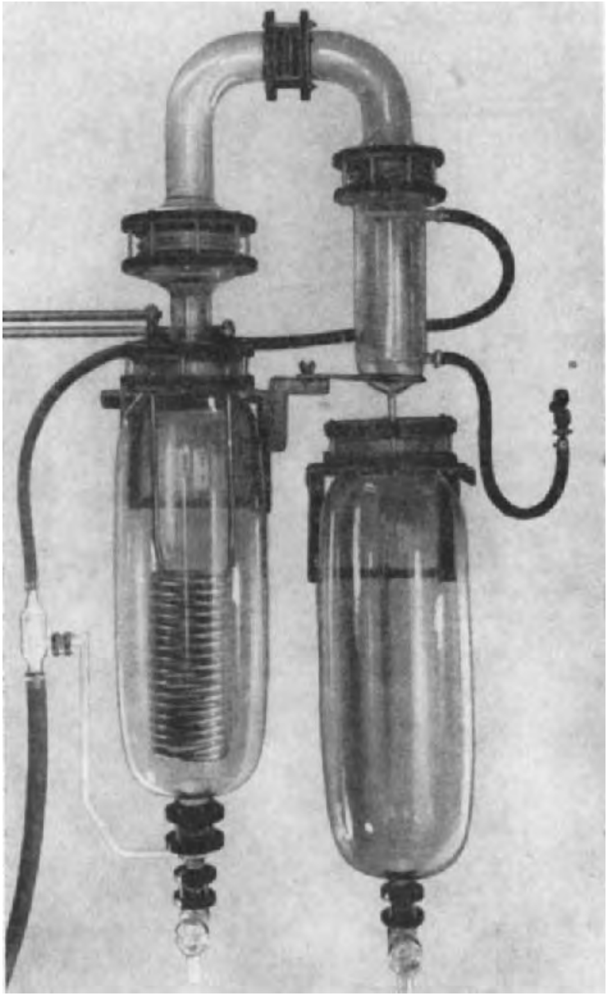


Fig. 316
Jena suspended vessels (16 to 150 l) as still pots

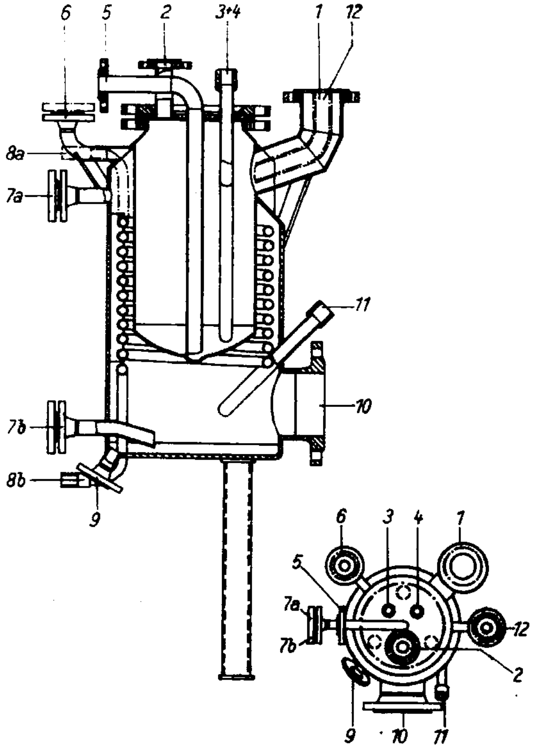


Fig. 317
Metal boiler with welded-on oil-heated jacket (Stage [98])

1 = joining socket for column, *2* = socket for pressure measurements, *3*, *4* = sockets for temperature measurements, *5* = outlet socket, *6* = socket for oil expansion vessel, *7a*, *b* = joining sockets for circulating pump, *8a*, *b* = joining sockets for cooling water, *9* = outlet socket for oil, *10* = socket for heater, *11* = sockets for temperature measurements, *12* = inlet socket for oil

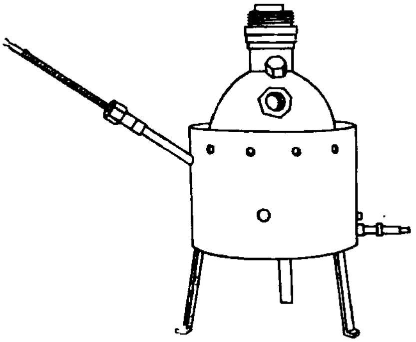


Fig. 318
Armoured glass flask with metal-bath heating

For micro- and semi-micro-distillation smaller flasks are frequently necessary. As a rule these are made with pointed bases, in order that distillation may be continued down to a small residue (Fig. 127).

Flat-bottomed flasks have proved to be favourable (Fig. 315) since the evaporating surface remains almost constant down to the residue whereas in round-bottomed flasks the liquid surface decreases more and more as the level sinks.

For continuous distillation a satisfactory arrangement consists of a flask provided with an overflow tube, which maintains a constant liquid level and through which the bottom product is continuously drawn off.

In low-temperature distillation it is usual to employ cylindrical flasks which are generally placed inside a Dewar vessel (Figs. 173, 175, 176, 180). Other forms of flask may sometimes be necessary, depending on the method of heating (section 7.7.2).

For semi-technical plants of glass, short-necked round-bottomed flasks of capacities up to 4 l and three-neck round-bottomed flasks of capacities up to 10 l (TGL 10102) are available. The glassware manufacturers can now offer spherical distilling flasks and cylindrical vessels with capacities up to 200 and 375 l, respectively. Connection pieces may be placed at the top, at the side or at the bottom. Cylindrical vessels are usually provided with caps which hold the connection pieces.

Fig. 316 shows suspended vessels which are available in sizes of 16 to 150 l [1, 5]. Adapters for connecting the necks to ball and conical ground joints can be purchased for both types. Flasks of this size are best heated by steam, by some kind of bath, or by electric immersion heaters or mantles.

For combustible or explosive substances the use of a stainless steel boiler is advisable. A metal vessel developed by Stage has a nominal capacity of 10 to 200 l (Fig. 317) and is provided with a jacket for oil-bath heating. Here again an adapter is available for joining the ground flange to a glass ball joint. If the use of glassware is essential on account of corrosion, an armoured glass flask heated in a metal bath gives the greatest safeguard against explosions (Fig. 318). Such flasks are made in sizes from 1 to 20 litres [99]. The flask is surrounded by a metal jacket and the intervening space is filled with bismuth or an alloy. The metal bath ensures an even transfer of heat; two opposed sight-glasses allow the contents of the still to be seen.

7.6.2 Receivers and fraction collectors

Practically any form of vessel may be used to collect the distillate (Fig. 238). For measurement of volume it is preferable to employ graduated cylindrical receivers (Fig. 238—9) which can be provided with a jacket for dealing with high-melting or low-boiling distillates; the jacket also encloses the drain cock (Fig. 319). In accurate work it is always advisable to include a distillate cooler and to jacket the receiver, so that the amounts of distillate can be measured at the same temperature. In distillation at normal pressure the receivers should be in communication with the atmosphere, at reduced pressures they are connected to the vacuum line. A satisfactory arrangement is that shown in Fig. 320 where the vacuum connection is also cooled [100]. By means of Bredt's rotating receiver (Figs. 238/*11* and 321) and that of Brühl (Fig. 238/*12*; *cf.* also Figs. 127, 130) it is possible to collect 4 and 7 fractions, respec-

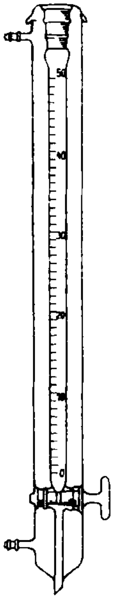


Fig. 319
Receiver with jacket

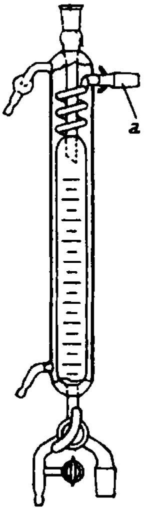


Fig. 320
Receiver with jacket and cooled vacuum connection *a*

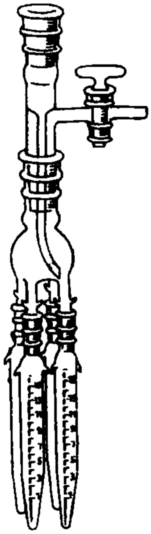


Fig. 321
Bredt's rotating receiver with graduated tubes

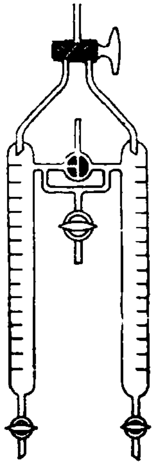


Fig. 322
Stage's receiver for vacuum distillation

tively, in vacuum distillation without interrupting the operation. Any number can be collected with the Anschütz-Thiele adapter with interchangeable receivers (Fig. 238-8, *cf.* section 7.5.1). Fig. 322 shows Stage's receiver for vacuum distillation and Figs. 137 and 142 illustrate the arrangement used for work on a larger scale; the latter again obviates interruption by the provision of vacuum and air connections. The receiver of Rock and Jantz is also of the "pig" type and has a magnetic switch-over device [101] (Fig. 323). The magnet *a* attached to the ring *c* pulls the rod *d*, hanging from hook *b* to the appropriate receiver. This arrangement has the advantage that the distillate does not become contaminated by tap grease. For taking off gaseous distillates in low-temperature distillation special devices are used (Figs. 183 to 185).

Of late *automatic fraction collectors,* as employed in chromatographic work, have also become of importance in distillation at atmospheric pressure. These devices generally have a rotating table, on which test-tubes are arranged in a circle or spiral. The principles according to which they can function are the following:

1. drop counting;
2. control of the volume by a syphon or photo-electric cell;
3. control by time.

Modern fraction collectors can mostly be employed selectively according to these three principles. Pneumatic devices are also available now for work in rooms where the danger of explosions is great.

In the automatic collectors based on *drop counting* a falling drop brings about an electric contact or activates a photo-electric cell. The resulting pulses are passed through a relay to a counter, which can be so set that after any desired number of drops a mechanism releasing the table is set in motion, whereby the latter moves on to the position of the next receiver. At the same time the counter automatically returns to zero.

In analytical work it is common practice to collect fractions of a definite volume and to read the distillation temperature at each cut. The volume of the fractions depends on the size of the charge and generally lies between 1 and 20 ml. Whilst fractions of 1 to 5 ml can be collected satisfactorily by the drop-counting method, those above 5 ml are best obtained by *syphon control* (Fig. 324). To a measuring vessel 1 a syphon is connected, which draws off the liquid as soon as it has reached a certain level. The stream of liquid flows past a photo-electric cell 2-3, that passes on its pulse to a relay. The latter, after a delay of a few seconds, moves the rotating table on. The collecting vessel 1 in the author's apparatus is provided with a plunger with which its capacity can be regulated to within 0.1 ml, so that it is unnecessary to change the vessel for samples of different volume.

The fully automatic fraction collector of Grassmann and Deffner [102] functions by *photo-electric volume measurement.* A pencil of light measures the volume directly in the test-tube (Fig. 325); this volume can be regulated between 0.5 and 8 ml (with an accuracy of one drop, 0.03 ml) by raising or lowering the light source *L*. The mechanism changing the receiver is actuated by the photo-electric cell *K* when it is struck by the light reflected down (via the walls of the tube) from the meniscus *M* as this passes the light source, the round bottom of the tube acting as a collecting lens.

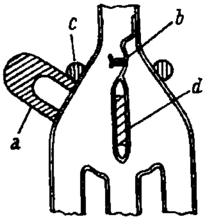


Fig. 323
Receiver with magnetic control (Rock and Jantz)

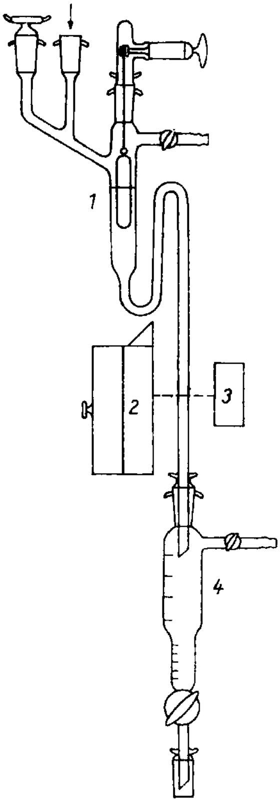


Fig. 324
Syphon arrangement according to Krell with volume regulation by plunger

1 = collecting vessel with plunger,
2 = photo-electric cell, *3* = light source,
4 = measuring pipette

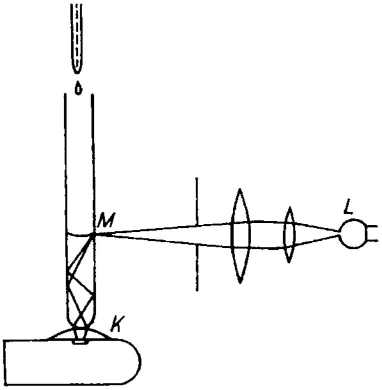


Fig. 325
Photo-electrically operated fraction collector of Grassmann-Deffner

M = meniscus, *L* = light source,
K = lens and photo-electric cell

For the measurement of small volumes in the order of 1 ml the pulse required for operating the table can also be obtained from the current passing between two electrodes [103]. The current required is extremely weak (about 0.1 micro-ampère) and the method can therefore be used for most liquids except the hydrocarbons. The error is said to be not more than 0.1%.

In the *time-regulating method* the table is merely made to rotate one step further at certain intervals of time. If fractions of the same volume are to be collected this procedure obviously entails an accurate regulation of the speed of distillation. It has proved particularly satisfactory in micro-distillations (Fig. 257b).

7.7 Insulation and heating devices

In order to start and maintain a distillation a continuous supply of heat is required. This goes principally to preheat the feed, to form reflux and to evaporate the fractions. A further part of the heat is consumed in compensating for heat losses. When the temperature of distillation lies below 100 °C, these losses can as a rule be sufficiently reduced by good insulation only, but at higher temperatures some form of heating inside the insulation becomes necessary.

Thus we distinguish these heating systems:

- the heating of still pots and flasks;
- the heating of feed-stock and bottom;
- insulation.

Stage and Gemmeker [104] have dealt with all aspects of evaporation and heating, including numerous constructional details.

7.7.1 The heating of still pots and flasks

Still pots may be heated either directly by gas or electricity or indirectly by a heat carrier. Bunsen burners are now as a rule used only for heating small flasks, as in an Engler distillation (Fig. 235) or micro-distillation. When foaming liquids have to be distilled a Bunsen burner is also useful, as it can be manipulated in such a way that "puking" of the flask contents is counteracted. Large flasks are now rarely heated by gas, firstly because of the danger of superheating, secondly because an accurate temperature control is not easy to achieve with gas heating and thirdly besause of fire risk. These difficulties may to some extent be avoided by placing asbestos wire-gauze below the flask or surrounding it by an air bath [105]. Heat transfer then takes place more uniformly by conduction from the hot gases of combustion. By the use of a chimney (Fig. 326) the heat of the flame is utilized economically.

Electrical heating, on the other hand, is easily regulated. It can be applied in various forms:

1. by open and encased heating elements;
2. by shaped heaters;
3. by immersion heaters;
4. by infrared radiation heaters.

Hot-plates with bare heating elements have the advantage of providing sensitive control, as is necessary, for instance, when the heat input is controlled by the pressure drop over the column (*cf.* section 8.4); a covered hot-plate in this case has too long a temperature lag, which may result in flooding. It is advisable to leave an air space between the hot-plate and the flask and to avoid heat losses by radiation as far as possible (Fig. 327).

Another form of heating are the so-called "mirror cookers" or electric Bunsens. These "burners" depend on the concentration of the radiation emanating from an

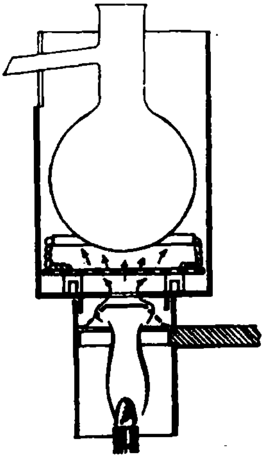


Fig. 326
Hübner's air bath

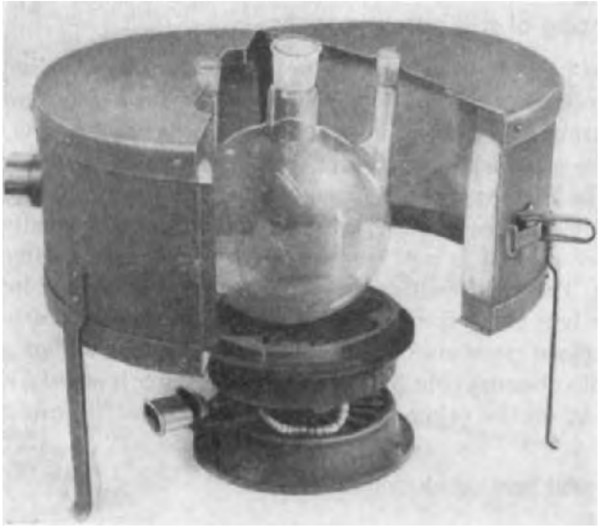


Fig. 327
Destinorm flask-heating unit

electric heater to a point by reflection from a concave mirror [106]. The temperature is adjusted by means of a regulating shield ("electro-tap"). With Hoffmann's [107] burner temperatures up to 800 °C can be reached.

Heating elements with resistance wires conforming to the shapes of the surfaces to be heated are known as shaped heaters (Figs. 149, 184). If the contents of the flask are to be stirred electromagnetically an apparatus such as the one shown in Fig. 328 is convenient; it combines a hot plate and a magnetic stirrer.

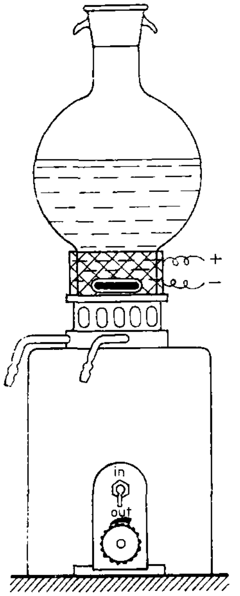


Fig. 328
Hot-plate magnetic stirrer

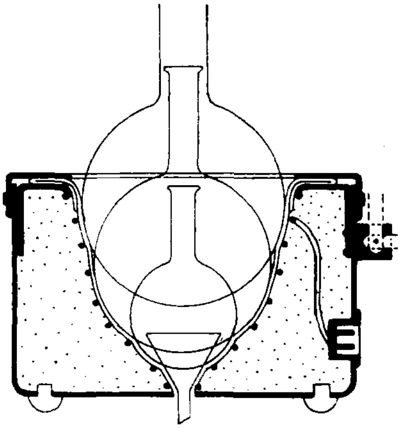


Fig. 329
Multi-heating jacket for temperatures up to 450° C

When combustible or explosive substances have to be distilled, flexible heating mantles provide additional safety; they can be obtained in individual sizes or the multi-size design can be employed for various sizes of flask. The heating elements are secured in a glass fabric; the maximum temperature is about 400 °C. In the multi-size mantle a system of circular springs gives the flask a secure seating, and an opening in the base prevents the formation of air cushions and allows the heater to be used for flasks with a bottom drain and for funnels (Fig. 329) [108]. The proximity of the heating jacket to the wall of the flask ensures a good transfer of heat and helps to prevent bumping, especially in the case of viscous liquids.

Efficient heat transfer is also a feature of *immersion heaters* (*cf.* chap. 7.6.1). This type of heating requires the presence of heating wells. Fig. 147 shows a water still having a heating element made of quartz. In another construction the flask has a well in its base containing a vertical heater (Fig. 330). Junge's "Intus" heater (Fig. 331) is equipped with an immersion heater passing through a central opening in its top and projecting down into an extrusion in its base, so as to allow distillation to be continued to a small residue. The flask, however, is surrounded by a container filled with insulating material and it is consequently difficult to watch the contents. Good mixing of the liquid is ensured by the use of a flask with circulation heating (Fig. 332). The well for the immersion heater has a layer of glass powder fused onto its surface to promote regular ebullition. Immersion heaters such as the THQ 6 heater of VEB Jenaer Glaswerk Schott & Gen., Jena, with a rating of 6 kVA (*cf.* chap. 5.1.3.3) may also be used in semi-technical and pilot plants.

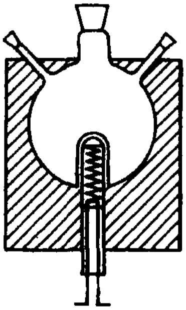


Fig. 330
Flask with immersion heater in its base

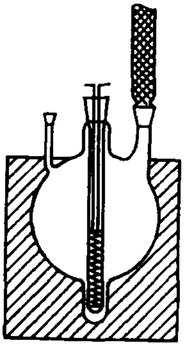


Fig. 331
Junge's flask with immersion heater

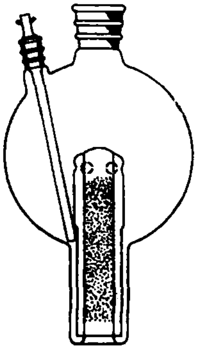


Fig. 332
Flask for circulation heating

At the present time the methods of heating based on conduction are being replaced to some extent by the gentler and more uniform method of radiant heating and especially by *infrared lamps.* Among the latter we can distinguish between bright radiators, which have the shape of a large electric light bulb and are most commonly used in the 250 Watt rating, and dark radiators in the form of a metal tube, with ratings up to 1000 Watt. By the use of several bright radiators temperatures up to 300 °C can be established. Dark radiators are easier to adapt to the surface to be heated and in particular have proved valuable for micro-distillation. A distinct advantage of infrared heating lies in the extremely small differences in temperature that occur between the outer and inner walls of the glass vessel heated. The methods of infrared heating have been described by Klees [110].

Indirect heating of the flask by a heat carrier should always be considered if direct heating is not advisable for reasons of safety, or if a very even transfer of heat is essential for the prevention of local superheating. It should, for instance, be employed for preference if a low-boiling light fraction is to be separated from a high-boiling residue, as a drastic increase in temperature after removal of the "tops" can otherwise scarcely be avoided. Indirect heating can be carried out by the use of open liquid baths (Fig. 203), or by passing a heat carrier through a coil in the flask (Fig. 333) or through a jacket surrounding it (Fig. 334). If high-pressure steam is not available for temperatures above 100 °C, low-pressure steam may be superheated as described in section 6.1. Liquid heat carriers, such as glycerin, lubricating oil or triglycol, are heated by being passed through a directly heated coil (Fig. 317) or a coil placed in a bath. In glass-made pilot and semi-technical plants steam and fuel oil are chiefly used as heat carriers. Fig. 335 shows immersion heaters with and without stirrers. The following substances are suitable for open baths.

Substance	For temperatures
Water	up to 80 °C
Oil	up to 330 °C; *cf.* Table 46
Salt mixtures	150—500 °C; *cf.* Table 46
Sand	any temperature
Metal alloy	above 70 °C; *cf.* Fig. 318

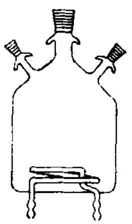


Fig. 333
Destinorm flask provided with heating coil

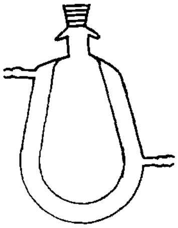


Fig. 334
Destinorm flask with heating jacket

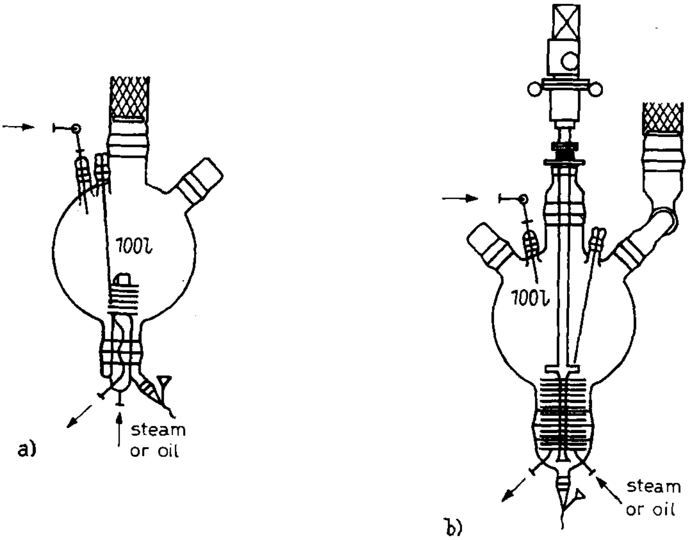


Fig. 335
Immersion heaters for pilot and semi-technical plants

a) without stirrer b) with stirrer

It should be noted that it is very difficult to control the temperature of a sand bath, and that when using salt or metal baths one should remove the flask before the bath has solidified. Some suitable alloys for metal baths are:

Wood's metal (M.P. 71 °C): cadmium 1—2, tin 2, bismuth 7—8 parts;

Rose's metal (M.P. 95 °C): bismuth 2, lead 1, tin 1 parts.

Mercury and alloys containing large amounts of lead should not be employed, owing to their poisonous nature.

7.7.2 The heating of feed-stock and bottom

In continuous distillation the incoming feed-stock has to be heated to a temperature corresponding to the point at which it enters the column (Figs. 142, 167). If this temperature is not higher than 100 °C, it is often possible to use an ordinary coil-type condenser (chap. 7.4) as heat exchanger, a liquid of constant temperature being passed through the coil. Conversely, the liquid to be heated may be run through a coil immersed in an oil bath controlled by a thermostat. Semi-technical and pilot plants made of glass usually employ coils which are protected against displacement. These devices are operated with steam (3 atm. overpressure, 147 °C) or fuel oil (maximum temperature, 220 °C) (Fig. 336). The upper connection serves as steam inlet, the lower as condensate outlet. The left-hand upper connection is used for temperature measurements.

Fig. 138 shows a pre-heater with external electric heating coil and Fig. 337, the Labodest VD 2 pre-heater which is provided with an electric immersion heater. These units may be operated at a base load, the regulating load being controlled via contact thermometers and relays (*cf.* chap 8.2.2).

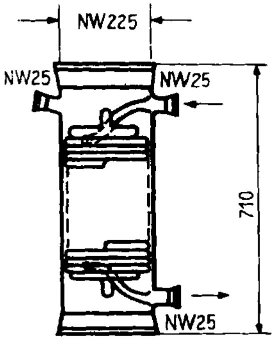


Fig. 336
Heating coils with protection against displacement

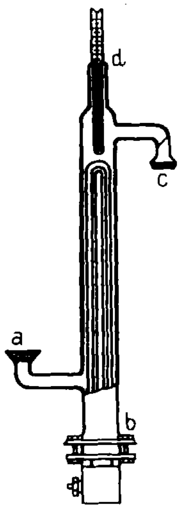


Fig. 337
Labodest VD 2 pre-heater with immersion heater flanged to it

In continuous operation the bottom may be heated as shown in Figs. 328 to 335. By employing circulation heating the amount of column bottom and particularly the mean residence time can be decisively reduced [104]. Some possible designs using vertical or inclined immersion heaters are demonstrated in Fig. 338. The Labodest horizontal circulation heater (Fig. 339) was designed for vacuum work with high-

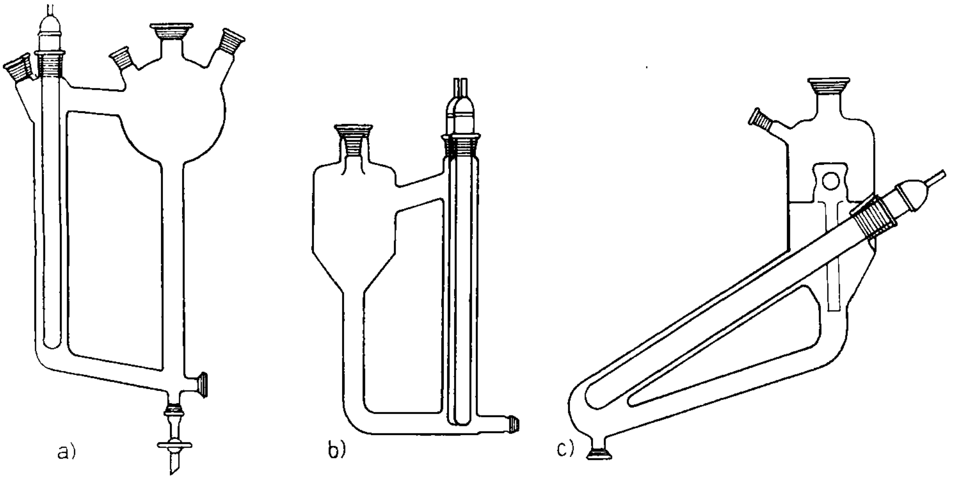


Fig. 338
Circulation heaters with vertical and inclined immersion heaters
a) "Normschliff" model b) "Normag" model c) "Schmidt" model

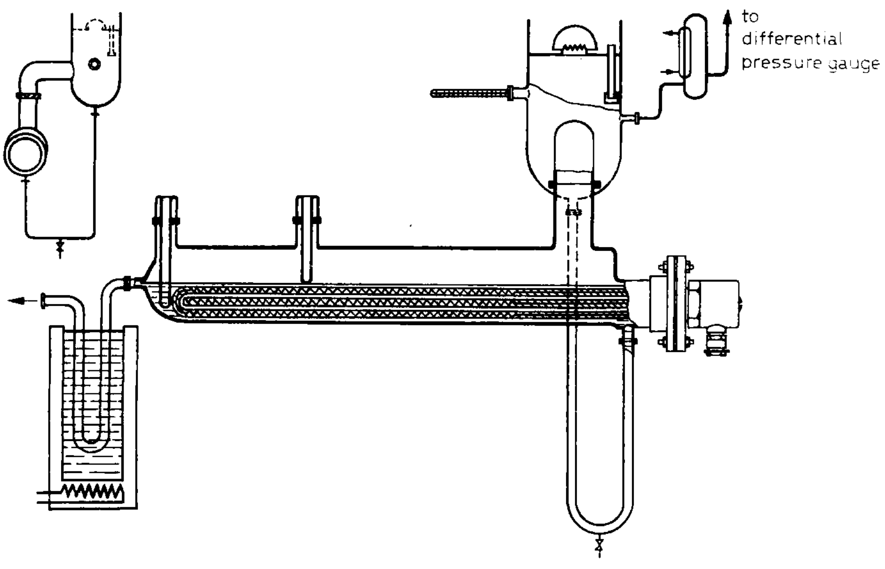


Fig. 339
Labodest horizontal circulation heater with separate pipes for vapour and reflux (Stage)

boiling liquids. It has separate pipes for the vapour and reflux. This arrangement is particularly suitable for large-scale plants. Circulation heating is appropriate for pilot plants as well, as can be seen from Figs. 141 and 142.

7.7.3 Insulation

The vapour ascending from the boiler should in general reach the condenser without the introduction or removal of heat, other than by exchange with the reflux. When the usual insulating materials are used this requirement can be satisfied sufficiently closely up to a temperature of about 100°C only; above this temperature, heat must be supplied to make good what is lost by convection and radiation to the surrounding air. The still pot and all parts of the apparatus up to the condenser should therefore be insulated. Proper insulation not only improves the sharpness and reproducibility of the separation in question, but also ensures that the heat is economically utilized (*cf.* section 4.12).

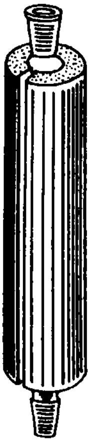


Fig. 340
Semi-circular glass-wool sheaths for insulation

The following means of insulation for laboratory and semi-technical apparatus are available.

a) Coatings of a material having a low heat conductivity;
b) Vacuum jackets;
c) A jacket containing a heat carrier in circulation [111];
d) Electrical heaters in an insulating jacket.

In simple forms of distillation, not requiring an accurate control of the reflux ratio, asbestos cord is still largely employed as insulation in the laboratory. As a rule it is applied in too thin a layer; the thickness should amount to about 50—60 mm (2 inches). More convenient in use are lengths of pipe insulation made of glass wool, which are easily fitted to the column and can be cut to any desired length (Fig. 340). Around these sheaths a layer of glass-fibre tape is wound. If a loose material such as magnesia or mineral wool is to be used, a metal jacket is required as container. The efficiency of insulation is improved if the column is first coated with a reflecting sheath of aluminium foil. Insulating jackets of the above-mentioned type are, however, good enough only for operating temperatures not exceeding 80 °C; the same applies to air jackets.

Vacuum jackets provide satisfactory insulation up to 150 °C or more if they are evacuated to 10^{-4}—10^{-6} mm Hg [112]. They are usually silvered inside to reduce radiation. The quality of the silver layer has a great influence on its efficiency. A strip of 5—10 mm width is often left clear in the silvering for purposes of observation, but it should preferably be only 2 mm wide. A much better method is to place metal cylinders or curved aluminium foil in the jacket. Perforated foil is claimed to provide the same insulation as a completely silvered surface and has the advantage of allowing all parts of the column to be seen [113]. If it is essential for some reason to have an unobstructed view of the column contents, no other course is open than to dispense with the silvering or foil. Then it is advisable to keep the jacket constantly evacuated to the high vacuum mentioned above by connecting it to a diffusion pump. Commercial vacuum jackets should be checked to ensure that they are sufficiently evacuated.

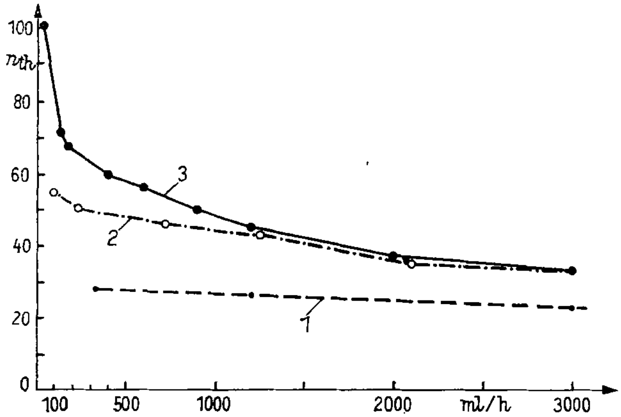


Fig. 341

Relation between load and number of theoretical stages, n_{th} [141]

Test column: length 1200 mm, diameter 25 mm, with silvered vacuum jacket

1 = wire-gauze packing with large mesh size, DNW 1, for small pressure drop, *2* = wire-gauze packing with small mesh size, DNE 2, *3* = packing as in 2 but with electric compensation heating jacket

The strain produced by the difference in expansion of the outer and inner walls of a vacuum jacket is reduced if the outer tube is provided with expansion bellows (Figs. 257b, 282), or the inner tube with an expansion coil. If the column has diameter of less than 10 mm and a length of more than 500 mm, or if the temperature exceeds 150 °C it is advisable to wind an electric heating tape around the outer wall of the vacuum jacket. A rough estimate of whether the insulation is sufficient can be obtained by feeling it; the outer surface should not be appreciably above room temperature.

Fischer and Weyand (chap. 8, Ref. [27]) could prove that providing a column with an electric heat-compensating jacket in addition to a vacuum jacket may improve the efficiency considerably (Fig. 341).

A warning must be sounded here against the use of jackets through which a heating medium, such as steam or a thermostatically controlled liquid (*cf.* section 7.7.1) is passed. There is necessarily a temperature gradient in any column [112]; an isothermal jacket therefore produces either a "false reflux" or an additional evaporation along the column wall. Kolling and Tramm [114], when using this method, placed a layer of insulation between the column and the oil circulating jacket and also insulated the latter externally.

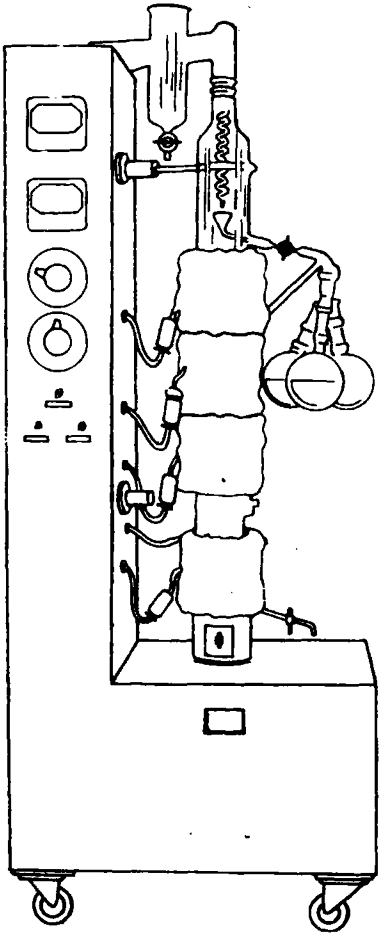


Fig. 342
Heating sections in glass-fibre cloth, applied to a molecular still

A satisfactory method for insulating laboratory and pilot plant columns is to use *electric heat-compensating jackets* which themselves should be effectively insulated. This type of jacket is particularly necessary in vacuum distillation, where the heat capacity of the vapour is small. Fig. 342 shows such insulation made in the form of sections lagged with glass fibre; these are obtainable as components for insulating flasks, columns and molecular stills [115]. Von Weber [112] demonstrated that the flow of heat through the column wall is independent of the position of the heating wire within the insulation. There is thus no drawback in winding it directly around the column.

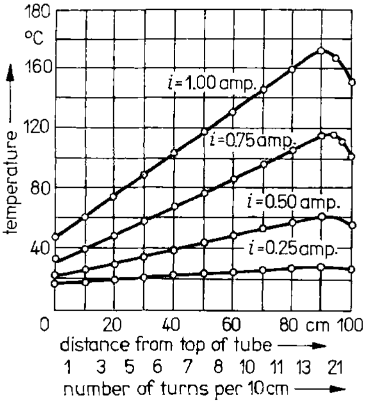


Fig. 343a
Temperature gradients at various currents in the heating system of Kortüm and Bittel

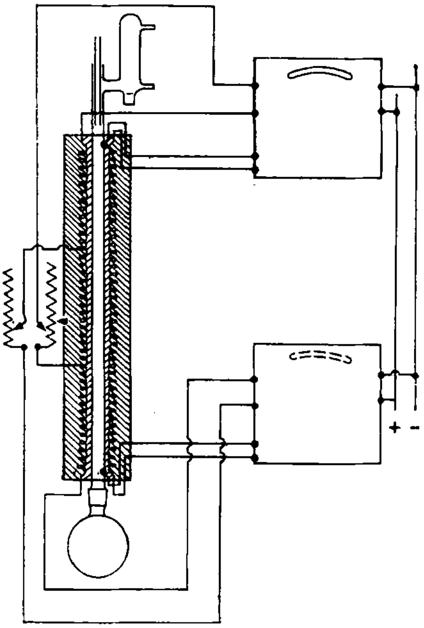


Fig. 343b
Diagram of a heating jacket circuit with thermocouple

The fact that a *temperature gradient* exists in the column must of course be taken into account in designing an electric heat-compensating jacket. For this reason the Destinorm jackets, mentioned above, are made in lengths of 50 cm, each of which can be adjusted to the corresponding interior temperature of the column. A satisfactory method of doing this is to have a thermometer indicating the inner temperature of the column in each section and to adjust the jacket temperature to a value 1 or 2 deg. C below this reading. It is incorrect to regulate the jacket temperature in accordance with that in the column head, even if the temperature gradient in the column is not more than 1 or 2 deg. C.

Kortüm and Bittel [116] have evolved an arrangement of two heating elements by means of which an arbitrary temperature gradient can be maintained along the column. Two heating circuits wound on an iron tube are employed, the first of which is so spaced that the distance between the turns becomes smaller toward the lower end of the column. The temperature gradient is measured at distances of 10 cm by thermocouples. It will be seen that an almost linear temperature profile is obtained at all current strengths (Fig. 343a). The second heating element, insulated by beads, is wound with constant spacing over the first, the spacing being equal to that in the centre of the "gradient" heater. The whole is insulated externally with thick asbestos cord and by a jacket of magnesia or kieselguhr. Two contact thermometers are fitted in such a way that their bulbs are in direct contact with the packed column at distances of 10 cm from its upper and lower ends. The upper contact thermometer controls the second element, the current in which can be set at any value; the lower contact thermometer controls the "gradient" heater. Only a fraction of the total current is controlled.

In Fig. 343b the schematic diagram of a heating jacket regulated by means of thermocouples [117] is shown. A power of 85 W (220 V, 0.39 A) is sufficient for temperatures up to 200°C whereas higher temperatures require jackets with 100 W (220 V, 0.46 A).

Table 69

Calibration of a heat-compensating jacket

Electrical input	Watts	14	42	77	114
Temperature	°C	75	157	219	297
Heat input per metre	cal/m · h	9300	28700	51000	76000
Condensate corresponding to heat input	mol/m · h	1.27	3.2	5.0	6.3

Jackets may be calibrated as follows. A column of the proper length is placed inside the jacket; thermometers are so inserted into the upper and lower ends of the column that their bulbs are at one third of the length from the top and the bottom. The temperatures established at various current inputs are then observed, the average of the two thermometer readings being taken. As an illustration of such measurements, the values found by von Weber [112] for a jacket are listed in Table 69.

The figures for the heat input correspond to the amount of heat that would be lost at that temperature if the column were operated without heat compensation. The heat input refers to one metre of column length and the amount of condensate has been calculated for a typical liquid obeying Trouton's rule and boiling at the observed temperature.

Given such a calibration, a heat-compensating jacket can be regulated to the inner temperatures occurring in any distillation with a variable resistance and an ammeter or wattmeter. A more accurate, automatic heat control is obtained by the use of thermocouples or gas thermometers (*cf.* section 8.2.2).

It is also necessary to insulate the parts between the still pot and the column, between the individual column sections and between the column and the condenser. If these portions are not lagged they act as dephlegmators and produce additional reflux. It is usually difficult to get the vapour of high-boiling substances out of the column without adequate insulation. To prevent condensation in the vapour tube it may be surrounded by a vacuum jacket (Figs. 309, 310), but this measure is effective only up to about 150°C. For higher temperatures the vapour tube or the vacuum jacket can be heated by a winding of resistance tape in glass-cloth insulation (Fig. 344). Heating tapes of this type are made in lengths of 60—250 cm (2—8 ft.) and widths of 6—90 mm ($^1/_2$—$3^1/_2$ in. [118]). Their ratings range from 36 to 850 Watt; at an average surface load of 0.4 Watt/cm^2 they can produce temperatures up to 450°C. For use at still higher temperatures, flexible heated tubes in a sleeve of heat-resisting stainless steel plaiting can be obtained; they are manufactured in various lengths, for maximum temperatures of 450°—800°C. Their diameter is 6 mm ($^1/_4$ in.) and the surface load 4.65 Watt/cm^2.

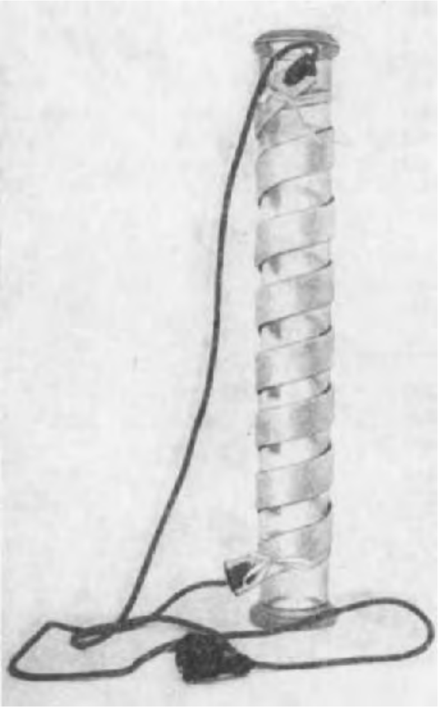


Fig. 344
Chemotherm heating tape

Heating tape manufactured by Electrothermal Engineering Ltd., London, is also available in extended lengths on rolls. The manufacturer provides a nomogram for determining the length needed for a given purpose, and the amount required is cut off. Electric terminals are supplied and can be fixed without difficulty.

When heating elements are used on the column head care must, of course, be taken that the vapour is not superheated, as this would vitiate the temperature readings. A calibration as described for column jackets must therefore be carried out first. If distillates having a high melting point are produced, they can easily be handled by the use of heating tape on the connections to the receiver and on the receiver itself.

Table 70

Test data for packed columns

Packing						Column
Type of packing	Material	Diameter (mm)	Height (mm)	Wall thickness (mm)	Surface area of one litre (m^2)	Column diameter (mm)
Raschig rings	Glass, smooth	3.0	3.0	0.7	1.320	
	Glass, smooth	4.0	4.0	0.6	1.109	
	Glass, smooth	4.5	4.5	0.5	1.382	24
	Glass, smooth	5.0	5.0			35
	Glass, smooth	6.0	6.0			20
	Glass, smooth	6.5	6.5	0.5	1.109	24
	Glass, smooth	10.0	10.0			50
	Porcelain	5.5	5.5	1.1		24
	Porcelain	8.0	8.0	1.1		24
	Earthenware	10.0	10.0	1.7		24
Dixon rings	Wire mesh	3.0	3.0			25
	Wire mesh	5.0	5.0			20
	Wire mesh	6.0				50
Prym rings	Metal	2.2	2.5			
Wilson spirals	Glass	3.0	1.5–3.0	4.0		24
	Glass	5.0	5.0	0.65	1.66	
	Glass	6.3				25
Fenske helices	Glass	2.1				10
	Glass	3.1				13
	Glass	3.1				20
	Glass	6.3				25
Helices	Stainless steel	1.6	1.6	0.2		40
	Stainless steel	2.0	2.0	0.2	4.55	24
	Stainless steel	4.0	4.0	0.4	1.49	24
Beads	Glass, smooth	3				24
	Glass, smooth	4			0.9	
	Glass, matt	4				24
	Glass, matt	7.5				24
Saddles	Porcelain		4		1.5	30
	Porcelain		6		1.15	30
	Porcelain		8			30
	Porcelain		10		0.72	30

Sigwart: No further data supplied.
Thormann: The lower HETP's are for smaller loads and conversely.

		Height equivalent to a theoretical plate, cm					
Cross-sectional area (cm²)	Packed height (cm)	Schultze and Stage Ch. 4. [216]	Sigwart Ch. 4. [217]	Thormann Ch. 4. [218]	Myles et al. Ch. 4. [192]	Other	References
				5–7			
				6–9			
4.5	60	5.82–9.52					
9.6	90		11.1	7–12			
3.1	125		15.5	8–14			
4.5	60	5.0–14.3					
16.9	95		18.2				
4.5	60	3.69–7.5					
4.5	60	7.07–11.3					
4.5	60	7.23–12.8					
4.9	100					1.4–2.8	chap. 7.8
3.1	60		4.35				
19.6	100					1.4–3.5	
				3–5			
4.5	60	8.0 –13.35					
				7–12			
4.9	107				7–9.2		
0.8	80		4.8				
1.3	126		7.4	4–6			
3.1	125		9.5				
4.9	107				3.6–4.2		
12.5	100					1.4–2.0	Author's measurements
4.5	60	1.25–3.32					
4.5	60	1.82–5.0		2–5			
4.5	60	6.00–6.06		5–6			
				6–7			
4.5	60	5.82–7.22					
4.5	60	3.31–7.50					
7.0	45					4.7–6.3	Author's measurements
7.0	45					6.0–9.0	Author's measurements
7.0	45					7.5–11.4	Author's measurements
7.0	45					9.0–12.8	Author's measurements

Myles et al.: Test mixtures are n-heptane—methylcyclohexane and n-dodecane—cyclopentylcyclohexane; the HETP's are for various pressures and a medium reflux flow.

For glass piping steam-heated copper or lead tubes are used which are placed along the glass pipes and isolated. The elastic Calorex profile tubes [119] of synthetic rubber have a wide range of heating applications. Their base widths are 8, 15 and 30 mm. The heat transfer coefficient for Calorex on glass (wall thickness, 1.5 mm) ranges from 165 to 260 kcal × h × m² × deg.

7.8 Packings

Packings, placed in the column in a random fashion (*cf.* section 4.10.2), are intended to provide the surface necessary to carry the thin film of liquid (section 4.2) with which countercurrent exchange takes place. In a few cases a space-symmetric arrangement may turn out to be advantageous [118a]. The effective surface of packing is that taking part in the exchange of material and heat. The smaller the size of packing unit of a given shape, the larger is the area per unit of column volume. There is, however, also a corresponding increase in the hold-up, which tends to reduce the separating efficiency (section 4.10.5). As so often in distillation one must therefore take several factors into account and make a compromise when deciding on the shape, size and material of the packing to be chosen. Leva [120] has compiled data and calculations concerning the choice of packing units, particularly for semi-technical and technical columns.

7.8.1 Shape of packing units

Although bodies of various shapes have been proposed as packing, cylinders are by far the most usual form. Of the non-cylindrical types, balls and saddles are those most often encountered in the laboratory. Some of the other shapes that have been suggested are: single-turn glass spirals, glass wool, chain links, tacks, nails, metal bellows. Data for packings are listed in Table 70.

Kerényi [121] has made a systematic study of the methods of selecting highly effective packings for particular distillations. The dependence of the separating efficiency on shape and size of the packing units and on material and operating parameters is represented in a number of diagrams. Besides, a relation for characterizing efficiency in terms of a quality factor G was derived:

$$G = \frac{n_{th}}{\sqrt{H \times \Delta p}} = A \times t^{-B}, \tag{200}$$

$$\lg G = \lg \frac{n_{th}}{\sqrt{H \times \Delta p}} = \lg A - B \lg t, \tag{201}$$

where n_{th} = number of theoretical stages, H = liquid hold-up, Δp = pressure drop, t = throughput, ml × h^{-1}, A and B = constants.

A double logarithmic plot of G vs. load (ml × h^{-1}) gives rectilinear dependences according to which the most efficient packing units may be chosen. Fig. 345 exhibits the data for new packing units developed by Kerényi (*1* to *4*) as compared to those for helices with close and wide spacing (*5* and *6*).

A study of ring-type packing units (Fig. 346a to *i* and *m*, spaced wire helices, Perfo rings and expanded-metal rings) carried out by Reichelt [121a] has revealed that while a great variety of ring-type packing units have been developed no satisfactory comparative assessment of their efficiency in material exchange and of their fluid dynamic behaviour can be made.

Fig. 346 shows various forms of *cylindrical* packing units, all of which are based on the Raschig ring, a. Some non-cylindrical types are illustrated in Fig. 347. Among the latter we must include the wire "Heli-Pak" [122] and wire-gauze "Octa-Pak"

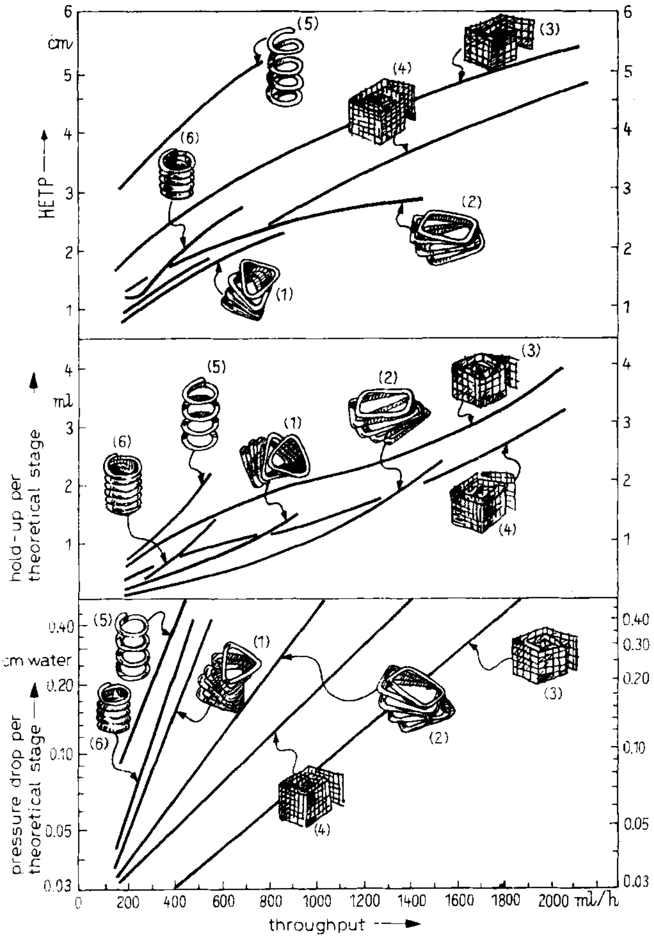


Fig. 345
Comparison of the separating efficiency of various packing units (Kerényi [121])

Column: 24 mm diameter, effective separating length 50 cm
Pressure: atmospheric
Reflux ratio: ∞
Test mixture: n-heptane-methylcyclohexane

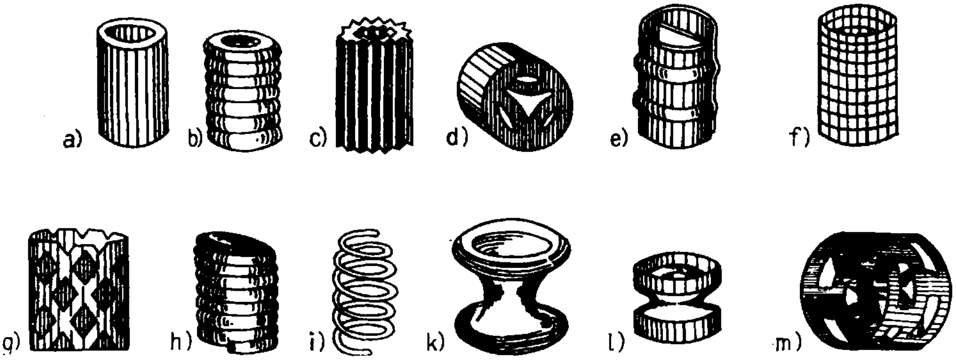


Fig. 346
Cylindrical packing units (based on the Raschig ring)

a) Raschig, smooth and matt
b) Idem, with circular grooves
c) Idem, with lengthwise grooves
d) Idem, with internal structure
e) Prym ring
f) Raschig ring of wire gauze (Dixon ring)
g) "Intos" ring
h) Helix
i) Wilson spiral
k) Spool
l) Pulley
m) Pall ring

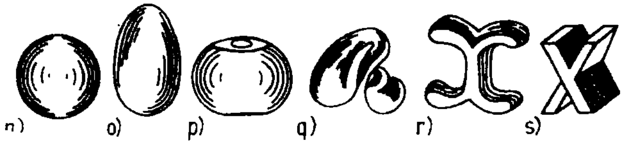


Fig. 347
Non-cylindrical packing units (based on the Raschig ring)

n) Sphere, smooth and matt
o) Kirschbaum's packing
p) Bead, smooth and matt
q) Berl saddles
r) Twin sectors
s) Cross packing

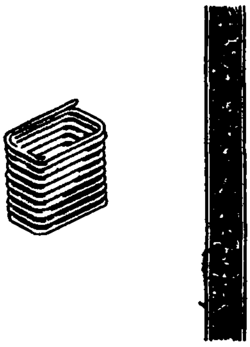


Fig. 348
Podbielniak's "Heli-Pak"

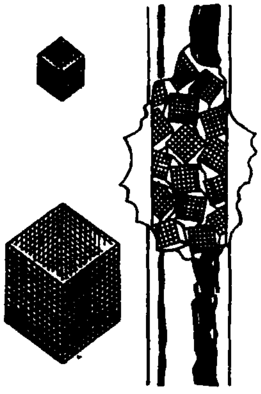


Fig. 349
Podbielniak's "Octa-Pak"

bodies of Podbielniak (Figs. 348 and 349) and the perforated metal semi-cylinders of Cannon (Fig. 350), all of which are very efficient.

The cylindrical forms that are most commonly used in the laboratory and in pilot plants are:

Fig. 346*a*, Raschig rings of glass (smooth and matt), of ceramic material or of metal, 2—10 mm;
Fig. 346*e*, Prym rings of metal, 2—10 mm;
Fig. 346*f*, Raschig gauze rings, with or without partition, 3—10 mm;
Fig. 346*h*, Helices of glass or metal, 1.4—10 mm;
Fig. 346*i*, Wilson spirals of glass, 3—6 mm.

Prym rings are as a rule made of metal and are used for comparisons with industrial columns. Data on their stage efficiency are scarce. According to Thormann [19] 2.5 × 2.2 mm Prym rings give the same HETP as 4 × 4 mm metal helices. The metal Raschig ring is now available also with circular holes as Perfo ring [123].

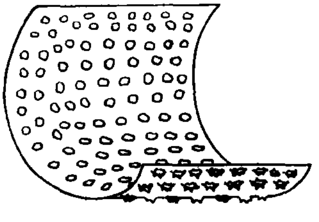


Fig. 350
Cannon's perforated metal-sheet semi-cylinders

Dixon's Raschig rings of wire gauze (about 100—140 mesh), with one or two turns and with or without partitions, are used to an increasing extent [124, 125]. Brass-wire netting Dixon rings of sizes 4.3 × 3.3 mm and 5.1 × 5.1 mm were investigated with chloroethane/benzene and H_2O/D_2O as test mixtures by Zelvenskii et al. [125a]. The measurements were performed in a column of 43 mm diameter and 1000 mm packing height in the pressure range of 50 to 750 torr. Chemical pretreatment of the rings with 25 to 30% NaOH or KOH resulted in different permeabilities, pressure drops and retaining powers as compared to unpretreated rings. The results are represented graphically.

Data for wire-gauze packings have been collected by Ellis and Varjavandi [126]. This packing is not made in sizes smaller than 1.5 mm ($^1/_{16}$ inch), but gives HETP values of about 1.5—2.5 cm and better. A favourable feature of this type of rings is that the efficiency drops but little with increasing column diameter. Measurements carried out by Kirschbaum [127] showed that a column of 100 mm diameter, containing a 1-metre layer of bronze wire-gauze rings (single turn without partition, 3 × 3 mm), gave an HETP of 1.67—2.8 cm at vapour velocities of 0.02—0.27 m/sec (Fig. 3 [51]). The test was performed at infinite reflux ratio with an n-heptane-methylcyclohexane mixture.

Helices of thin wire (Grosse-Oetringhaus) have an extremely high efficiency. The author's experience shows that they can also deal with high loads. If such helices are to be resistant to corrosion they should be made of stainless steel (*e.g.* 18:8); furthermore, their manufacture to a constant length in sizes smaller than 2 mm is difficult. Their price is consequently high. On the other hand the efficiency of the small sizes (1.3—2 mm) is exceptional; an HETP of 1.0—1.6 cm can be obtained with them. The latter sizes are made of 0.15—0.2 mm wire. For one litre of column space the number of rings required is approximately as follows:

2 mm	115,000
4 mm	12,500
20 mm	100

It was an obvious step also to make such helices of glass (Fenske helices). The writer carried out some tests on closely-wound glass spirals of 4 × 4 × 0.3 and 7 × 7 × 0.3 mm at atmospheric pressure with benzene-CCl_4 mixture and obtained the results shown in Table 71. They are available as both single and multi-turn helices.

The glass packing known as Wilson spirals differs from metal and Fenske helices (which have turns of close pitch) in being made with spaces of 0.6 mm between each turn (Fig. 346i). Their efficiency is of the same order as that of equally large Raschig rings, but they can handle large loads.

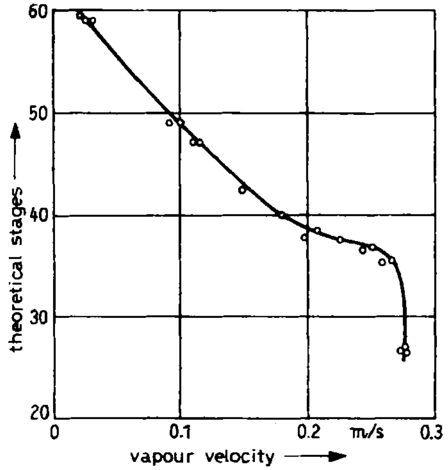


Fig. 351
Tests with bronze wire-gauze rings, 3 × 3 mm, single turn, no partition, by Kirschbaum

Column diameter: 100 mm; packed layer: 1000 mm; test mixture: n-heptane-methylcyclohexane; $v = \infty$

Table 71

Tests with 4 and 7 mm spirals

Load (ml/h)	100	200	400	800
HETP with 4 mm spirals (cm)	5.2		5.6	6.1
HETP with 7 mm spirals (cm)	5.4	6.4	8.0	

Column height, 1 m; diameter, 30 mm; effective length, 920 mm; reflux ratio $v = \infty$; charge: 40 mol%

Data for glass helices with one turn are given in Table 70. Single-turn wire helices have also been investigated; Thormann [19] reported the HETP's listed in Table 72 for this packing. Single-turn wire helices hence have about the same efficiency as glass Raschig rings or glass spheres of the same size.

Of the *non-cylindrical* forms of packing the following are employed in the laboratory and in semi-technical plants.

Table 72

Values of the HETP for single-turn wire helices

Diameter (mm)	HETP (cm)
1.6	2.5–3
2.5	4
4.0	4–8
5.0	12

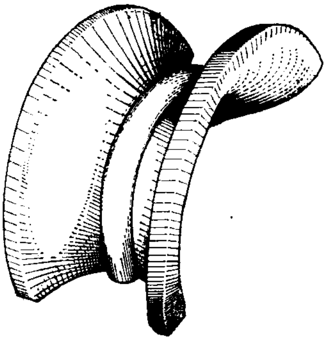


Fig. 352
"Intalox" packing

Fig. 347*n*, Spheres of glass, smooth and matt, 3—8 mm;

Fig. 347*q*, Saddle-shaped packing of porcelain, special compositions or wire gauze, 4—10 mm;

Fig. 348, "Heli-Pak"; wire gauze, 1.8—4.5 mm;

Fig. 349, "Octa-Pak"; wire gauze, 5 and 7.5 mm.

Spheres, smooth or matt, are still used to some extent, particularly in preparative work. Their large weight, however, limits the length of the column.

Saddles (Fig. 347q) probably represent the best solution of the packing problem from the aspect of flow. Every surface of such a body lies at a slant, whatever its position, so that there are favourable conditions for contact between vapour and liquid. For the liquid flowing centrally the angle of distribution is 55—60°; the surface area of a saddle exceeds that of an equally large Raschig ring by 30 to 60%, in the size range of 4—10 mm. The resistance to vapour flow is very low; 8 × 8 mm saddles, for instance, cause only half the pressure drop of Raschig rings of the same size. A requirement for high efficiency of these packings is, however, that they are properly made and do not have a ridge. Saddle packing has also been manufactured of 100-mesh brass wire gauze (MacMahon packing [128]. A development of the saddle is the so-called "Intalox" packing [129] (Fig. 352); it has larger surface area and an increased free space, so that the pressure drop is still smaller than with saddles of the original type. It is made in 6 and 12.5 mm ($^1/_4$ and $^1/_2$ inch) sizes for laboratory and semi-technical use. Another variant is furnished by the Hydronil "Plastic Intalox" [130] which has two holes (Fig. 353) and is equivalent in efficiency to ceramic Intalox

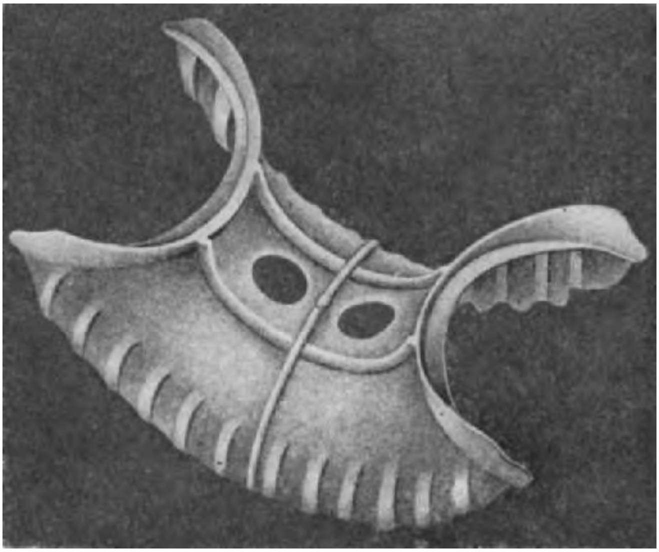


Fig. 353
"Hydronil Plastic Intalox" packing, of various plastic materials and sizes 1, 2 and 3 in.

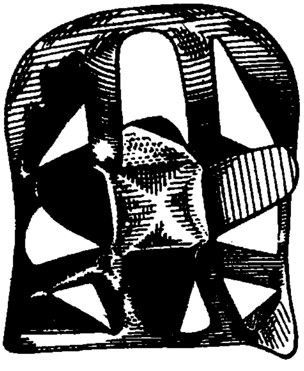


Fig. 354
"Supersaddle" (Kirschbaum)

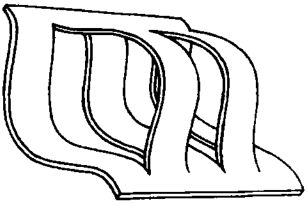


Fig. 355
Metal-made "Interpack" unit

Table 73

HETP values for non-cylindrical packing bodies

Type	Size (mm)	HETP (cm)	References chapter 7
Perforated sheet-metal semi-cylinders (Cannon)	4	1.3–2	[19]
Heli-Pak	1.8	0.5	

Type	Size (mm)	HETP (cm) at a load of				
		200 28.3	400 56.6	600 84.9	800 113.2	ml/h ml/cm^2 · h
Porcelain saddles	4	4.73	5.29	6.00	6.43	
	6	6.00	6.92	8.18	9.00	
	8	7.50	8.18	9.00	11.24	
	10	9.00	10.00	11.24	12.87	

Test mixture: CCl_4-benzene, 40 mol%
Column diameter: 30 mm; effective length 450 mm; $v = \infty$

packings. While the pressure drop is the same the throughput is twice as large as with Pall rings. A further evolution is found in Kirschbaum's "Supersaddle" [131] which has partitions extruded from the saddle surface (Fig. 354).

Almost all metals are used in the manufacture of "Interpack" packing units (Fig. 355) which are available in sizes 10/10/0.3; 20/25/0.4; and 30/35/0.8 mm [132]. They are characterized by a relatively small pressure drop. Plastics are under consideration as constructional material.

The HETP's for non-cylindrical packing, which have not been included in Table 70, are listed in Table 73. The values for procelain saddles were measured by the author.

7.8.2 Constructional material of packings

In chap. 4.2 it was already pointed out in how far the chemical nature of the material of which the column packing is made may influence the separation. The materials in question are glass, porcelain, earthenware, various metals and their alloys and recently also plastics. Glass or a ceramic material is in general preferred on account of its resistance to corrosion and low price. Porcelain should be hard-baked and free from iron, as catalytic effects may otherwise occur. For high efficiencies packing made of 18:8 stainless steel wire or wire gauze is unsurpassed.

The differences in the separating effect found with wire-gauze packing made of various alloys are explained by Fuchs [133], on the strength of work done by Forsythe et al. [134], as being due to differences in the wettability of the metals and to different adsorption effects that may arise as a result of their respective chemical activities. Wolf and Günther [135], however, later examined the surface behaviour of various metals with respect to test mixtures of increasing polarity and found that the differences in activity were of the same order as the accuracy of the experiments, *viz.* 10 to 12%.

The author was able to demonstrate that the degree of wetting of packings — and consequently also the separating efficiency — depend to a marked extent on the average degree of roughness of the material in a given liquid-solid system [136]. It was further found that polymers having swelling values of about 10% show excellent wetting properties.

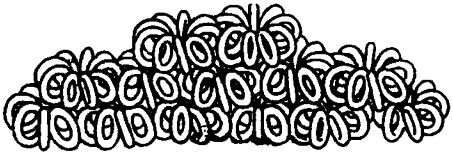


Fig. 356
Teller's polyethylene "Tellerettes"

The basic advantages of packings made of plastics as compared to other materials are [137]:

— high accuracy to size;
— low weight;
— large relative free volume of packing (due to small wall thicknesses);
— high breaking strength;
— high cleanability;
— relatively high resistance to corrosion.

The relatively high separating efficiency of packings made of plastic material with a low wettability is interpreted by Teller [138] as resulting from the formation of an interstitial hold-up due to the low energies of adhesion involved (*cf.* chap. 4.2). This hold-up extends the residence time of the liquid phase in the column. Teller's polyethylene "Tellerettes" (Fig. 356) yield a relative free volume of 83%. They are shaped such that the two phases encounter relatively small solid surfaces by which they are divided and diverted.

Ponter et al. [144] have suggested that packings with a low wettability may be advantageous for the separation of positive azeotropes. The admixture of 10 to 50% Teflon rings to glass Raschig rings of the size 0.6 × 0.6 × 0.4 cm yielded favourable results. It was further shown [145] that with PTFE Raschig rings the pressure drop is twice as large as with glass Raschig rings of the same size, using water as liquid. However, increasing the PTFE proportion in packing mixtures up to 80% leads to a pressure drop increase by only 20%. With Teflon rings, flooding starts at smaller gas loads than with glass rings.

Tests have shown that the polymers polytetrafluoroethylene and polypropylene are suitable packing materials for columns using concentrated sulphuric acid or acid water as liquids [143].

Miniature rings are made of metals, porcelain or high polymers [139]. The shaping of highly efficient packings made of thermoplastic material has been discussed by Egberongbe [140].

The use of polyethylene packings in separating columns of glass or steel involves the risk of increased wall flow. The difference in adhesion between the systems liquid-column wall and liquid-packing unit gives rise to changes in the adhesion process in favour of the column walls (*cf.* chap. 4.2). According to Stürmann [141] wall flow may be checked by the use of undulating column walls. Krell [137] has shown that an optimum shaping of the inner column walls from the point of view of interface physics ensures favourable flow density spectra even when plastic packings are used. Polyethylene or Teflon sheet placed on the inner wall eliminates wall flow [142].

8. Automatic devices, measuring and control equipment

Only by using accurate methods of measurement can high separating efficiency and good reproducibility be obtained in laboratory and pilot plant distillation. The principal measurements to be performed in distillation are those of temperature, pressure, reflux ratio and load. The determination of data on the products of distillation will here be discussed only in so far as they are actually performed during the course of distillation. In addition, reliable measurements are an essential requirement for reliable control and recording of processes in distillation, and consequently for automation. Control methods employed in industry are also applied to some extent on a laboratory and pilot plant scale. The latest developments in the field of control are regularly reported by a number of specialized journals.

8.1 Automatic equipment

In practically all modern apparatus for laboratory distillation certain functions are now automatic. Heating is often controlled by contact thermometers, and the rate of evaporation of the charge with differential manometers. Reduced pressures are also frequently kept constant with automatic units. In fact, the present trend is towards fully automatic control of the conditions of distillation and simultaneous recording of the data measured, an object that has already been reached in many industrial installations. The ideal procedure is for the mixture to be merely introduced into the apparatus and the latter switched on; it then automatically yields the required products of distillation and at the same time prepares a diagram of the top and bottom temperatures and other data that may be needed.

The extent to which measuring and control devices are employed in batch and continuous distillation depends on the nature of the work and, to a considerable degree, on financial considerations [12]. In practice a distinction can be made between semi- (or partly) automatic and fully automatic apparatus. In the latter all operations except starting up are performed automatically; in partly automatic apparatus only some of the functions are governed by regulating devices.

The following possibilities may be distinguished:

I. Partly automatic operation

a) Control

1. Still pot heating: by contact thermometers and contact manometers via electronic proportional controllers (*cf.* sections 8.2.2 and 8.4.2);
2. Column heating jackets: by thermocouples, contact thermometers or air thermometers (sections 7.7, 8.2.1, 8.2.2);
3. Feed heating in continuous distillation: by contact thermometer (section 8.2.2);

4. Feed rate in continuous operation; by metering devices (section 8.6);
5. Boil-up rate (and thereby the load): by contact manometer (section 8.4.2);
6. Reduced pressure: by pressure controller (section 8.3.);
7. Amount of cooling water: by constant level device and flowmeter (section 8.6) together with safety switch;

b) Recording (*cf.* section 8.2.1)

As a rule for top temperature, feed temperature, bottom temperature and wall temperature in column heating jackets (section 7.7.3) by the use of thermocouples or resistance thermometers instead of glass thermometers.

II. Fully automatic operation

a) Control

As for partly automatic operation, with the addition of:

8. Feed rate: by means of small metering pumps or automatic level control in a supply vessel (section 8.6);
9. Reflux ratio: by an automatic column head, actuated by mechanical or electronic means (sections 7.5. and 8.4.1);
10. Distillate take-off: by an automatic fraction collector (section 7.6);

b) Recording (*cf.* section 8.2.1)

1. Top temperature as a function of the amount of distillate: by temperature recorder;
2. Feed, bottom and heating jacket temperatures: by temperature recorder;
3. Reflux ratio: indirectly, by recording the difference between top temperature and temperature in the middle of the column;
4. Pressure: by pressure recorder.

8.1.1 Fully automatic equipment for standardized boiling point analysis

A good example of a fully automatic apparatus is provided by that designed for ASTM distillation method D 86 [1], a procedure which is employed to determine boiling point curves of fuels etc. The operations that have to be carried out manually are confined to the introduction of the charge into the flask, switching on the heating, the removal of the flask after the analysis and detaching the recorded diagram. Fig. 357 gives a block diagram of the apparatus. Besides the provisions already mentioned, the apparatus includes the following devices.

1. A heating arrangement, responding to rapid changes in temperature and so set that the first drop of distillate falls within the specified time of 5 to 10 minutes after the start.
2. A device by which time markings are recorded at every 2nd and every 10th minute on the chart.
3. An arrangement for the automatic determination of the 95 vol% distillate point and the subsequent maintenance of a constant heat supply, as required by the specification.
4. Automatic cooling of the receiver to 15 ± 3 °C.
5. A mechanism for setting the whole apparatus to its initial state after termination of the distillation.

The accuracy of the temperatures recorded is 0.5 deg. C, that of the distillate volumes 0.1 ml. The apparatus maintains a speed of distillation adjustable at either 4.5 or 9 ml/min and is designed to run 24 hours a day.

A similar apparatus, Asda Mark 3, of Messrs. Gallenkamp, London, is designed to cover the following operations:

- ASTM D 86-JP 123, groups 1, 2 and 3, and D 1078, DIN 51751 and 51752;
- ASTM D 86-JP 123, group 4;
- rapid distillation (no standard).

Thus it was possible to carry out 80,000 boiling point analyses within 8 months in a laboratory equipped with 15 Asda apparatuses. This corresponds to 666 analyses per month and apparatus.

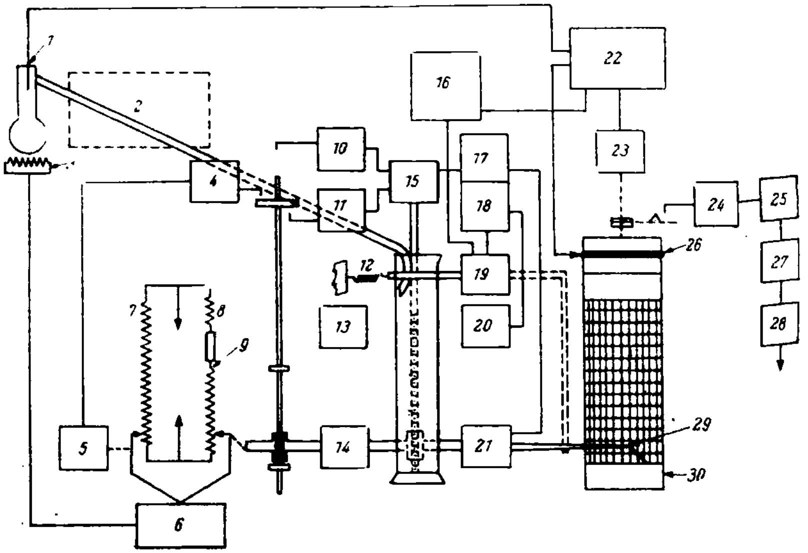


Fig. 357
Block diagram of automatic apparatus for ASTM method D 86

1 = Thermocouple, *2* = Condenser ice bath, *3* = Heater, *4* = Switch for 95% distillate point, which sets heater to fixed voltage, *5* = Timing motor for control of distillation rate, *6* = Heater control, actuated by *5*, *7* and *8*, *7* = Potentiometer for time measurement, *8* = Potentiometer for volume measurement, *9* = Contact for 95% distillate point, *10* = Upper limit switch, to stop volume follow-up, *11* = Lower limit switch, to stop return of volume follow-up, *12* = Spring to return receiver to starting position, *13* & *14* = Light sources for photoelectric cells, *15* = Motor for volume follow-up drive, *16* = Motor and switch for "correction temperature", *17* = Amplifier and switch for volume follow-up, 18 = Amplifier for first drop, *19* = Electromagnet for putting pen on chart and moving receiver after first drop so that distillate runs down wall, *20* = Photoelectric cell for recording first drop, *21* = Photoelectric cell for volume measurement, *22* = Amplifier for thermocouple, *23* = Motor of recording drum, controlled by temperature, *24* = Final boiling-point switch, *25* = Cut out, *26* = Potentiometer slide-wire, *27* = Relay, *28* = Starting switch, *29* = Pen, *30* = Drum and chart

It should be quite possible for a single analyst to attend to ten sets of automatic apparatus. The main advantage, however, lies in the fact that subjective errors are eliminated.

In the Soviet Union a piece of automatic equipment, due to Kanterman et al. [3], is employed for the distillation of petroleum products; it operates with an accuracy of ±2 deg. C. An automatic apparatus for the distillation of fuels and solvents according to DIN 51751 developed by Salzer [4] is manufactured by AEG, of Berlin.

Fig. 358 shows another apparatus which has been described by Jirmann [5]. It consists of the switch cupboard with compensation recorder for a resistance thermometer and two distilling units for alternate operation. The apparatus covers the temperature ranges +100 to +385 °C and 0 to +285 °C. The automatic Herzog apparatus [6] also operates on the digital principle and prints the results immediately on a strip of paper. For standardized boiling point analyses at reduced pressure the apparatus shown schematically in Fig. 359 [6] was developed by Zappe et al. [7].

8.1.2 Fully automatic equipment for fractionation

Basically, any apparatus for batch or continuous distillation may be automated to such an extent that it may be called fully automatic. A fully automatic apparatus was developed by Ulusoy [8] especially for preparative work. In the section on low-temperature distillation, a fully automatic apparatus due to Podbielniak was mentioned (Fig. 178) the block diagram of which is given in Fig. 360. A number of

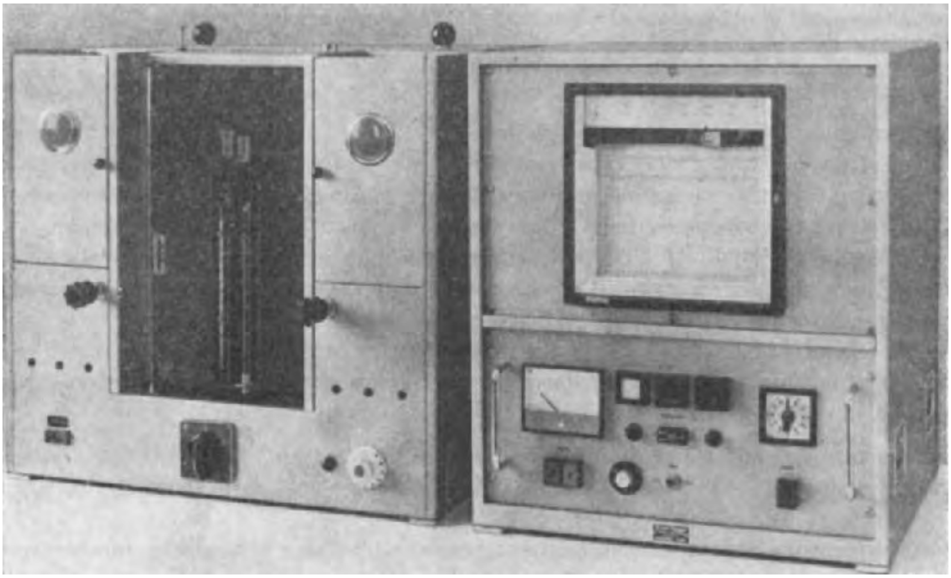


Fig. 358
Automatic apparatus for the distillation of fuels according to DIN 51751 on the basis of the ASTM D 86 or the D 158, D 1078 and ISO 3405 apparatus with compensation recorder (recording width, 210 mm)

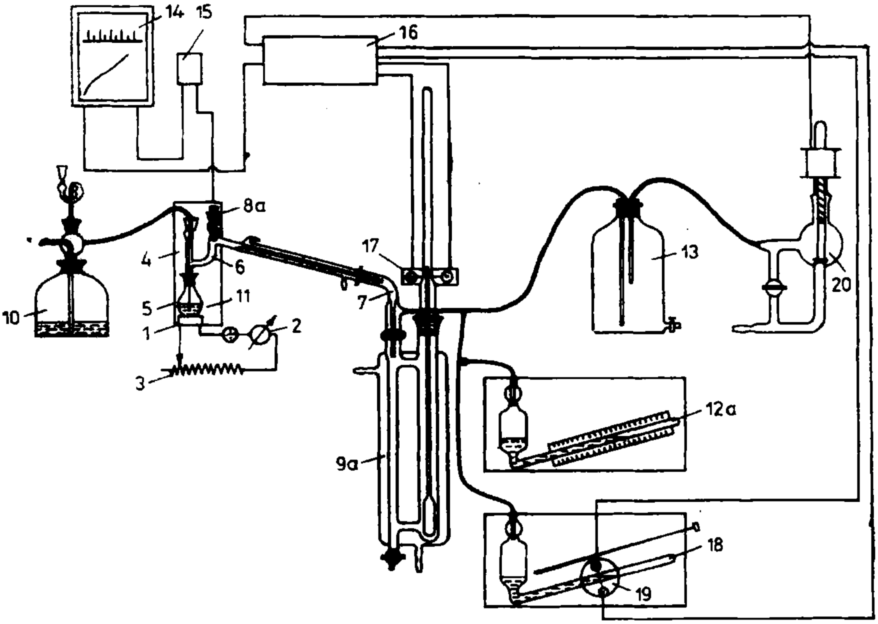


Fig. 359
Apparatus for boiling point analyses at reduced pressures with automatic temperature control (Zappe et al. [7])

1–*3* = still pot heating and control, *4*–*9a* = distillation apparatus with heating jacket, still pot, Claisen still head, adapter and receiver, *10*, *11* = bubble counters with boiling capillary, *12a*, *18* = manometers with inclined tube, *17*, *19* = photo-cells, *14*–*16* = recorder with thermostat and amplifier, *20* = pressure controller

automatic Labodest plants were developed by Stage [9]. One of these is the concentric-tube column for work on a semi-micro scale (Fig. 257 b). Such designs offer the advantage that the measuring and control devices can be used for various columns [10], *e.g.*, for the concentric tube column with charges of 5 to 100 ml, at atmospheric or reduced pressure down to 0.1 torr, with an efficiency of about 40 theoretical stages; or for the wire gauze column with charges of 100 to 1 000 ml, at atmospheric or reduced pressure down to 5 torr, with an efficiency of about 60 theoretical stages.

The front part of the apparatus (Fig. 257 b) carries the various units which can be pulled out by means of telescopic rails. For all functional groups there are plug-in printed circuit modules. The following circuits are distinguished:

- temperature control of the oil bath by electronic proportional controller: setting the temperature between 0 and 300 °C or otherwise setting the load in drops per minute;
- temperature control of the heat-compensating jacket: setting the temperature between 0 and 300 °C or automatic follow-up control according to the vapour temperature in the column head;
- control of the reflux ratio with vapour division in steps of 0.5 to 200 sec;
- collection of the fractions with change of receiver at preset intervals (in minutes);

- vacuum control;
- protection against failures, such as interruption of cooling water supply, overtemperature or overcharging of receivers;
- recording of the various temperatures and of change of fraction.

For packed columns, the load is relatively easy to control via the pressure drop whereas concentric-tube columns with pressure drops of the order of 10^{-3} torr required a novel control system. Fischer and Weyand [10] solved the problem by electronically measuring the reflux dropping rate. Depending on the desired load the still pot heating is controlled linear-proportional to the difference of actual and preprogrammed drop number. Thus it is possible to cover loads from 50 to 250 ml/h exactly and absolutely reproducibly, the pressure in the still pot ranging from 760 to 10^{-3} torr.

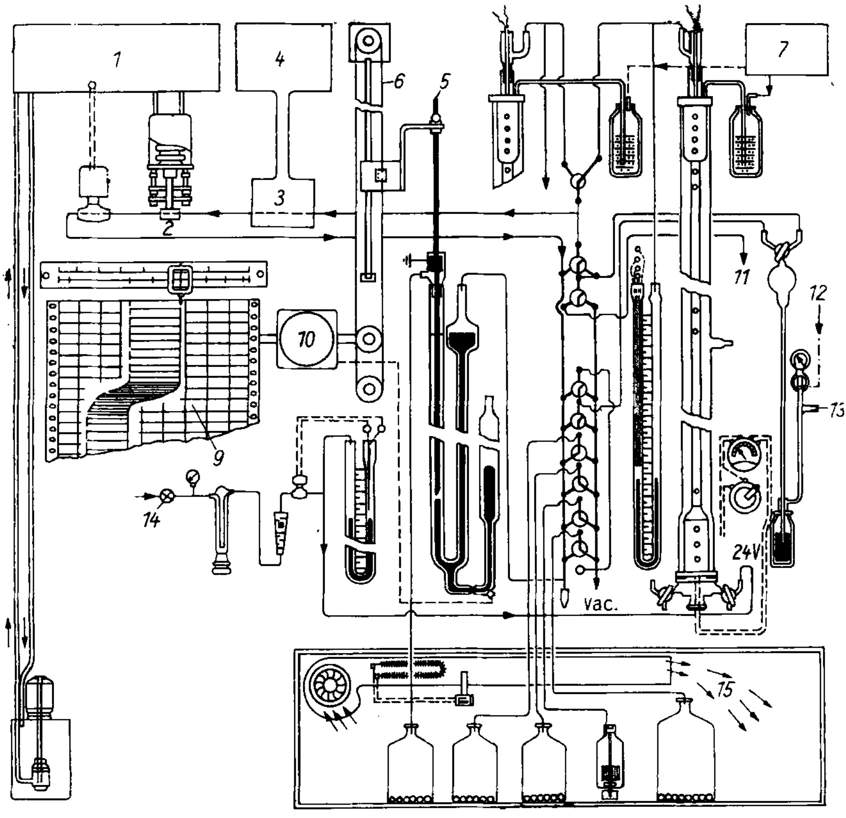


Fig. 360
Block diagram of the fully-automatic low-temperature apparatus "Thermocon" (Podbielniak) (cf. also Fig. 178)

1 = electronic control for distillate, *2* = distillate vapour, *3* = photo-electric measuring cell, *4* = circuit for heat conductivity measurements, *5* = recording manometer, *6* = connection to drive of recording drum, *7* = pressure and reflux condenser control, *8* = temperature, *9* = heat conductivity recording, *10* = motor, *11* = vapour outlet, *12* = air, *13* = connection to atmosphere, *14* = automatic introduction of gas samples, *15* = heated air bath

The author's automatic Destinorm apparatus "Automatic 62" (Fig. 361) possesses the following features [11]:

1. Flask with electric Intus heater.
2. Means for sampling or measuring the bottom reflux just above the flask.
3. Automatic electronic control of the column heating jacket to the average inner column temperature (Fig. 368).
4. Automatic reflux control by a magnetically operated swinging funnel and timer (Fig. 312).
5. An automatic fraction collector, containing 60 receivers, with syphon control (Fig. 324).
6. An electronic thermostatted vacuum controller, with an accuracy of ±0.1 mm Hg (Fig. 377).
7. An automatic control of the boil-up rate (load) by contact manometer (Figs. 387, 388).
8. Temperature reading at eye level by means of an optical system, or temperature recording by an electronic recorder.

The distillate removed by the swinging funnel first passes through a heat exchanger (Fig. 361) where it is brought to the required temperature; low-boiling fractions are cooled, solidifying fractions are heated thermostatically. The magnetic valve *14* which follows measures off the fraction in the graduated tube. Next there is an arrangement for taking single-drop samples *18* for analysis. At this point a thermometer may also be introduced, or a funnel for calibrating the syphon system. The latter is provided with an adjustable plunger *20*, allowing the fraction size to be set with an accuracy of ±0.1 ml. The change in pressure caused by the action of the syphon acts on a manometer *22* containing an organic contact liquid, and the resulting pulse, after passing through an electronic relay, brings the mechanism of the fraction collector into action and causes it to move up one step. The same pulse can be used to actuate an auxiliary pen on the temperature recorder and so to record the cut points between the fractions.

Fig. 361
Fully-automatic distillation apparatus "Automatic 62"

1 = 1 still pot, *2* = 1 measuring device for bottoms reflux, *3* = 2 transition pieces, *4* = 1 drop-forming tip, *5* = 1 column, *6* = 3 thermometers, *7* = 3 air thermometers, *8* = column heating jacket, *9* = 3 differential pressure manometers, *10* = 1 column head, *11* = 1 condenser, *12* = 1 vacuum connection, *13* = 1 cold trap, *14* = 2 magnet coils, *15* = 2 thermometers, *16* = 1 connecting piece, *17* = 1 stopper, *18* = 1 sampling device, *19* = 1 metering device, *20* = 1 sinking body, *21* = 1 vacuum receiver, *22* = 2 electrical contact manometers, *23* = 1 fraction collector, *24* = 60 test tubes, *25* = 1 vessel for fraction collector, *26* = 1 ground glass piece, *27* = 1 distillate distributor, *28* = 1 length of piping, *29* = 1 length of piping, *30* = 1 distillate tube, *31* = 1 distillate tube, *32* = 1 condenser for pressure drop measurements, *33* = 1 heat exchanger, *34* = 1 vacuum receiver (Anschütz-Thiele), *35* = 1 receiver pipette, *36* = 1 thermometer, *37* = 1 funnel for feed, *38* = 1 stopper, *39* = 1 switchboard

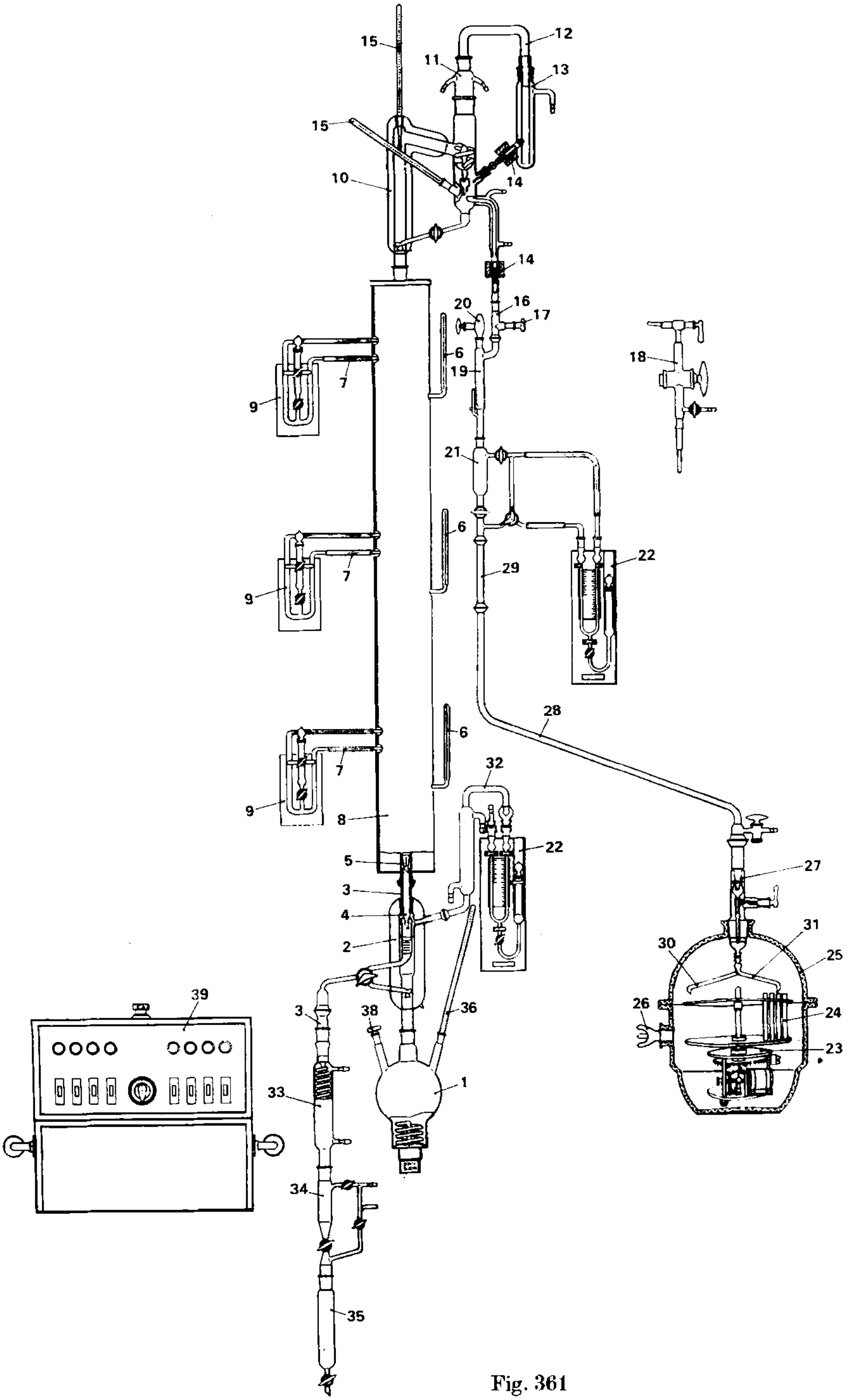

15
12
11
13
15
10
14
14
20
16
17
18
6
19
7
9
21
6
22
7
29
9
28
6
32
7
9
8
22
5
27
3
4
31
30
25
2
39
3
38
36
26
24
23
1
33
34
35

Fig. 361

The fraction collector *23* normally contains sixty 20 ml receiving tubes and is built into a vacuum desiccator with a wire-gauze safety cover. It can be employed at atmospheric pressure and at reduced pressures down to 1 mm. After 30 tubes have been filled a signal sounds; alternatively, the apparatus may be made to switch over automatically to the next circle of tubes. When all the tubes are full there is another signal and the reflux controller is switched off so as to stop the distillate take-off.

The part of the apparatus between the syphon and the fraction collector can easily be taken apart and is so constructed that the distillate is not contaminated by grease.

For preparative distillations correspondingly larger syphons and receiving tubes are used; alternatively, receivers may be arranged to ring a bell when filled to a certain level and at the same time switch over the column head to total reflux.

An automatic fractionating still designed by Koukol et al. [12a] is employed in the distillation after Micko for testing the quality of wines. The heating is controlled as a function of the amount of distillate collected per unit time. The constant distillation rate enables a mixture to be separated into several fractions of equal volumes in a pre-set constant time of, say, 15 minutes. The volume is measured by means of a thermistor filler which is adjustable as to the level and ensures a reproducibility of a fraction volume of 25 ml to within ± 0.1 ml.

Automatic apparatus for continuous distillation has been developed by Kolling and Tramm (Fig. 166) and Stage (Fig. 167).

Röck et al. [13] have mentioned a number of very useful components for automating laboratory columns, including protections against lack of cooling water and against fire. Extensive surveys of the control of laboratory apparatus have been given by Abegg [14], Kössler and Vohdenal [16] and Kadlec [17].

Pilot plants for continuous operation whose flow chart is identical with that of the subsequent large-scale plant should be largely automated in order that real comparative values may be obtained. Fig. 362 shows a pilot plant for the simulation of crude oil production conditions. The plant operates continuously and has a main column and three additional strippers. It is used for the separation of multicomponent mixtures which are taken off in 4 distillate fractions. The bottom product is pumped out of the main column. The columns are designed as vapour-collision plate columns. The results obtained with these columns are intended to be transferred directly to a large-scale plant. The metering of the material flows is done by means of pumps P (*cf.* chap. 8.6). The rates of evaporation, the heating jacket temperatures and the reflux ratios are controlled from the switch cupboard *1*. The vacuum controller *2* ensures a constant reduced pressure and the safety relay *3* switches off the plant as soon as the supply of cooling water is interrupted. Naturally, the more important temperatures are continuously recorded on electronic recorders [17a]. Fischer Labor- und Verfahrenstechnik have also developed automatic apparatus for the determination of mineral oil compositions according to ASTM 2892 and DIN 51567. The device is equipped with a falling-film column with wire-netting insert. It permits charges from 500 to 4000 ml and operates at normal pressure or vacuum to 2 torr and at temperatures to 350 °C. The separating power is reported to be about 14 to 17 theoretical plates.

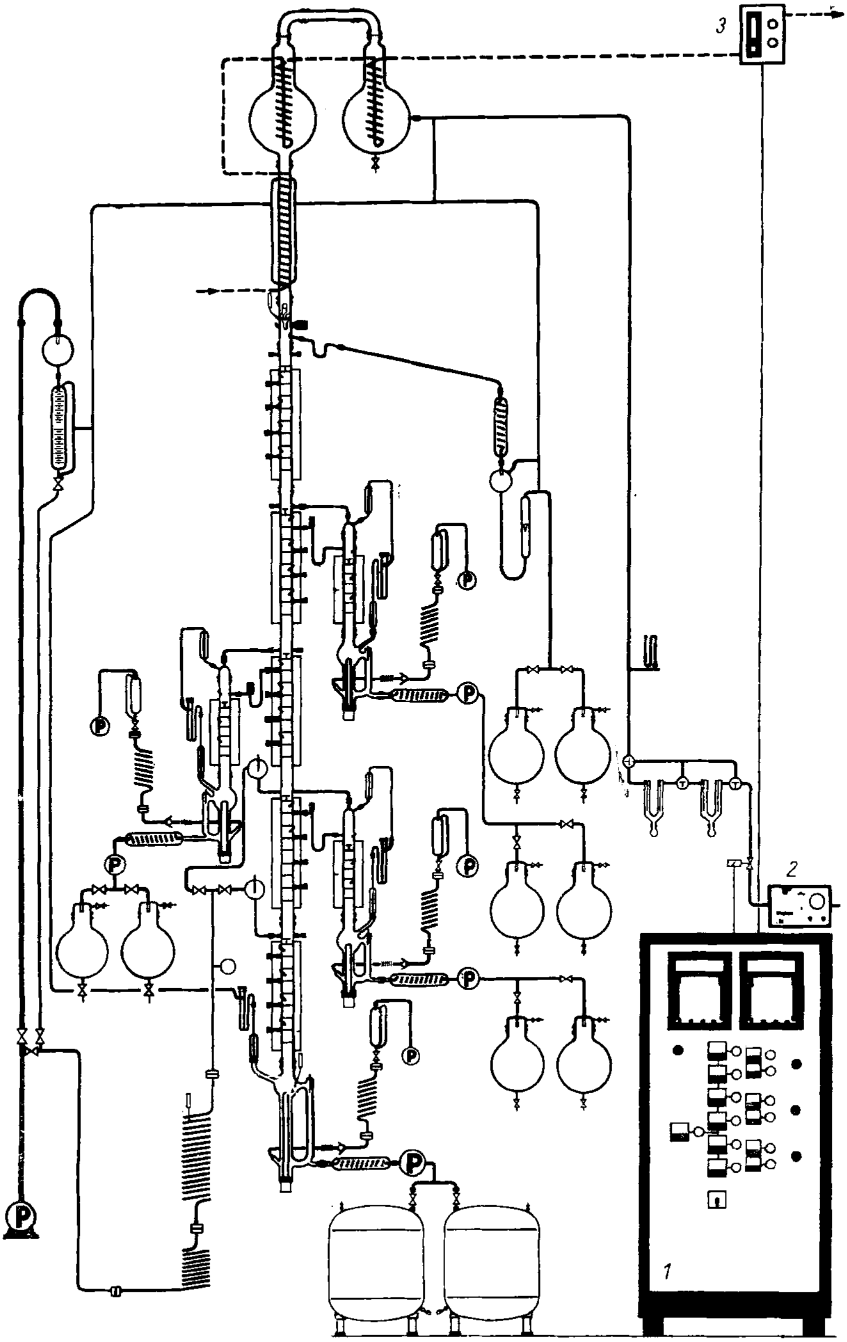


Fig. 362
Continuously operating pilot plant with vapour-collision bubble-plate columns for the simulation of crude oil production conditions

8.2 Temperature measurement and control

8.2.1 Temperature measurement

In distillation the most important temperatures to be measured are those of the overhead vapour, close to the point of condensation, and of the liquid in the still pot in the case of readily decomposable substances. In continuous operation it is necessary to know the temperature of the preheated feed at the inlet. Other temperatures often required are those in heating jackets and heating media (liquid baths or vapour jackets).

Table 74

Standardized glass thermometers for distillation

Standard	Component
TGL 40-335	liquid thermometer, distillation thermometer
40-336	liquid thermometer, thermometer for testing fuel oils and fuels, thermometer A and B for boiling course
40-339	laboratory thermometer with conical joint NS 14.5/23
DIN 12779/71	distillation thermometer
12784/55 Sheet 1	thermometer with standard ground joint, distillation thermometer (to be calibrated)
12784/63 Sheet 2	thermometer with standard ground joint, thermometer with bulb (to be calibrated)
12785/58 Sheet 1	thermometer for boiling course (to be calibrated)
12788/63 Sheet 1	thermometer well with standard ground joint 14.5/23

In laboratory and pilot plant distillation glass thermometers are still largely employed. If the temperatures lie within a restricted range it is, however, often more useful to carry out the measurement electrically, *i.e.* with thermocouples, thermistor or resistance thermometers, since it is then possible to record the temperature automatically. The possibilities of temperature measurements in the laboratory have been reviewed by Vanvor [18]. The measurement, generation and control of temperatures from high to low have been discussed by Laporte [15].

It is important to place the measuring point in the optimum position. In the column or still head it should be about 10 mm below the junction of the vapour tube. The temperature in the still pot should be measured at its lowest point, so that superheating may immediately become apparent. In flowing vapour or liquid the measuring point should be well insulated and should lie in the centre of the stream.

Standardized glass thermometers for distilling purposes are listed in Table 74.

Besides those specified in the standards, there are numerous types made for special purposes, such as angle thermometers (useful for measuring inner column temperatures), flanged thermometers and thermometers having capillaries backed with another colour to facilitate reading [19].

The thermometers most usually employed in distillation are of the enclosed type, in which the capillary and the scale are fused into a protective jacket (Fig. 363). For the temperature range of —58° to +360 °C, the normal thermometer liquid is mercury or its alloys; for low-temperature distillation (—58° to —200 °C) it may be pentane or a liquid with good wetting properties.

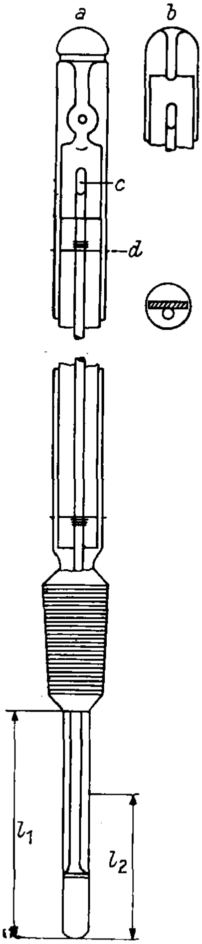


Fig. 363
Distillation thermometer with standard ground joint 14.5
a = Richter's scale-mounting, b = Stift's scale-mounting, c = safety bulb, l_1 = stem, l_2 = immersion depth

It should be noted that all the thermometers listed above except the ground-joint type (Fig. 363) are calibrated for total immersion; in other words, they read correctly only when the whole of the mercury thread is at the measured temperature. Short thermometer wells can thus give rise to appreciable errors. According to Piatti and Marti [20] the error is small only if the mercury bulb is just immersed in the oil in the well. In practice, total immersion thermometers should be mounted so as to be completely immersed in the vapour or liquid, although the ease of reading is thereby adversely affected. Otherwise a correction for emergent stem has to be applied (*cf.*

section 4.13). For this reason the use of ground joint thermometers is to be preferred. The data for such a thermometer are given in Table 75.

Ground joint thermometers are also commercially available for ranges of 50 °C and a graduation to 0.1 °C and as angle thermometers. This type, officially gauged, serves as standard for ground joint thermometers and for sharp distillations. The gauging certificate specifies the constant depth of immersion and the mean thread temperature during gauging. With a graduation to 0.1 °C the reading error is of the following orders:

Table 75

Data of the distillation thermometer with standard ground joint according to TGL 40-339, DIN 12784/55

Type	Measuring range (°C)	Graduation (to °C)	Temperature range (°C)	Calibration error (°C)
A or B	0 to +110	0.5		±0.5
	0 to +250	1	0 to 50	±0.7
			50 to 100	±1.0
			100 to 200	±1.5
			200 to 250	±2.0
	0 to +360	1	0 to 50	±0.7
			50 to 100	±1.0
			100 to 200	±1.5
			200 to 300	±2.0
			300 to 360	±2.5
Stem l_1 =	50	110	200 mm	
Immersion depth l_2 =	32	92	182 mm	

0 to 50 °C: ±0.05 °C
50 to 100 °C: ±0.05 °C
100 to 150 °C: ±0.2 °C
150 to 200 °C: ±0.2 °C
200 to 250 °C: ±0.5 °C

Since the errors of simple thermometers lie between ±0.2 and ±6 deg. C and glass undergoes a process of aging, it is apparent that thermometers used for distillation need to be checked at intervals. As already stated, some thermometers are provided with auxiliary markings with which corrections can be determined. Others should be tested by comparison with standard thermometers. (The apparatus of Junge and Riedel, designed for this purpose, functions in the same way as the Thiele melting point apparatus and is suitable for checking thermometers calibrated at total immersion up to 300 °C.) For testing ground-joint thermometers the author employs the equipment shown in Fig. 364; this can also be used for checking thermocouples. Standard compounds in the vapour phase provide the temperatures required; Table 76 lists a number of compounds that can be used in the temperature range of +34° to 210 °C. For higher temperatures, glycerin or some other stable, high-boiling

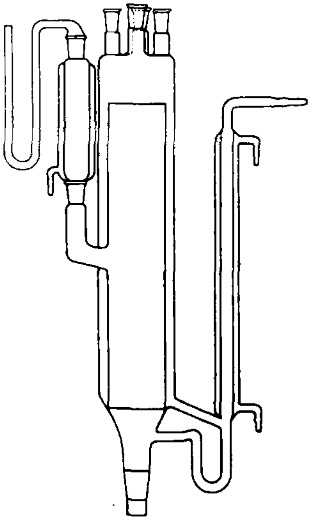


Fig. 364
Krell's thermometer calibration apparatus for ground-in thermometers and thermocouples

Table 76

Substances suitable for vapour baths for testing thermometers

Compound	*Kp*.$_{760}$ °C
Diethylether	34.6
Methylenechloride	40.67
Acetone	56.13
Methylacetate	56.96
Chloroform	61.0
Methanol	64.72
Carbontetrachloride	76.69
Ethylacetate	77.06
Cyclohexane	80.8
Water	100.00
Toluene	110.6
n-Butanol	117.75
n-Butylacetate	126.2
Chlorobenzene	131.69
Isoamylacetate	142.0
Bromobenzene	155.6
Decane	174.0
Aniline	184.4
Ethyleneglycol	197.4
Benzylalcohol	205.2
Nitrobenzene	210.6
Naphthalene	217.96
Diphenyl	254.9
Benzophenone	305.9

substance is employed at a reduced pressure. Three thermometers can be tested at the same time; the fourth is a standard one provided with an official calibration certificate, stating its errors at various temperatures. Care should be taken that the temperature of the exposed thread does not depart appreciably from that prevailing during its calibration; otherwise a correction must be applied.

For electric temperature measurements thermocouples and resistance thermometers are universally applicable. They are commercially available in a variety of designs [18].

For automatic recording, thermocouples or resistance thermometers are used. An advantage of thermocouples is that they can be used in small cavities and thin layers, for instance in the film flowing down the wall of a heater in molecular distillation. Thermocouples and small resistance thermometers give a rapid response and can be used over a wide temperature range; for thermocouples this range is approximately −200 to 1800 °C.

For the cold junction zero thermostats operating on the Peltier principle have proved to be appropriate [21].

Resistance thermometers usually contain a platinum resistance element and can be used from −220 to +750 °C. They rely on the resistance of a platinum element, (a thin layer, a cylinder, a straight or coiled wire) which changes by about 0.4% with every degree centigrade. It follows that if temperatures are to be determined to within 0.01 deg. C the resistance must be measured with an accuracy of a few hundred-thousandths of the total value. The methods used for this purpose depend on the accuracy required. If a Wheatstone bridge is employed, the changes in resistance can be used for recording and for control, for example to control the temperatures of column jackets to follow column inner temperatures, and to record the reflux ratio indirectly.

The evaporation of metal onto a surface forms a resistance element capable of determining the temperature of the surface accurately [22]. Data for surface heaters can be obtained in this way.

In pilot plants, resistance thermometers are commonly used to measure vapour and liquid temperatures. They often make use of two coils, one for recording and the other for control. The Quickfit all-glass version (Fig. 365) has joining sockets of nominal widths 25 and 40 mm.

Semi-conductors (thermistors), in combination with a recorder/controller, allow temperatures to be measured and controlled over a narrow range with a precision of ±0.001 °C, and for this reason are particularly suitable for use in vapour pressure measurements and the determination of phase equilibria. The "Thermophil" eletronic thermometer appears to be useful for measuring temperatures on surfaces, as in thin-film distillation and on outer column walls. The sensing point, encased in a glass or metal coating, contains a germanium semi-conductor 0.25 mm in diameter, which withdraws negligible amounts of heat from the place of measurement. The apparatus is made for various temperature ranges between −50 and +450 °C and is accurate to 1−2 deg. C. The signal produced is amplified electronically and actuates a pointer on a scale. Up to 10 points may be connected to the apparatus by leads of any desired length. The newly developed digital thermometers can be used with thermistors, thermocouples and resistance wires for sensing.

Temperature recorders are generally designed to serve one, two, four, six or twelve measuring points.

Since temperature ranges of 200 deg. C occur in laboratory distillation the recorder should give a relative accuracy of 0.1% or better and an absolute accuracy of 0.25% of the full scale, if the recording is to be as accurate as observation from glass thermometers. These requirements are fulfilled by various types of electronic recorders which are connected directly to a platinum resistance thermometer (100 ohm at 0 °C). In continuous distillation the instrument can also be employed for recording deviations from a specified temperature.

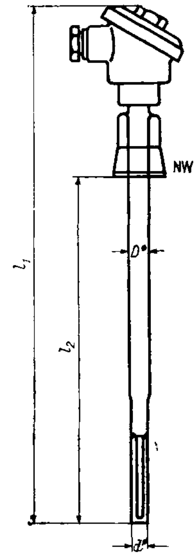


Fig. 365

All-glass resistance thermometer
Measuring range: −200 to +300 °C

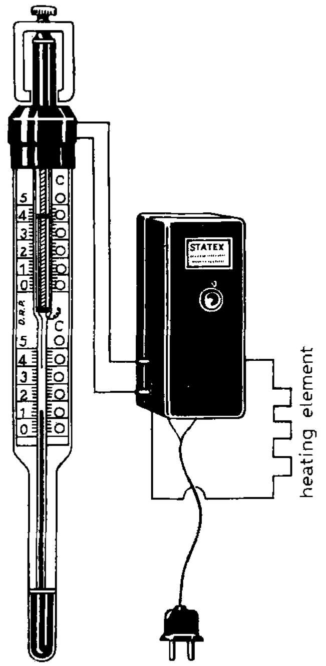


Fig. 366
Contact thermometer adjustable by means of a rotating magnet

8.2.2 Temperature control

For controlling the temperature of baths or flowing liquids and of various portions of an apparatus (such as column jackets, tube heaters, etc.) *contact thermometers* are largely used; they are obtainable with standard ground joints (*e.g.*, NS 14.5). Contact thermometers can be obtained either with contacts set to definite temperatures or with variable temperature. In the variable type (Fig. 366) the upper thermometer scale is used to set the required temperature, while the lower one carries the electrical contact. A contact thermometer with a spiral bulb with a large surface area (Fig. 367a) gives a more rapid control. Fig. 367b shows the difference between the speed of response of this type and the usual cylindrical bulb [23].

Contact thermometers of a maximum-minimum type are also manufactured; these make contact both on exceeding an upper limit and on dropping below a lower limit. By means of a fine adjusting screw the temperatures may be set with an accuracy of 0.1 °C [23]. Temperature control may be arranged to follow a variable reference temperature by moving the thermometer contact with a synchronous motor.

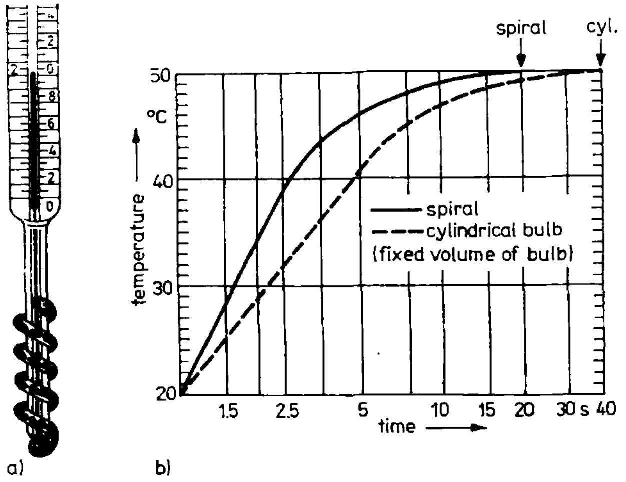


Fig. 367

a) Contact thermometer with spiral bulb

b) speeds of response of contact thermometers with spiral bulb and with cylindrical bulb

Quite satisfactory experience has been gathered with contact thermometers having a special three-pole plug and sliding ground joint, the latter ensuring that immersion can be continuously varied [24].

Between the contact thermometer [25] and the controlled apparatus a *relay* is placed, since a contact thermometer is not capable of carrying a normal heating current. Relays with vertical mercury switches have proved the most satisfactory in laboratory use, as they contain no parts subject to wear, such as bearings, levers or flexible leads [26].

Transistor relays may also be used in connection with contact manometers (*cf.* chap. 8.3.1 and 8.3.1.1). They are commercially available as a combination of standing or supported device. They operate on the "normally open" and "normally closed" principles where a circuit is switched on and off, respectively, on making a contact. These relays are further employed for photoelectric circuits, *e.g. in the* level control of liquids and in vacuum control (*cf.* chap. 8.6 and 8.3.1.1). As safety relays they switch off the circuit if the contact thermometer fails.

Universal electronic control devices have been discussed by Fischer [27]. He reports the use of proportional controllers besides electronic relays for temperatures between −200 and +800 °C. In this case the sensing is done by resistance thermometers having ground joints or flanges. A special advantage is the low surface load since the full electrical input is required only for starting up the heating.

A frequent requirement in laboratory distillation is the control of a *heating jacket temperature* in accordance with that inside the column. Methods for the thermal insulation of columns have been discussed in section 7.7.3.

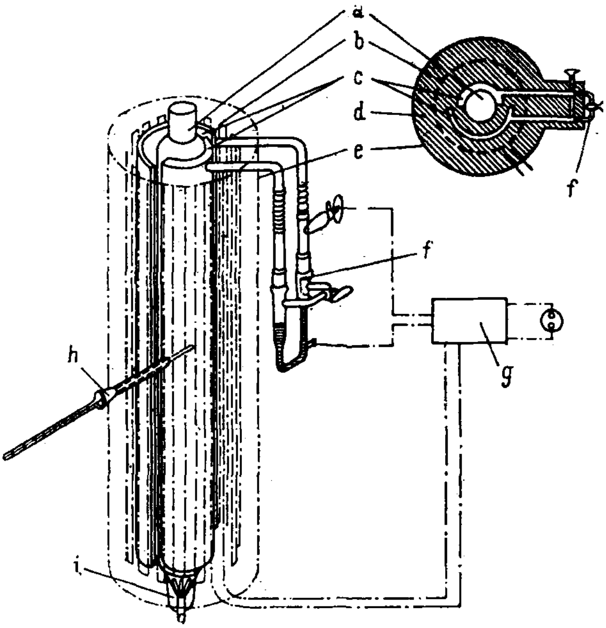


Fig. 368
Automatic control of the column jacket temperature according to the inner column temperature

a = Column, *b* = Heating element, *c* = Air thermometer, *d* = Glass wool insulation, *e* = Column jacket, *f* = Control manometer, *g* = Electronic relay, *h* = NS 14.5, *i* = NS 29

In batch distillation the column temperature increases during the course of the operation, frequently by sudden increments; the adjustment of the jacket temperatures by hand is consequently a matter of some difficulty. As the result of temperature lag, differences up to 30 deg. C between the jacket and column may occur, but these differences may be reduced considerably by automatic control. For this purpose air thermometers, thermocouples or resistance thermometers can be employed as sensing devices. Thermocouples are placed at the top and bottom of the column; these together act on the coil of a galvanometer, the position of which is "sensed" at short intervals by an electric switching device. The latter opens or closes the circuit of the heating jacket [28]. A circuit for the control of the heating jacket based on the internal column temperature has been described by Hutla [29].

The distillation controlling device Minitron V (Fig. 386) of Fischer [27] is equipped with two electronic proportional controllers serving the still pot heater and the heating jacket, respectively. Resistance thermometers of the type PT 100 do the sensing in the temperature range of 0 to 350 °C. The heating jacket may be controlled by adjusting the temperature on a helipot or by automatically following up the internal column temperature. A resistance thermometer in the column head instead of the helipot in the controlling device sets the desired value. The heating jacket temperature is then automatically regulated according to the vapour temperature in the column.

With *air thermometers*, one limb of which is placed inside the column and the other in the jacket, the author [11] was able to control to within ±0.5 deg. C. This accuracy could be achieved by the use of a contact manometer containing a conducting organic liquid, coupled by an electronic relay to the jacket heating circuit (Fig. 368). Up to 400 switchings per hour could be obtained with this arrangement. The temperatures in the jacket and the column remained completely parallel, even during sudden increases in temperature. The advantage of the method is that the jacket (which should preferably be subdivided into sections of 25—50 cm length) is controlled by the inside temperature of the column section. If the upper jacket section is controlled, in the more usual manner, by the temperature in the still head, during the distillation of a transition fraction the jacket will be cooler than the inside of the column. The upper column section then acts as a dephlegmator and produces additional reflux. The method of control just described also makes it possible to maintain a fixed temperature difference between the jacket and the column, if required.

8.3 Pressure measurement and control

The pressure ranges in which various forms of distillation are carried out can be defined as follows:

Pressure range	*Type of distillation*
Above 760 mm Hg	Pressure distillation
Between 760 and 1 mm	Simple and fractional distillation "Flash" distillation Thin-film distillation
Between 1 and 10^{-6} mm	Thin-film distillation Molecular distillation

In these various ranges different methods for the measurement and control of pressure are employed [2]; these will be discussed in the following sections [30]. A good review of the methods of pressure measurement has been compiled by Leck [31].

8.3.1 Pressure measurement and control above 760 mm and from 760 to 1 mm Hg

When distillation is carried out at pressures up to 2 atm absolute — *cf.* section 5.4.5 — mercury manometers of 1 m length are suitable for measuring the pressure above atmospheric (Fig. 369).

The distillation pressure is then given by the relation

$$b + \Delta p = p_1, \tag{202}$$

where b = corrected barometer reading (torr), Δp = pressure difference with respect to atmospheric as indicated by the manometer, p_1 = distillation pressure in the apparatus.

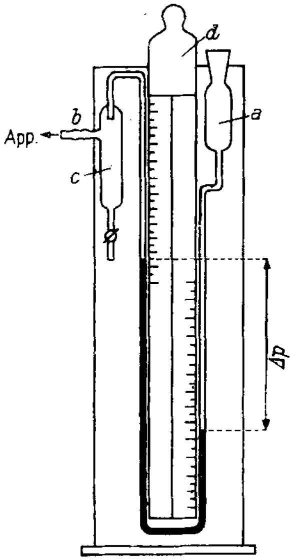


Fig. 369
Manometer for determining the difference between distillation pressure and atmospheric pressure

At higher pressures, diaphragm or Bourdon gauges are used. A method for controlling pressures above atmospheric has already been described in section 5.4.5.

The aneroid absolute pressure controller of the FA 149 type (manufactured by Wallace & Tiernau-Chlorator GmbH, Günzburg) allows absolute pressures to be controlled in the range of 20 to 1520 torr with an accuracy of 0.25 torr.

When distillation is performed at atmospheric pressure it is necessary to read the barometer, from time to time, so that boiling points may be corrected to 760 mm (see section 4.13). A reliable mercury barometer should be used [32]. The one after Gay-Lussac or that after Schrodt-Kiefer is often used in the laboratory. For an accuracy of ±0.1 mm the vernier should be employed in reading the mercury level. The liquid pressure gauges developed by Nickel [32] make allowance for the surface tension of the measuring liquid and enable corrections for zero deviations such as those caused by temperature changes.

It is advisable to have barometers checked occasionally against a standard instrument so that the corrections to be applied at various readings may be known. Aneroid barographs should be calibrated in the same way. These instruments — which generally have an accuracy of not more than ±0.5 mm — are provided with charts running either for a day or a week. The charts should be filed, in order that the atmospheric pressure at any time can be subsequently found. Aneroid barographs are as a rule compensated for errors due to temperature in the range of —40° to +40 °C by bimetallic strips.

The barometer reading is similarly required if reduced pressures are determined by means of open manometers (Fig. 369). The mercury, after thorough cleaning, is introduced, without air bubbles, through the safety vessel *a*, and the apparatus is connected at *b*. Vessel *c* is also a safety trap, functioning in the event of a sudden decrease in pressure. By means of the adjustable scale d the difference with respect to atmospheric pressure Δp is read off. The pressure p_1 is then found to be

$$p_1 = b - \Delta p, \tag{203}$$

with p_1 = pressure in the apparatus (torr), b = corrected barometer reading (torr), Δp = pressure difference as indicated by the manometer (torr).

The use of open manometers for pressure measurement has the advantage that the whole range from atmospheric pressure down to a few millimetres can be covered. For greater precision the mercury levels should be determined by cathetometer. An arrangement for reading and recording the mercury levels automatically has been described by Farquharson and Kermicle [33]. At a height of 80 cm the repeatability of operation is better than ±0.05 mm and the absolute accuracy better than ±0.11 mm.

Differential pressure determinations, as described above, are simplified considerably if the pressure gauge and the barometer are combined in a single apparatus (Fig. 370). Instruments of this kind are made for a barometer range of 600—820 mm and a pressure range of 1—310 mm Hg. By using tubing with an inside diameter constant to ±0.01 mm and with automatic zero correction [32] high accuracy may be obtained.

Short manometers (so-called Bennert manometers) have a closed evacuated limb (Fig. 371) and are usually designed for a pressure range of 0—180 mm Hg. They can be read to within 0.5 mm. Frequently, however, the closed limb is not sufficiently evacuated, and air bubbles tend to pass into this limb during use. In practice therefore, they can give rise to appreciable errors, especially in the 0—10 mm range. Frequent calibration of these instruments against an open manometer is therefore desirable. A manometer of this type, due to Ströhlein, is provided with a mercury seal at the end of the closed limb, whereby it is possible to pump out any entrained air.

The major sources of error involved in work with liquid manometers have been described by Dosch [34]. If a precision scale and a vernier for the readings are employed the pressure can be read off with a maximum deviation of 0.2 mm.

The vacuum manometer due to Holland-Merten [35] gives measurements with an accuracy of ±0.5 mm in the 200—20 mm range; by the provision of an inclined limb its accuracy is ±0.1 mm Hg between 20 and 0 mm (Fig. 372).

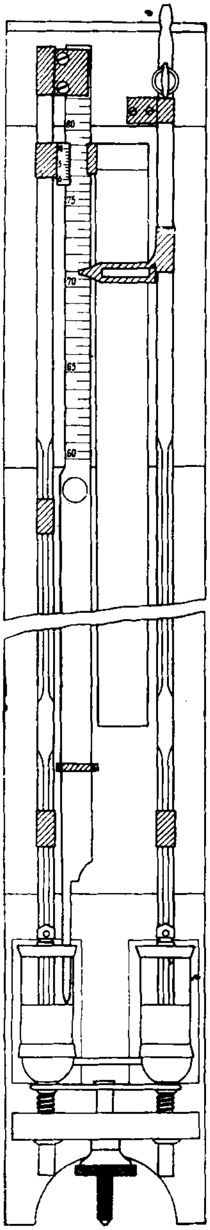


Fig. 370
Baro-vacuum meter

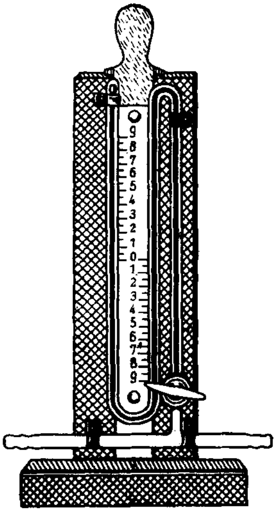


Fig. 371
Short Bennert-type manometer, range 0 to 180 torr

If instead of mercury, a silicone oil is used as manometer liquid, the precision of reading increases tenfold. Thus the Laporte manometer uses such a filling for the range of 0.2 to 20 torr. A vacuum gauge working on the displacement principle [35] which serves for precision measurements between 0 and 10 torr exhibits an accuracy of 0.01 torr. Vacuum pump oil, purified paraffin and Amoil S cannot be recommended as manometer liquids since they absorb water and thus yield appreciable errors [36]. Following a suggestion of Bachmann, in the case of water some additives should be used which reduce the surface tension.

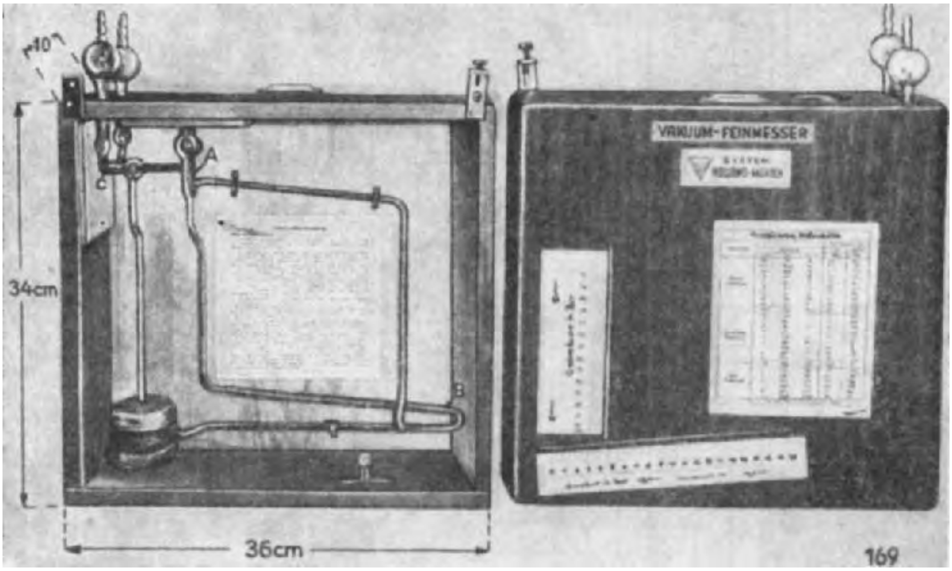


Fig. 372
Fine-reading vacuum manometer (Holland and Merten)

Compression manometers of the McLeod type can also be employed in the 760—1 mm range. Since, however, their main field of application lies in the range of 10^{-1} to 10^{-6} mm pressure, they will be discussed under the latter heading. For the range of 0 to 60 mm water column electronic contact manometers are now in use [36a].

Diaphragm gauges have the advantage of giving a reading independent of the nature of the vapour or gas [37]. Their sensing component is a thin metallic membrane. The diaphragm gauge VM-M of Heraeus (Fig. 373) indicates pressures between 50 and 10^{-1} mm with the same accuracy as a mercury manometer. It is particularly suitable for laboratory and pilot plant work. An essential feature of the device is that its sensitivity is not changed by the entrainment of air. A variety of precision pressure gauges in the form of mercury and aneroid manometers, especially such as used for calibrating purposes, are manufactured by Wallace & Tiernau-Chlorator GmbH, Wasserburg. For pilot plant distillations various models of spring manometers are suitable [2].

Whatever kind of manometer is used *a cold trap* should be placed between it and the apparatus to remove condensable vapours. Care must also be taken that there is no pressure drop between these two points. This may be checked by carrying out comparative pressure measurements on the evacuated apparatus before use, the manometer being connected first to the thermometer joint and subsequently after the cold trap.

In the control of reduced pressures in the 760—1 torr range mechanical devices as well as those combining the mechanical and electronic principles are in use [38]. Two methods can then be adopted to control the pressure: the method using an air leak and that of controlled evacuation.

With the vacuum pump running continuously, enough air is admitted into the buffer vessel through a tap for fine regulation or needle valve to maintain the required pressure. Requirements for this method are that the vacuum pump operates very uniformly and that the apparatus is leak-free (Fig. 374a).

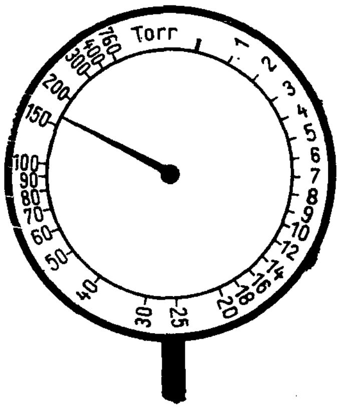


Fig. 373
Diaphragm manometer, type VM-M

8.3.1.1 The method of controlled evacuation

In this method evacuation of the apparatus takes place only when the pressure in the buffer vessel begins to exceed the required value. A pressure controller and relay can either start the pump or open a valve. A schematic diagram is shown in Fig. 374b.

In the 760—10 mm pressure range a device containing a *fritted glass disc* and mercury as sealing liquid can be used for control [39] (Fig. 375). The mercury level should be about 3 mm above the upper level of the fritted disc. With all taps of the controller open, evacuation is allowed to proceed until the pressure in the apparatus is 1—2 mm above the predetermined value. Tap C is now closed. The level of the mercury surrounding the fritted disc then falls, owing to reduction of the pressure in vessel B, until the disc is at the point of becoming uncovered. At this moment valve D is closed. The pressure in B is now equal to that in the apparatus minus the difference in level of the mercury in the two vessels. If the pressure in the apparatus then increases, the level in A falls further and gas is withdrawn by the vacuum pump through the fritted disc until it is again sealed off. By this method a vacuum constant to ± 0.5 mm can be maintained, provided that the regulator is kept at a uniform temperature.

Gilmont's pressure regulator [40] operates on the principle of the *Cartesian diver* and can be used for pressures down to 6 mm. Fig. 376 shows this apparatus, mounted on a console together with a Stock manometer and a Friedrichs-Antlinger non-return valve [41]. Its accuracy is about ±0.5 torr.

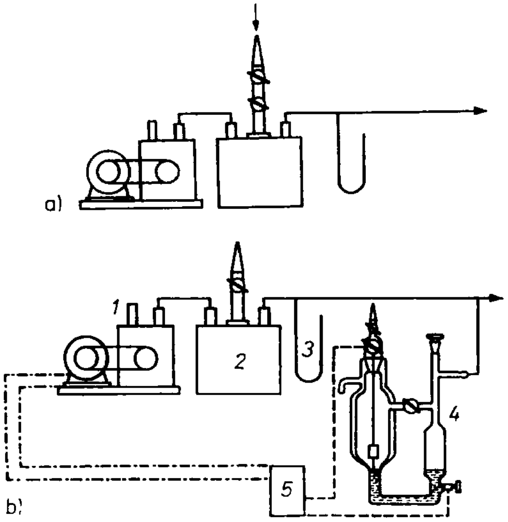


Fig. 374
Pressure control

a) air-leak method
b) method of controlled evacuation

1 = vacuum pump, *2* = buffer vessel, *3* = manometer,
4 = pressure controller, *5* = electronic relay

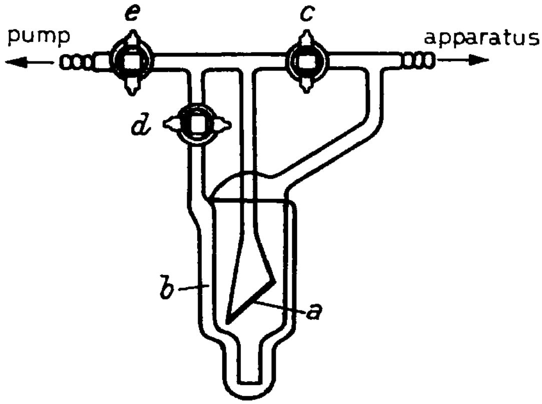


Fig. 375
Pressure regulator with fritted glass disc

a = fritted glass disc, *b* = residual pressure space, *c*, *d*, *e* = taps

A higher precision, *viz.* ±0.1 mm, can be attained by *electronic methods*. The mercury manometer is replaced by one containing a high-boiling organic liquid, increasing its sensitivity by a factor of about ten. A pressure difference of 1 mm Hg then corresponds to a difference in level of 10—13 mm in the limbs. The lower limit of the field of application is determined by the vapour pressure of the filling. A photo-electric method may be used, in which a thin pencil of light is directed over the float of a Dubrovin gauge onto a photo-electric cell. An increase in the pressure in the apparatus results in an interruption of the light by the float; the darkening of the cell causes the opening of a relay, which in its turn switches on the pump [42].

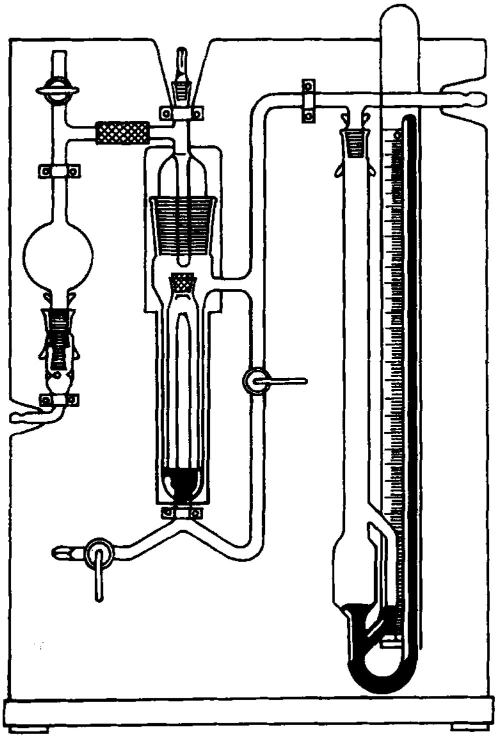


Fig. 376
Gilmont's pressure regulator (principle of the Cartesian diver)

Another electronic method is based on the use of a manometer liquid such as butyl glycol that has been made feebly conducting by the addition of a small quantity of a salt such as sodium nitrite. The current passing at 6—8 V need be only about 10^{-6} A; with an electronic relay it can be made to switch a current of 10—15 A at 220 V. The controller functions as follows. In one limb of a U-shaped vessel, maintained at a constant temperature, the required control vacuum is established (Fig. 374b). If the same pressure is present in the apparatus connected to the other limb, the contact liquid is at the same level in the two limbs. An increase in pressure in the apparatus causes the liquid in the limb joined to it to fall; contact is then made in the other, and an electronic relay starts the pump, which continues to run until contact

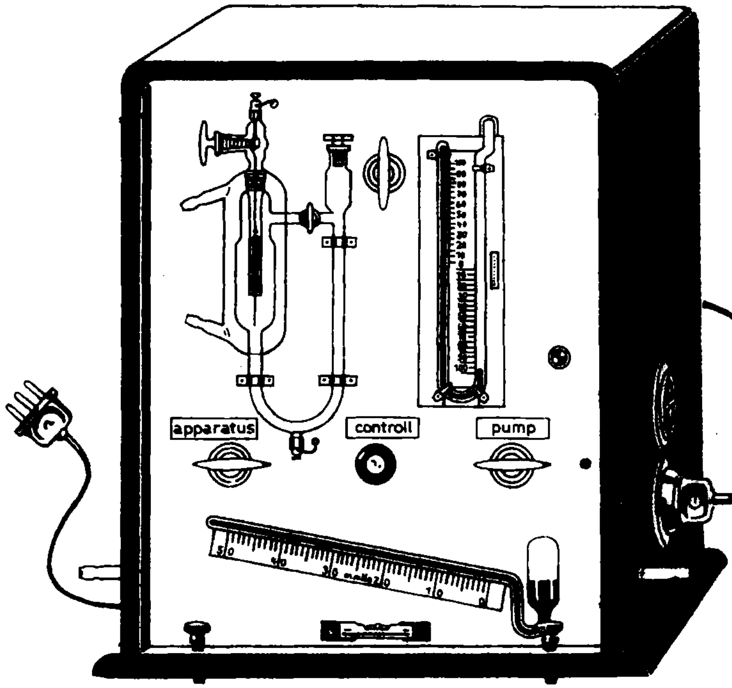


Fig. 377
Krell's automatic vacuum assembly

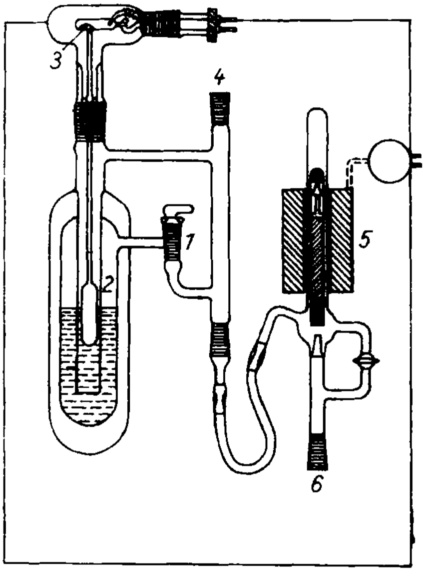


Fig. 378
Stage's automatic pressure regulator

is again broken. In the author's automatic vacuum assembly (Fig. 377) an accuracy of ±0.1 mm Hg could be obtained in the 300—1 mm range, shown by tests carried out with pure substances [43]. With phenol, pressure deviations of ±0.1 mm correspond to boiling point deviations of ±0.1 deg. C. In the separation of the isomeric xylenes at 70 mm pressure, where boiling points have to be determined to within 0.1 deg. C, the pressure should be controlled with an accuracy better than ±0.15 mm Hg [44]. Stage's pressure controller (Fig. 378) contains a float, which is so placed in the inner limb of an oil manometer 2 that mercury switch *3* is just kept level. If the pressure in the apparatus, connected at *4*, rises, the oil level in *2*, and with it the float, falls. By the action of a relay a magnetic valve *5* then opens, and the apparatus is connected to the vacuum pump via *6*. The vacuum controller due to Fischer [27] uses a differential manometer with inclined limb which is surrounded by a silvered vacuum jacket (Fig. 379).

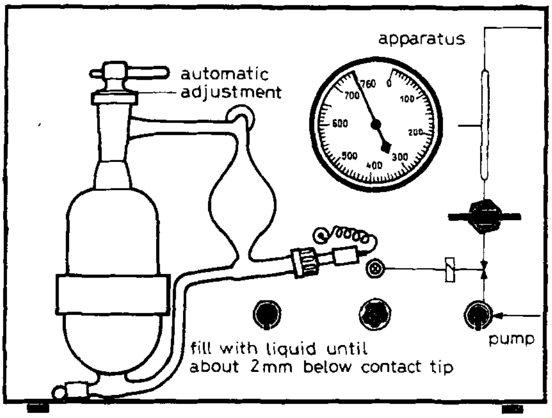


Fig. 379
Vacuum controller, type VK 1

8.3.2 Pressure measurement and control from 1 to 10^{-8} mm Hg

The measurement of very low pressures is a matter of considerable difficulty; since differential readings with respect to atmospheric pressure then become too inaccurate, indirect methods must be adopted. Observations of glow discharges enable the pressure to be determined only approximately. The fluorescence vacuscope due to *Burger* covers the measuring points 10^{-1}, 10^{-3} and 10^{-5} torr. Intermediate values may be estimated. Reproducible measurements in thin-film and molecular distillations require methods which are summarized in Table 77.

Measuring techniques for ultra-high vacua of 2×10^{-10} to 10^{-12} torr have been reported by Hoch [46]. Advantages and disadvantages of the gauges given in Table 77 have been discussed by Steckelmacher [47].

The Alphatron is an ionization gauge in which ions are generated by the bombardment of the residual gas with α-rays [45]. The mol-vacuum gauges (an absolute-manometer type due to Knudsen) make use of the radiometer effect. The design developed by Gaede [48] and the quartz thread vacuum gauge after Langmuir [49] are preferably employed. As is the case with the mol-vacuum gauge, the diaphragm microgauge does not include the kind of measuring gas in the calibration parameters. The latter device covers the range from 10^{-4} to 1.5×10^{-1} torr. The problems involved in pressure measurements in vacuum apparatus with mercury diffusion pumps have been discussed by Müller [50].

Table 77

Applicability and measuring range of various pressure gauges (after Mönch [45])

Type of gauge	Pressure measured (total or partial)	Dependence on nature of gas present	Range of applicability (torr)
Diaphragm and Bourdon gauges	tota.	independent	$760-10^{-3}$
Gas discharge manometer (Philips vacuum gauge)	total	dependent	$10^{-3}-10^{-5}$
Damping and friction manometers	total	dependent	$10^{-1}-10^{-4}$
Thermal conduction manometer (Pirani gauge)	total	dependent	$10^{-1}-10^{-4}$
Compression manometer (McLeod gauge)	partial (not vapour pressures)	independent (only for permanent gases)	$760-10^{-1}$ $10^{-1}-10^{-6}$
Ionization manometer	total	dependent	$10^{-3}-10^{-6}$
Radiometer (mol-vacuum gauge)	total	independent	$10^{-1}-10^{-8}$

It would take us beyond the scope of this book to mention all the vacuum gauges that are manufactured. They are fully described in the various monographs on high-vacuum technique [49]. In the 10^{-1} to 10^{-4} range the Pirani gauge is much used and in the 10^{-3} to 10^{-6} range the ionization manometer. Combinations of these two instruments into a single unit are available.

Vacuum gauges functioning electrically have the advantage that the pressure is indicated by a pointer, and that recording and controlling the pressure are possible. Thermal conductivity and ionization gauges both yield the *total* pressures of gases and vapours. To determine the residual pressure of any uncondensable gas it is necessary to place a cold trap before the gauge.

These instruments can be calibrated against a McLeod gauge; this is usually carried out with dry air. Calibrating curves are supplied by the manufacturers. The accuracy of Pirani gauges amounts to about 5% in the $1-5 \times 10^{-3}$ torr range, that of ionization gauges is about 3% in the $10^{-3}-10^{-6}$ torr range. The measuring tubes are provided with either NS 14.5/23 ground joints or flanges.

8.3.2.1 The McLeod compression manometer

The principle of this manometer, which gives a reliable reading only for permanent gases, is the compression of a certain volume of the gas, measured at the pressure to be determined, to a small volume in a capillary tube. The gas sample is in this way brought to a higher pressure that can readily be measured. The pressure p of the original gas can then be calculated with sufficient accuracy by means of the formula

$$p = \Delta h \frac{V_2}{V_1}, \tag{204}$$

in which p = the pressure of the original gas (torr),

Δh = the pressure at which the compressed gas is finally measured (the difference in mercury level in mm),

V_1 = the volume of sphere G and capillary tube K (measured from the junction at R),

V_2 = the volume of the compressed gas in capillary tube K.

Fig. 380 illustrates one of the commercial models of the McLeod manometer, in which the mercury level is not raised by means of a levelling bulb but by atmospheric pressure. The storage vessel V is partly filled with carefully purified mercury and the apparatus in which the pressure is to be measured is connected at A. P is connected to a filter pump. Whilst the apparatus is being evacuated the space in V above the mercury must simultaneously be pumped out. This is done by opening valve H to the filter pump to such an extent that there is not too large a difference in pressure

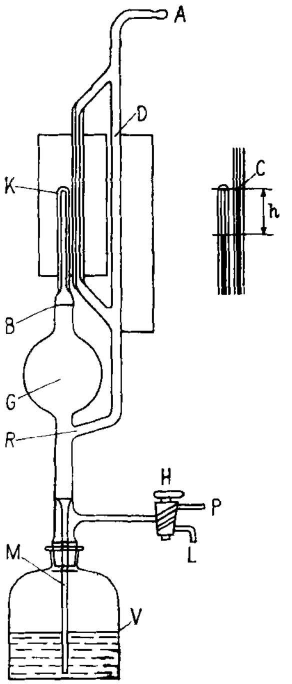


Fig. 380
McLeod gauge

Table 78

Volume of sphere and required amount of mercury in commercial McLeod gauges

Range (torr)	Volume of sphere (ml)	Amount of mercury (ml)
$2-10^{-5}$	300	450
$2-10^{-4}$	100	250
$15-10^{-3}$	15	50

between the manometer space and that in vessel V; otherwise mercury would rise in the manometer tube M or air would be sucked from M into V. To determine the pressure in the apparatus, valve H is turned so as to admit air slowly through tube L (the latter preferably being provided with an absorption tube to remove moisture and dust); the mercury is then forced up gradually into tube M. H is closed when the mercury has reached the mark C, level with the end of capillary tube K. The difference in height h is then read and p is calculated by formula (204). The volume V_1 is marked on sphere G and the volume V_2 on the scale against capillary tube K. Most manometers of this type, however, are so calibrated that pressure p may be read off directly from the scale. If the mercury is raised up to mark B the instrument provides measurements of pressures down to 10^{-2} mm; these are then read off on a scale along tube D. Prior to each subsequent pressure determination the mercury must again be brought back by the filter pump to below the tube junction at R. The volume of the sphere in commercial models and the amount of mercury required are shown in Table 78.

The numerous modifications of the McLeod manometer are dealt with in Ebert's book [51]. A pneumatically controlled model with automatic setting which is independent of the atmospheric pressure is described in detail by Peche [52]. A number of recommendations are made which are intended to ensure reproducible measurements.

As an example, Fig. 381 shows the "Vacuscope", a combination of a closed-limb U-tube manometer and a McLeod gauge. It covers the range from 80 to 1 mm as U-tube manometer and the $4-10^{-2}$ range as compression gauge.

A form of compression manometer that is very convenient for use in the distillation laboratory is the rotatable manometer of Moser (Fig. 382). It has three measuring

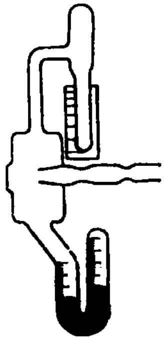


Fig. 381
Vacuscope

U-tube manometer: 80 to 1 torr
compression manometer: 4 to 10^{-2} torr

ranges, together covering from 760 to 10^{-4} mm, and contains only 6—7 ml of mercury. By turning the manometer anticlockwise around a ground joint one can adjust it for the ranges 760—1 mm, 1—10^{-2} mm and 10^{-2}—10^{-4} mm. The volume of the mercury must be so chosen that at atmospheric pressure bulb *G* is half full in position *4*. In each case the manometer is turned so far that the mercury meniscus is level with the mark *M*. The pressure is then read off against tube *n*. As in the case of the full-

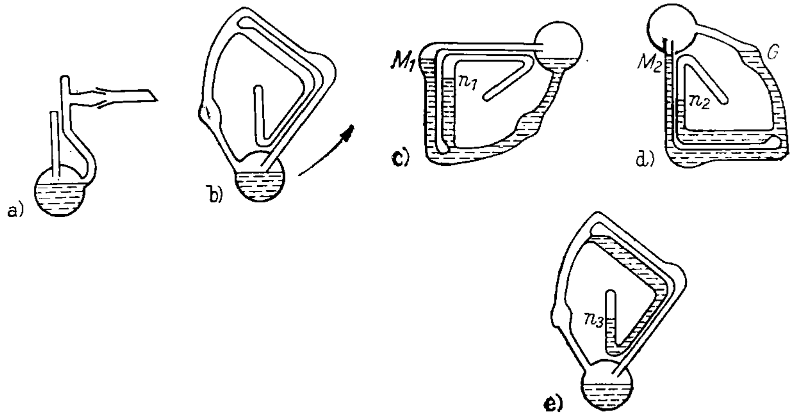


Fig. 382
Rotatable McLeod gauge of Moser

a) Side view
b) Position at start
c) Position for range 700—1 mm
d) Position for range 1—10^{-2} mm
e) Position for range 10^{-2}—10^{-4} mm

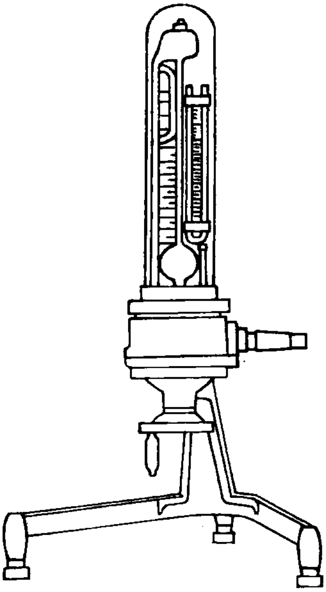


Fig. 383
Kammerer's compression manometer

10 to 10^{-3} torr: Hg-filling, 15 ml
1 to 10^{-4} torr: Hg-filling, 17 ml

sized McLeod gauge the device has to be reset to its original state before each measurement. The Moser gauge can be checked and calibrated by means of the large McLeod manometer.

The compression manometer due to Kammerer [53] also uses only a small amount of mercury (Fig. 383). Another advantage is that the filling is greatly facilitated by a new type of pumping mechanism. The instrument is supplied for the ranges of 10 to 10^{-3} torr and 1 to 10^{-4} torr and has an additional U-tube manometer for pressures up to 80 torr.

It should be pointed out again that all compression manometers indicate only the partial pressure of the gas component which is not condensable at the existing temperature. The presence of condensable substances is confirmed if different values of the pressure are measured in overlapping parts of two ranges [51].

8.3.2.2 Vacuum control to pressures of 10^{-6} mm Hg

Information on vacuum controllers for the medium and high vacuum ranges is scarce. Laporte [49] has described an instrument working on the thermal conductivity principle in which the Wheatstone bridge is connected to a signalling device which produces an acoustic signal when the pressure exceeds a given value.

Nisbet [54] has described an arrangement for regulating the pressure to 10^{-4} mm in a vessel containing air, and Melpolder [55] has published a method for controlling the pressure in the $10^{-3}-10^{-6}$ mm range. Melpolder's apparatus is shown diagrammatically in Fig. 384. It contains a McLeod manometer having four fused-in contacts $A-D$. By means of the device E the mercury in this manometer is forced up at intervals of 1 minute. Control takes place through the contacts A and B. When the pressure determined by contact D has been reached, this contact — via relays R_1

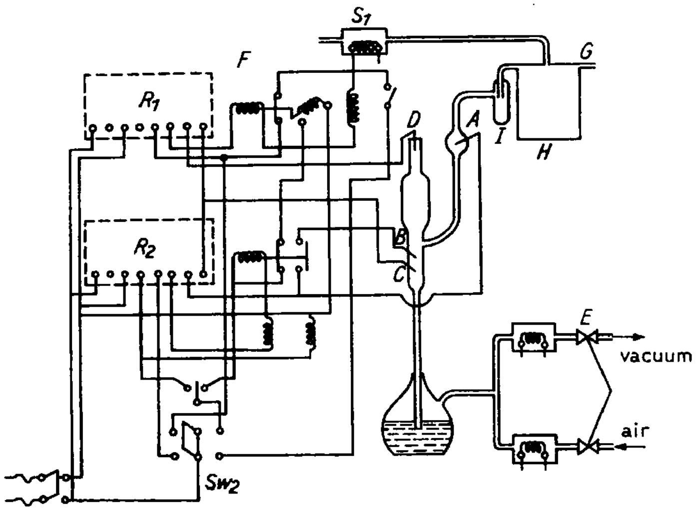


Fig. 384
Melpolder's apparatus for pressure control in the range 10^{-3} to 10^{-6} torr

and R_2 — closes the electromagnetic valve S_1 leading to the vacuum pump F. The apparatus to be evacuated is connected at G; flask H serves as buffer for smoothing out the variations in pressure. Cold trap I, cooled in liquid nitrogen, retains any condensable vapours. As soon as the required pressure is reached switch Sw_2 is put over to the position for "automatic control".

The electronic vacuum controller of Fischer [27] operates on the principle of thermal conductivity in the range of 100 to 10^{-3} torr (Fig. 385). The sensor is inserted in the vacuum line by means of a ground joint. The switching for the vacuum control can be continuously varied to cover any measuring range. The output of the potentiometer amplifier is connected to a directly controlled magnetic valve which is placed in the connection between the pump and the apparatus.

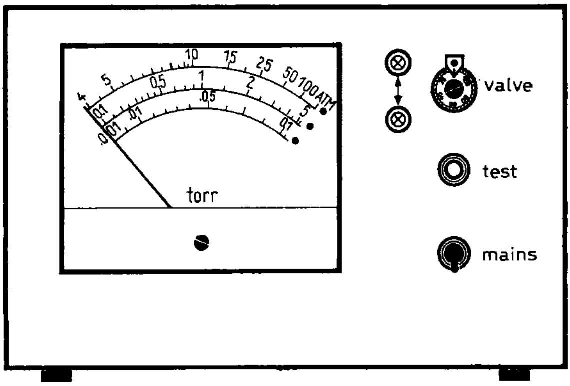


Fig. 385
Electronic vacuum controller, type VKH

8.4 Reflux and rate of evaporation

8.4.1 Time-operated devices for reflux control

As stated in section 7.5, automatic column heads are usually made to function by some timing device. The reflux ratio is then determined by the ratio of the periods during which the device is switched on and off. The timing apparatus used for this purpose should allow any required ratio to be established. At low ratios, say 1:1 to 5:1, the time during which distillate is taken off should be adjusted, for instance, to 1 sec; the corresponding periods of reflux return are then 1 to 5 sec. At higher reflux ratios, say 10:1 to 50:1, the period of distillate take-off should be low enough for the amount of liquid removed not to be greater than the quantity of enriched fraction present at the top of the column. It is therefore desirable to reduce the take-off periods progressively and to increase the periods of reflux return correspondingly, particularly during the distillation of transition fractions.

These requirements are fulfilled by the author's mechanical timing device [11]. It has a contact disc driven by a synchronous motor; the adjustment of the desired reflux ratio is done by means of a slider. The terminals are intended for connection to an electronic relay, which causes the electromagnet at the column head to function at a potential of 220 V. As the reflux ratio is increased, the period of distillate take-off is progressively reduced:

at a reflux ratio of 5:1 it is 2 sec.
at a reflux ratio of 10:1 it is 1 sec.
at a reflux ratio of 20:1 it is 0.5 sec.
at a reflux ratio of 50:1 it is 0.2 sec.

If the electronic relay is equipped with a switch to convert it from "normally closed" to "normally open", the reciprocal reflux ratios (*e. g.* 1:2, 1:5 etc.) can also be obtained for coarse separations.

The contact disc can be replaced by others yielding different periods. A more accurate control may, for instance, be provided in the range from 20:1 to 100:1; on the other hand the apparatus may be adapted for take-off times up to 30 secs, so that it can be used in pilot-plant and technical distillations.

The timers functioning entirely on electronic principles allow take-off and reflux periods of 0.1 sec to 20 min. to be adjusted with an accuracy of 1% [56]. For an alteration of the reflux ratio they require a change to be made in both the take-off and reflux times. A number of electronic devices are commercially available most of which are provided with bubble-point control. The column head is set at infinite reflux ratio as soon as the pre-set temperature of the contact thermometer placed in the column head is reached. When the temperature falls below this threshold the pre-selected reflux ratio is automatically switched on again. As an example, Fig. 386

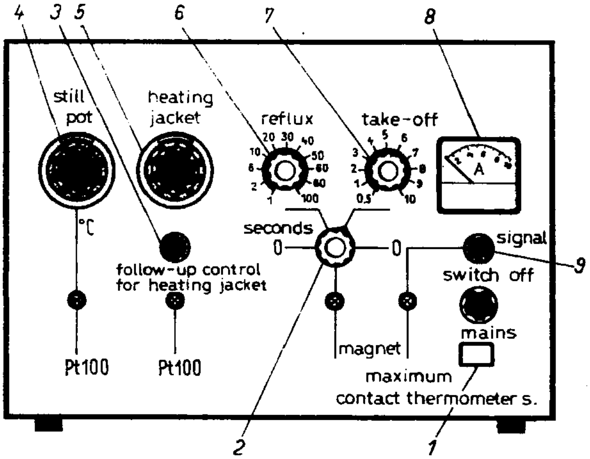


Fig. 386
Distillation control device Minitron 5

1 = mains key, *2* = switch, *3* = isotherm follow-up control for heating jacket, *4* = temperature control for still pot, *5* = temperature control for heating jacket, *6* = time decade for reflux, *7* = time decade for take-off, *8* = ammeter, *9* = change-over switch for maximum column temperature shows the distillation control device Minitron 5 which may simultaneously serve as timer and for flask and heating jacket temperature control (*cf.* chap. 8.2.2). The time-switching component has 11 steps for take-off periods from 0.5 to 10 sec and 11 steps for reflux periods from 1 to 100 sec, with the possible addition of a fixed period of 100 sec to the reflux time chosen. This yields reflux ratios between 1:1 and 400:1. Further, a transistor relay can actuate a limit contact which automatically interrupts the take-off indicating this by an acoustic or optical signal or switches off the apparatus altogether.

The accuracy of reflux control by means of electronic timers has been thoroughly studied by Röck et al. [13]. Gemmecker and Stage [57] have found that constant, reproducible and load-independent values for reflux can be obtained only with electromagnetically controlled components. Deviations may be due to the following effects.

The reflux ratio is larger than the time ratio if

- condensation occurs below the divider so that condensate thus produced is not handled by the divider;
- the condensate contained in the condenser does not completely flow to the divider so that again a partial stream is not handled by the divider;
- with vapour division the reflux condenser is accessible also during distillate take-off.

The reflux ratio is smaller than the time ratio if

- the dead volume of a magnetic valve always contains a small residue of liquid;
- vapours condense in the distillate take-off pipe;
- with vapour division the flow of liquid is obstructed in the condenser because the condensate cannot leave the reflux condenser during distillate take-off.

8.4.2 Control of boil-up rate

We have seen that the theoretical plate number is strongly dependent on load in some columns. In addition, if a column is operated near to flooding, the control of the boil-up rate should be close enough not to allow flooding to take place. Two methods of control are available:

1. that of keeping the heat input constant, especially in simple distillation and
2. control of the flask heater by the pressure drop in the column in countercurrent distillation.

The method of supplying the electric flask heater with a constant current can be unreliable since it involves frequent checking of the load, especially if there are large differences in the heats of evaporation of the components being distilled. As the pressure drop in a column depends on the vapour velocity (section 4.11), it provides a convenient means for controlling the heater. The method also has the advantage of not being seriously affected by mains fluctuations or by variations in the gas pressure [13].

Fig. 387 shows the arrangement employed in the Destinorm series of apparatus [11]. The bottom reflux measuring device, *a*, carries a side-tube connected to a guard condenser *b*. In order to prevent condensate from remaining suspended in the side-tube or the condenser itself, a small current of nitrogen may be blown in through a bubbler, or, more simply, the tube below the condenser may be heated by a resistance winding to such a degree that flooding cannot occur. The condenser is connected to a manometer *c*, provided with a contact wire *d* that can be adjusted during operation. The second limb *e* of this manometer is open if the distillation is at atmospheric pressure; for vacuum distillation it is connected to the vacuum lead at the column head. The contact manometer (Fig. 388) contains mercury if it is used with a mechanical relay (section 8.2.2), or an organic liquid when employed with an electronic relay. An organic liquid gives about ten times the sensitivity obtainable with mercury. By means of a resistance the flask heater is first adjusted to the desired load, producing a certain pressure drop; the wire *d* is then brought into contact with the manometer liquid and the heating current is increased slightly. The relay connected to the heater switches it off when contact is made. It is advisable not to switch the total current, but to keep about two-thirds of the heating capacity in circuit and to control only the remaining third. The use of a delayed relay can be recommended, since otherwise, if bumping occurs, every bump will produce a contact. Some forms of contact manometer are made with a hinged limb (Fig. 389), provided with a millimetre scale and angular graduations.

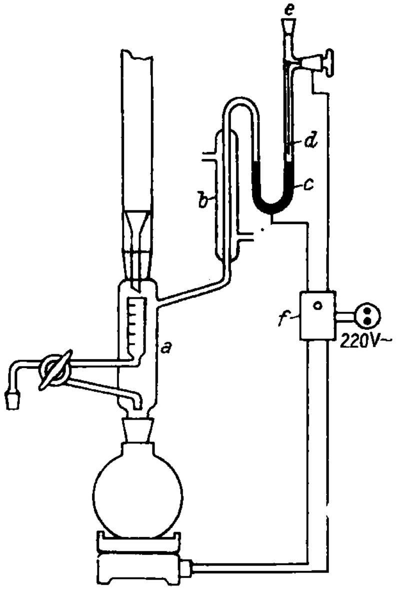


Fig. 387
Arrangement for controlling the load by the pressure drop in a column

a = bottom reflux measuring device, *b* = condenser, *c* = contact manometer, *d* = adjustable contact, *e* = to atmosphere or column head, *f* = relay

A much more elegant method has been described by Stage [58]. Electronic control is performed following either the temperature or a pre-set reflux rate in drops or ml/min. The reflux is optically scanned and controls the proportional and continuous heating. The still pot temperature is set according to the boiling point of the bottom product in question. The column load remains constant even after change of the fraction. An arrangement for automatic reflux ratio control dependent on the bottom temperature in batch distillation has been described by Fieberg [58a].

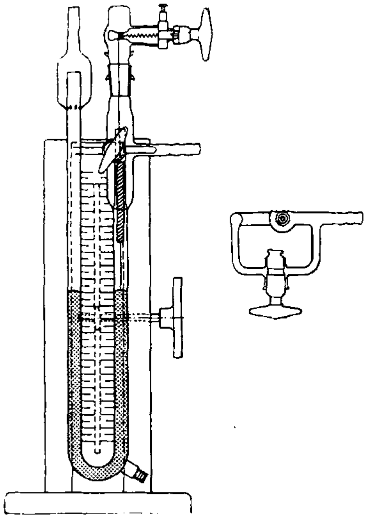


Fig. 388
Contact manometer (Krell)

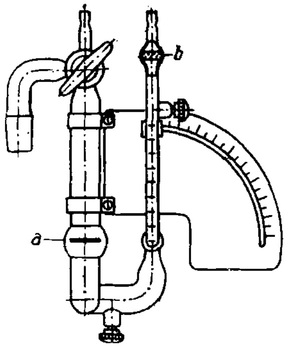


Fig. 389
Contact manometer with hinged limb

a = filling mark
b = G 1 fritted filter

8.5 Measurement of physical data during distillation

A correct boiling point is often not sufficient evidence for the purity of a component and it is therefore desirable to determine other properties during the course of a distillation. This should preferably be done without removing distillate, and the determinations must then be performed in the stream of reflux at the column head. Such measurements will allow the conditions of distillation to be altered if necessary, at the proper moment.

Continuous determinations of the following properties [59] are possible in laboratory and pilot plant columns:

melting point,
refractive index,
dielectric constant.

With the last two, however, difficulties are experienced in keeping the liquid at a constant temperature, since the distillate temperature normally rises during distillation.

8.5.1 Melting point

In the separation of high-boiling fatty acids Jantzen and Tiedcke used an ingenious device for determining the melting point of the distillate (Fig. 390). At *a*, the distillate or reflux drops into a capillary tube cooled by a thermosyphon loop, as in Thiele's melting point apparatus, and solidifies. In the first place this gives the freezing point, as indicated by thermometer *b*. The liquid in the mean time flows through *c* into receiver *d*. The temperature of the thermosyphon is then raised and the melting point is observed. An automatic apparatus on the same lines, yielding values with an accuracy of ±0.25 deg. C, has been developed by Müller and Zenchelsky [60].

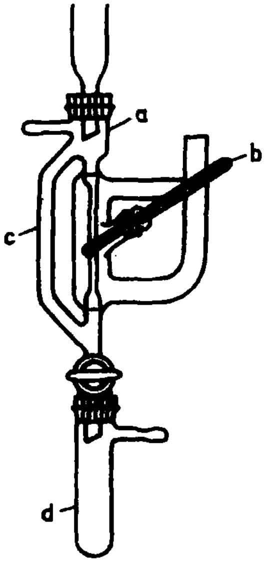


Fig. 390
Apparatus of Jantzen and Tiedcke for the determination of the melting point of high-melting fractions

8.5.2 Refractive index

The refractive index is widely employed in conjunction with the boiling point for characterising organic substances [59]. In the separation of close-boiling substances a continuous determination of the refractive index allows the conditions of distillation to be so chosen that the transition fractions remain as small as possible and yields are consequently increased.

Photoelectric refractometers indicate their reading on the scale of an electric measuring instrument and hence permit this reading to be recorded.

Automatic and continuously recording flow refractometers have been developed by Thomas et al. [61] and by Latchum [62].

The model Remat 10 of VEB Carl Zeiss Jena [63] is a differential flow refractometer. It compares the refractive index of the flowing sample with that of the reference liquid which can be arbitrarily chosen. Fig. 391 shows the front and back of

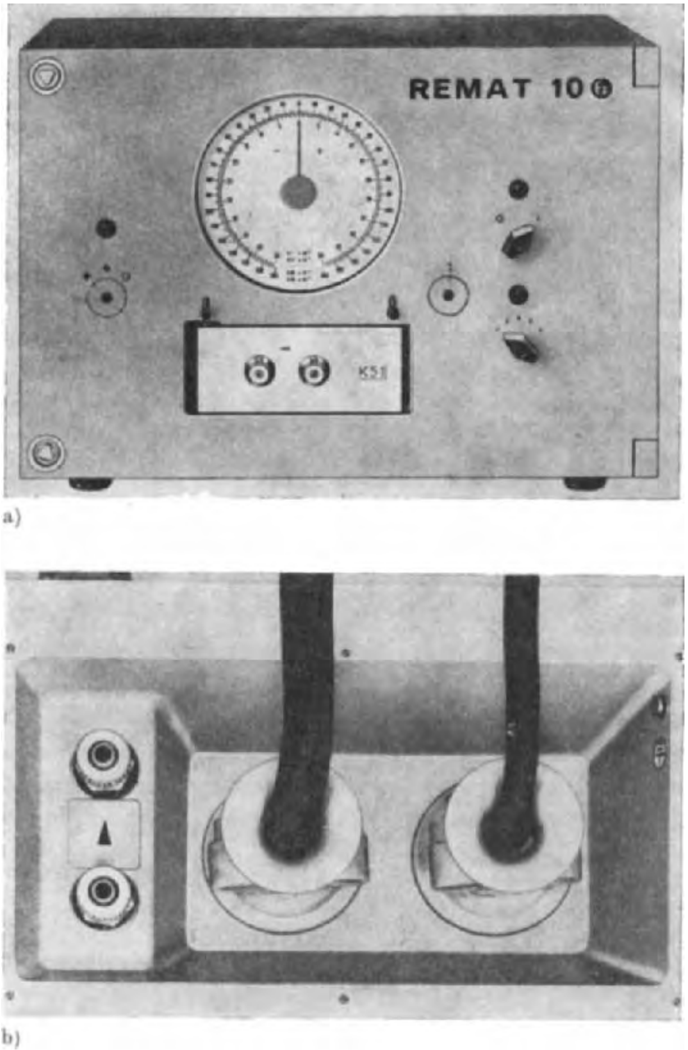


Fig. 391
Flow refractometer Remat 10

a) front part with 2 troughs K 51 and 2 linear scales
b) back with cables for power supply

the device. It works at temperatures in the range of −10 to +120°C and has 4 troughs with different measuring ranges.

Stage's arrangement (Fig. 392) designed for measurements of phase equilibria, appears useful. Two commercial flow refractometers are so arranged in the equilibrium apparatus that they indicate the refractive indices of the liquid and vapour phases and thus enable their compositions to be determined.

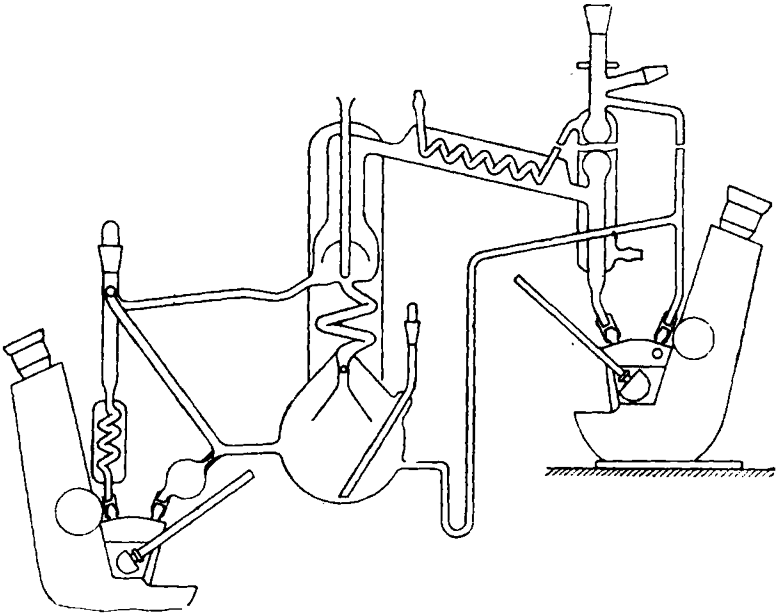


Fig. 392
Stage's apparatus for phase equilibrium measurements with flow refractometers

Interferometers can also be employed as automatic indicators, in this case of refractive index differences. Kegeles and Sober [64] used an apparatus containing a 25-mm cell; with the green mercury line as light source this gave readings accurate to 2 units in the 6th decimal place.

8.5.3 Dielectric constant

The increasing use of physical data in laboratory work has also led to developments in the technique of determining the dielectric constant. This constant is an especially useful quantity when the mixture contains water (diel. const. 80) or other components having widely different values. Examples are the mixtures acetic acid (diel. const 6.13)-acetic anhydride (22.2) and methanol-toluene. In the latter system the azeotrope has a dielectric constant of 26.8, whilst methanol and toluene have values of 33.8 and 2.37, respectively [65]. The dielectric constant has also proved convenient for determining toluene in benzene, in spite of the fact that the difference in the figures for these two components is only 0.08 units.

Fig. 393 shows an apparatus for determining the dielectric constant during the course of a distillation, as used by Oehme [65]. The measuring cell may of course also be placed in the reflux tube of a column head, where it will indicate the proper moment for altering the conditions of distillation. A book by Oehme contains a complete collection of values of the dielectric constant, together with the frequency and temperature at which they were determined and the temperature coefficient.

In Slevogt's dielectrometer, the "Multidekameter", the frequency is not restricted to a single value, but can be varied between 100 kilocycles and 12 megacycles [66]. Grant [67] has described a recording dielectrometer that appears suitable for distillation. The limitations of the dielectric constant technique in organic chemistry have been studied by Felloni and Tantillo [68]. The determination of the quasistatic dielectric constant as a parameter for the identity and purity of liquid raw materials is reported by Lertes and Niel [68a].

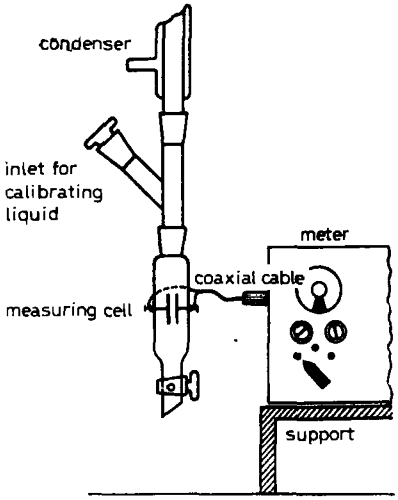


Fig. 393
Arrangement for measuring the dielectric constant during distillation (Oehme)

8.5.4 Various determinations

Laboratory and pilot plant work allows the same methods to be employed for the continuous determination of chemical and physical properties of the distillates and bottoms as work on a technical scale [2]. In many cases, however, the measuring arrangements will have to be modified appropriately.

The density balance due to Clasen [69] should be suitable for analytical work. It requires 8 ml of substance and has an accuracy of 10^{-3} g cm^{-3}. An arrangement for the continuous measurement of liquid density has been reported by Linford [70].

In large-scale work, particularly in the petroleum industry, considerable use is made of continuous methods for *viscosity determination*. Such a method might conceivably be modified for distillation on a laboratory scale. Fritzsche [71] has given a survey of viscosimeters for continuous on-line operation in oil refineries.

Other forms of continuous measuring devices utilized in chemical industry, such as the *infrared* and *ultraviolet spectrographs* and the *mass spectrometer*, might also find an application in small-scale distillation, particularly for analytical work [72]. A review of modern continuous analytical methods has been published by Siggia [73]. Of course, automatic analyzers have also come into use [74].

In chap. 4.2 it was pointed out how the surface tension of the liquid phase may influence the separating process in a countercurrent column. The Lauda tensiometer (DIN 53914, manufacturers: Meßgerätewerk Lauda) allows liquid interface tensions to be measured and recorded automatically.

At the present time, *radiometric methods* are becoming of increasing importance for following the course of a distillation. In the separation of multicomponent mixtures of compounds having similar physical properties these methods are both convenient and time-saving. To the initial mixture a certain amount of a labelled compound is added and its concentration in the distillate fractions is determined. Hughes and Malocoy employed the compound $^{14}CH_3OH$ to find the relationship between pressure and composition in the system methanol, ethanol and water and to observe the progress of the distillation.

Zelvenskij et al. [75a] labelled low-boiling components with the radionuclides C-14 and Cl-36 in order to measure diffusion and material transfer rates in falling-film distillations. It should be possible to test columns by similar methods [75].

8.6 Measurement and metering of gases and liquids

Laboratory work with gases has been extensively discussed in the books of Bernhauer [76], Wittenberger [77] and Müller and Gnauck [78] so that no details need be given here.

The measurement and supply of gases and vapours are required in low-temperature distillation (*cf.* section 5.3.1), in carrier vapour distillation (section 6.1) and in adsorptive distillation (section 6.3). A neutral atmosphere (usually nitrogen) is often necessary in the distillation of inflammable, oxidizable or hygroscopic material, and here again gas volumes may have to be measured.

Methods for the indirect measurement of the quantities of saturated or superheated water vapour have already been described in section 6.1. To determine the flow rates of gases or liquids under pressure, rotary flow meters ("Rotameter", a trade name), containing a float that is kept in rotation and suspension in a tapered tube, are now widely employed. Whilst bubble counters and capillary flow meters have to be calibrated against a wet gas meter, commercial "Rotameters" are generally supplied already calibrated for given gases or liquids. The forms of flow meters commonly used for laboratory and semi-technical work are shown in Fig. 394. Especially for pilot plant distillations, they may also be designed for pneumatic or inductive data transmission. For checking the amounts of cooling water employed in distillation, devices of the type SW 16.1 (Fig. 395) have proved convenient. The tapered glass tubes contain floats of a variety of materials, depending on the properties of the

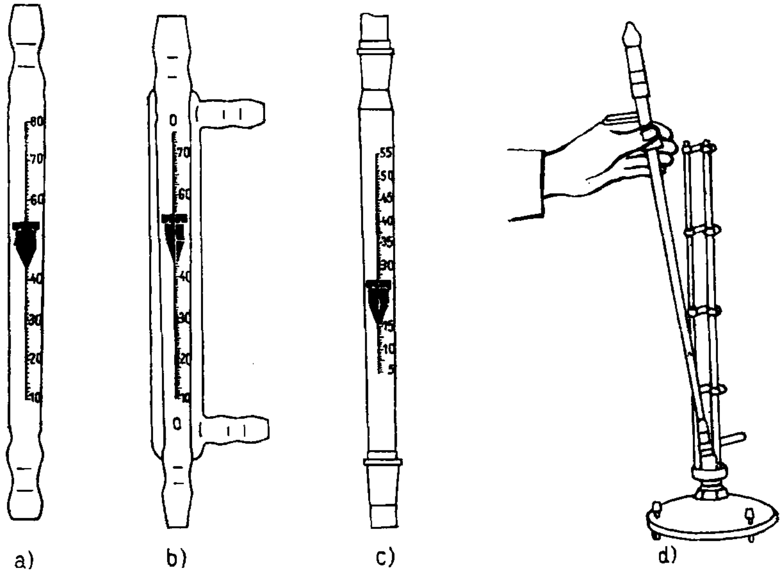


Fig. 394
"Rota" flow meters

a) with olive for tubing
b) with olive for tubing and with jacket
c) with standard ground joints
d) with armature

Fig. 395
Laboratory flow meter, type SW 16.1

Measuring range I: 0.5 to 3.0 l/min;
range II: 3.0 to 12.0 l/min

fluids. An automatic cooling water control has been described by Hinzpeter [79]. There are also flow monitors for liquid or gaseous media commercially available which switch off the power supply when the water supply is interrupted or is less than the pre-set value and switch it on automatically when the water supply is restored [80].

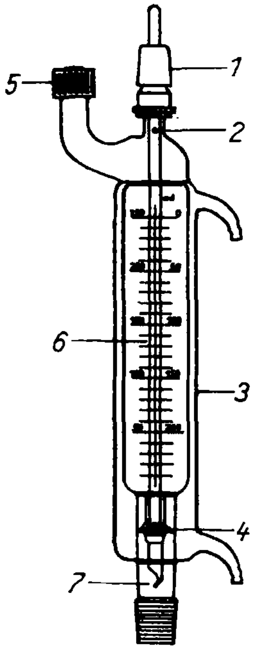


Fig. 396
Diagram of dropping funnel

1 = valve screw, *2* = opening, *3* = heating jacket, *4* = ball joint valve, *5* = screw-cap, *6* = valve spindle, *7* = drop-forming tip [81, 88]

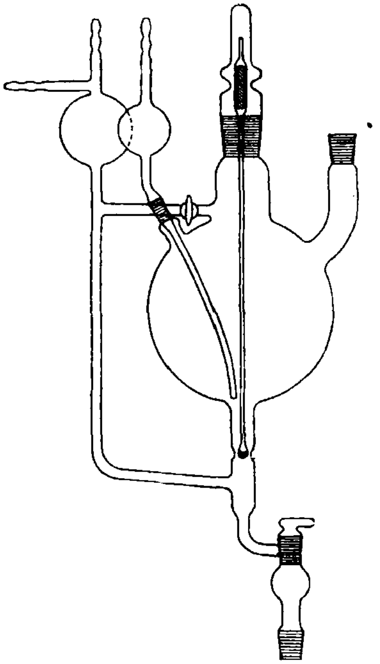


Fig. 397
Stage's automatic feed control

In continuous distillation the usual practice is to place a storage vessel for the feedstock at such a height that the resulting hydrostatic pressure is greater than the pressure in the column, and a steady supply is ensured. If an ordinary glass stopcock is used for control, it will have to be adjusted frequently, since the level in the storage vessel falls continually and a corresponding reduction in the feed rate would otherwise result. Although it is possible to control the rate accurately by the use of a needle valve and capillary drop counter, a constant-pressure (Mariotte) bottle (Fig. 224) is preferable. When necessary this bottle can be refilled from a large vessel by air pressure from a small hand blower.

The dropping funnel of Dammer and Kramer [81] (Fig. 396) employs a combination of the constant-pressure principle and valve control. The modified Mariotte bottle due to Hänel [82] with 6 interchangeable capillaries allows low dropping rates to be set quite exactly.

The various forms of Labodest automatic apparatus have been provided by Stage with a feed arrangement containing a magnetic valve, controlled by means of a timer (Fig. 397). The period during which the valve is open can be varied between 1 and 120 sec and the period of closure between 1 and 2 sec. Whenever the valve opens a definite quantity of liquid flows into the measuring device below and drains away during the period of closure. The feed vessel and its immersion tube function as a constant-pressure bottle as long as the liquid level is above the lower end of the immersion tube.

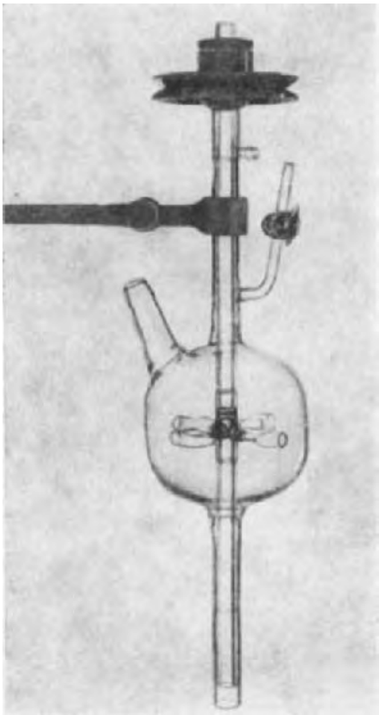


Fig. 398
Jena circulation pump, type 100

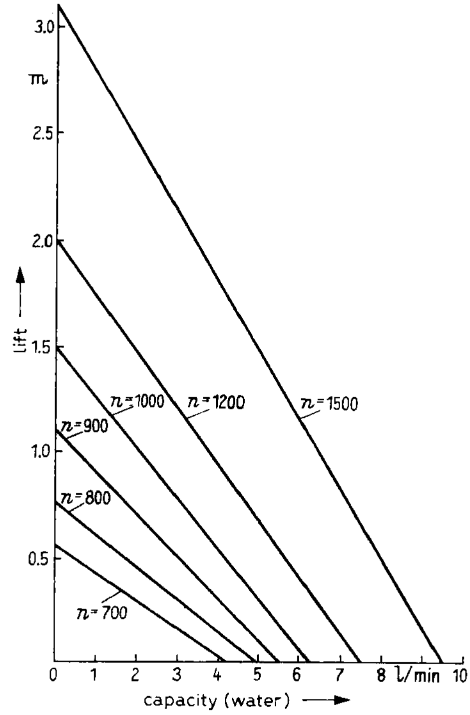


Fig. 399
Characteristics for the Jena circulation pump 100

Pinkava and Wichterle [83] have described a pneumatically operated glass valve with which, for instance, a water supply can be regulated in the 0.02—3500 ml/h range with an accuracy of ±1.5%. The book of Pinkava [84] deals thoroughly with metering problems encountered in the laboratory.

An appliance that finds many uses in the laboratory is the Jena Circulation Pump 100 (Fig. 398), a centrifugal pump of the simplest type constructed entirely of glass. Its lift and capacity as a function of the number of revolutions per minute of the motor are given in the diagram of Fig. 399. The electric spring bellows pump manufactured by Messrs. Haage serves for the continuously variable metering of gases and liquids. Its lift may amount to 20 m water column. The standard models, which have no stuffing boxes, are designed for capacities of 15 ml/h to 1,500 l/h and made of stainless steel, tombac-brass or plastic material (Fig. 400).

A special group is formed by peristaltic pumps with tubes made of various materials. They are mainly used for metering low-boiling liquids, emulsions, sludges,

Fig. 400
Electric spring bellows metering pump for liquids and gases

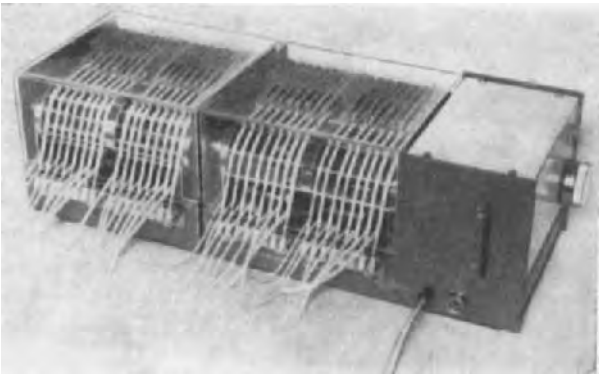


Fig. 401
Peristaltic pump, type DP 2-2, with 3 different speeds
Capacity: 3 to 2400 ml/h

gases and suspended solids [86]. Depending on the tube diameter (approximately 3 to 10 mm) and the revolving speed of the rollers amounts of a few ml/h to about 20 l/h may be handled in the temperature range of −90 to +150 °C. As an example Fig. 401 shows the weakly pulsating peristaltic pump of the type DP 2-2 which may be employed as pressure or suction pump and has 16 separate tubes. A contribution to the quantitative description of the pulsation of peristaltic pumps has been made by Engler and Kühnlenz [86a].

Plunger pumps have proved satisfactory for larger plants with continuous operation. Metering pump heads of glass with PTFE bellows were already mentioned in chap. 5.1.3.1 (Fig. 143) [88]. Circulation pumps made of glass are put to a variety of uses for a capacity range up to 20 m^3/h and lifts up to 15 m (Fig. 402). Metering pumps which may also be employed for the automatic mixing of various liquid streams (Fig. 403) in laboratory and pilot plant distillation [85] are manufactured by

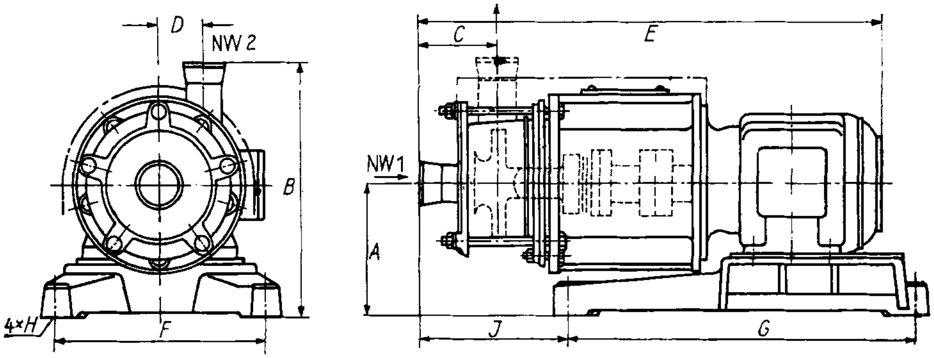


Fig. 402
Glass-made circulation pump with Teflon gasket

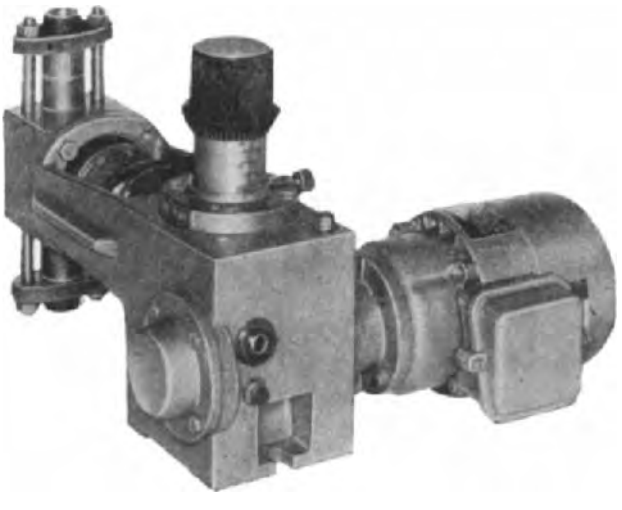


Fig. 403
Precision metering device Normados P 31

Messrs. Bran & Lübbe, Hamburg. Their Normados K and J series meet the requirements of laboratory and semi-technical work, the capacities ranging from 0.6 to 1,121 l/h. The machines can be controlled manually, electrically or pneumatically. Since the module system is strictly adhered to the components may be combined in many ways. The type Gnomodos is intended for small capacities (0.6 to 4.4 l/h) and is provided with a knurled flap for the fine adjustment of the stroke.

The model Gnomodos S 02 has several metering pump heads either with plungers or diaphragms. The drive is designed for strokes from 0 to 15 mm. Up to 5 pump heads can be operated simultaneously.

9. Arrangement of a distillation laboratory, starting up distillation apparatus

9.1 Lay-out

Points to be considered in designing a new laboratory are dealt with by Behre [1], Coleman [2] and Schramm [3], while the arrangement of a laboratory for analytical distillation is gone into by Kincannon and Baker [4].

A distillation laboratory should have long, high wall surfaces for supporting the frameworks for apparatus. Examples of satisfactory arrangements in various spaces are given in Figs. 404 to 407. The location of pilot plants is illustrated in Figs. 140, 141, 146 and 160. There is a tendency for the manufacturers of distillation apparatus to run test centres for work on problems of material and heat transfer. The testing apparatus is controlled from a measuring room. An associated laboratory is designed for complementary distillation experiments and the necessary analytical work on samples [21].

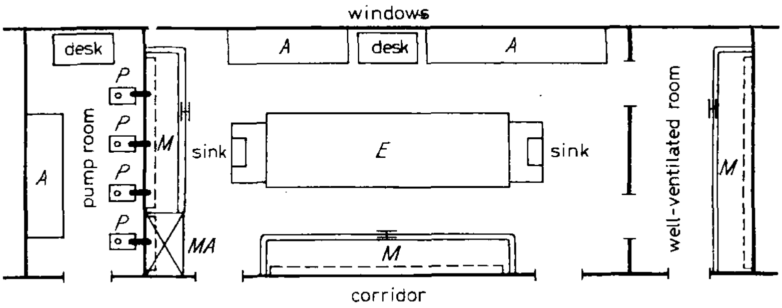


Fig. 404
Arrangement of a distillation laboratory (long type) with a well-ventilated room and a separate pump room

A = Laboratory bench, M = Framework, MA = Framework in fume cupboard, E = Laboratory bench

Lay-out I, Fig. 404

For the reduction of pump noise in the actual laboratory the vacuum pumps are placed in a separate pump room. The pumps P are close to the wall between this room and the laboratory, so as to make the vacuum lines as short as possible. The other side of this wall is provided with a framework M and is reserved for vacuum distillation. Automatic pressure controllers and vacuum gauges are placed on or behind the framework where they are accessible and can easily be watched. The pump room can also serve as a small workshop.

The window side of the laboratory is occupied by benches A with water and electricity supplies. This bench is intended for physical determinations, such as refractive index, solidification point, melting point, dielectric constant and optical rotation. The central bench *E* is reserved for chemical work. The main wall adjoining the passage is also provided with a framework. For the distillation of unpleasant or poisonous compounds such as ether, benzene, chlorinated hydrocarbons or organic nitro-compounds, a separate space is provided. It may be regarded as a large fume cupboard which can be entered; a 40-fold renewal of its air every hour ensures sufficient ventilation. The screen separating it from the laboratory is of wire-reinforced glass, so that the apparatus can be supervised from the laboratory. If automatic apparatus is used in this chamber the measuring and control equipment should be mounted on the wall outside it.

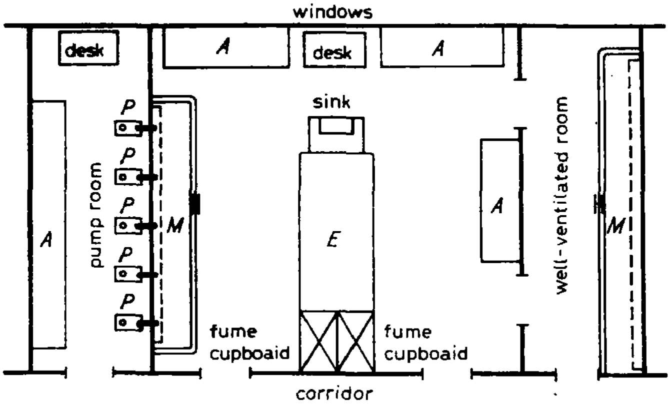


Fig. 405
Arrangement of a distillation laboratory (square type) with a well-ventilated room and a separate pump room
(for legend, see Fig. 404)

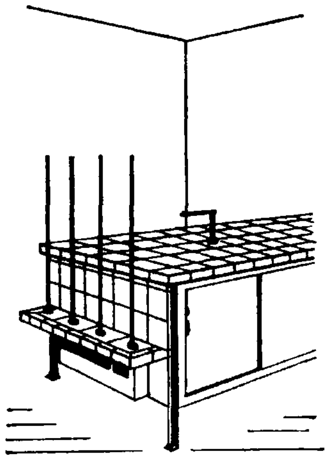


Fig. 406
Laboratory bench with stands for apparatus

Lay-out II, Fig. 405

The principle of this arrangement is the same as that of Fig. 404. As the longest free surfaces are the dividing walls, the frameworks are attached to them. The enclosed, ventilated room is again intended for the distillation of noxious substances. The central laboratory bench here starts from the wall adjoining the passage and can be fitted at its end with additional stands for small apparatus (Fig. 406).

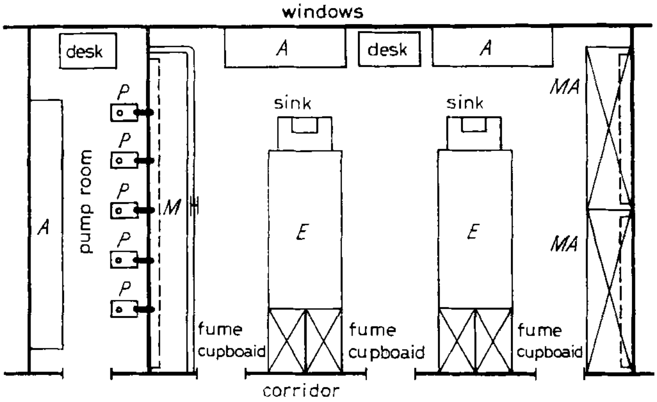


Fig. 407
Arrangement of a distillation laboratory (short type) with a separate pump room and high fume cupboards
(for legend, see Figs. 404 and 405)

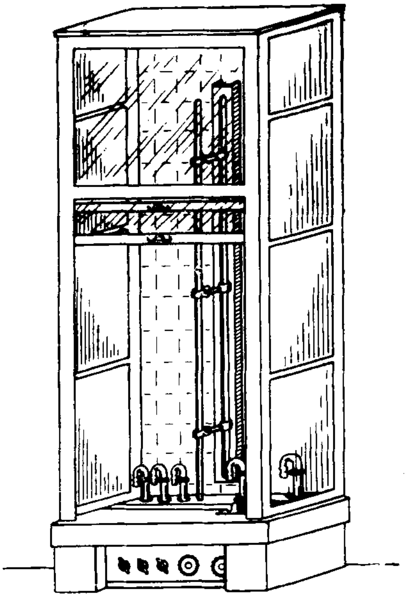


Fig. 408
Fume cupboard containing framework for apparatus

Lay-out III, Fig. 407

This laboratory, which is intended for distillations involving more extensive chemical work, is equipped with two large central benches. Instead of the ventilated room, it only has two fume cupboards *MA* containing frames. One of these cupboards extends from the floor up to the ceiling (Fig. 408); the second starts from table level, but also contains stands for small apparatus. The air speed at the openings of the cupboards is maintained at 1—2 ft/sec.

9.2 Frameworks and services

Frameworks to carry distillation equipment can either be built with sets of parts or be permanently attached to the walls. A framework which may be used to build any structure demanded by the apparatus, is shown in Fig. 409. Unit frames mounted on castors (Fig. 410) are obtainable, and have the advantage that the apparatus may be used anywhere in the laboratory. For extensive apparatus it is preferable to use frameworks fixed to the walls. Jordal rails (Fig. 411a) which are embedded in the walls are designed to take up special clamps (Fig. 411b) at any desired height [5]. By the use of cross-bars of various lengths the framework can be made to match the apparatus (Fig. 408).

The arrangement used by the author is illustrated in Fig. 412. The framework consists of interconnected units of 1 metre width, cemented into the wall; the wall is tiled to a height of 5 feet. On the floor below this framework there is a brickwork trough, 2 ft. 6 inches in width, to catch any liquid that may be spilt by breakage. This trough will also localize a fire.

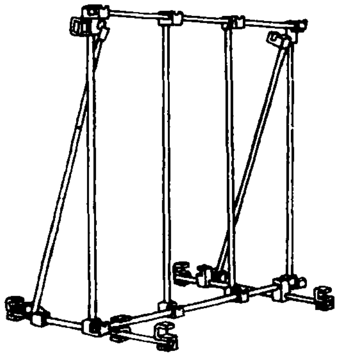


Fig. 409
Framework for components

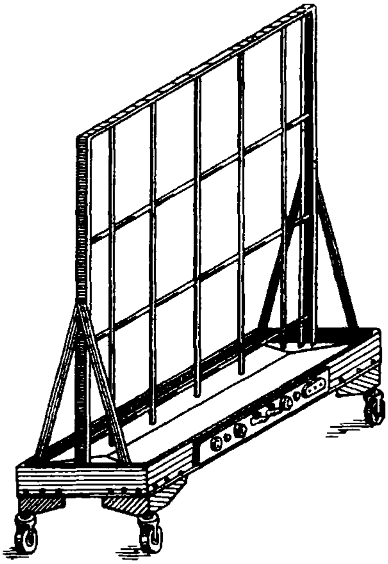


Fig. 410
Frame on castors

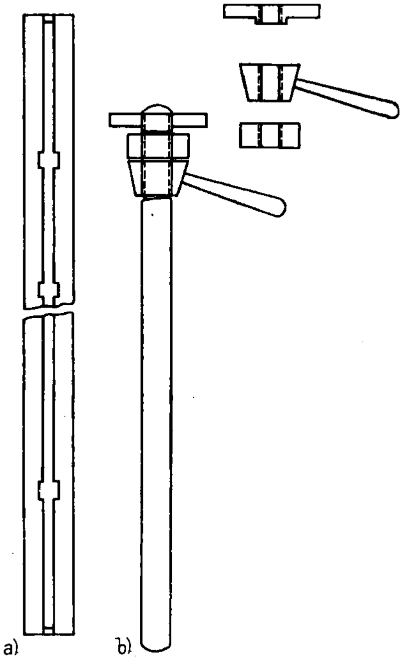


Fig. 411
Jordal rails

a) rail with holes for insertion of special clamps
b) special clamp

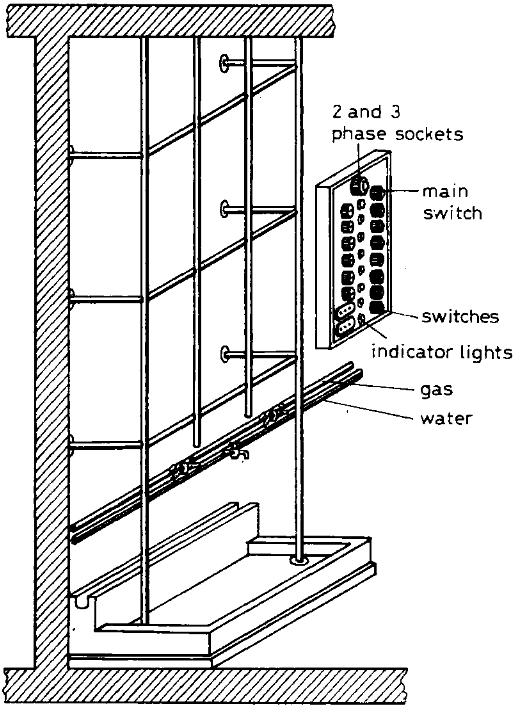


Fig. 412
Framework unit with brickwork trough, piping and electric panel

The piping for water, gas, compressed air, vacuum and steam should be laid along the walls, together with a drain. Bench instruments may be placed on shelves behind the framework. Electric power is taken from panels; the most convenient position for these is between each pair of frames (Fig. 412). The panels have 8 to 10 sockets, each with a switch and a neon lamp, so that it can be seen at a glance which parts of the apparatus are in operation.

A main switch should be installed to cut off the whole electrical supply except lighting in the event of danger.

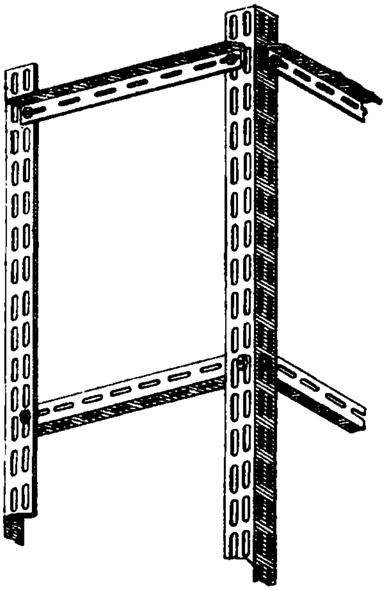


Fig. 413
Slotted angle iron for the construction of frames

Narrow sliding ladders, which can be kept in a corner behind the framework when not in use, are employed for reaching all parts of the equipment.

The *ventilation* should be so designed that fresh air enters along the floor behind the framework and the waste air leaves near the ceiling. Ten changes of air per hour is generally considered sufficient. If an appreciable quantity of gas is produced in a distillation it may be led away through the upper ventilation holes by tubes connected to condensers.

Semi-technical distillation apparatus should be provided with specially constructed frames and platforms (Fig. 424), which may if desired be built up from unit parts. Slotted angle iron (Fig. 413) greatly facilitates the construction.

9.3 Building up the apparatus

Before the equipment is assembled it is advisable, especially if the apparatus is complicated, to draw a sketch of it and, as a start, to arrange the components on the floor according to this plan. Next, the corresponding ground joints are examined by putting them together without grease and testing them for fit. By moistening the cone of the joint or drawing a circle of chalk on it, one can easily see whether irregularities are present. Loosely-fitting joints should be replaced. In vacuum distillation this procedure saves much time which would otherwise be spent in testing for leaks.

Assembling of the parts should start from the bottom. In the first place it should be possible to remove the still pot without dismantling other components. For this purpose flask heaters with a vertical adjustment (Fig. 327) can be used. Plain retort rings do not always give the flask a firm seating. In some cases the suspension of the flask in a spring cradle (Fig. 414) offers a solution.

The column should be mounted exactly vertically by means of a plummet. The lateral parts of the apparatus must not be connected to the main, vertical parts before these have been tested for vacuum-tightness. Testing for leaks should, in fact, always be performed step by step, as this method is by far the most rapid. Ground joints should

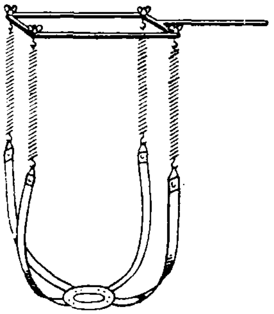


Fig. 414
Spring cradle for flask

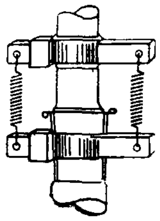


Fig. 415
Ground joint with metal clamps and springs

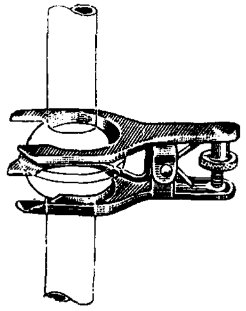


Fig. 416
Clip for ball joint

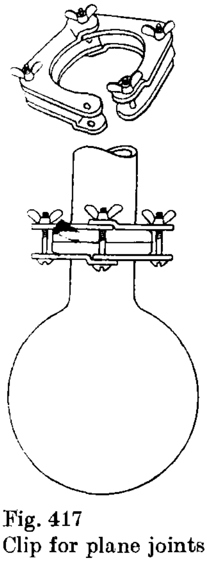


Fig. 417
Clip for plane joints

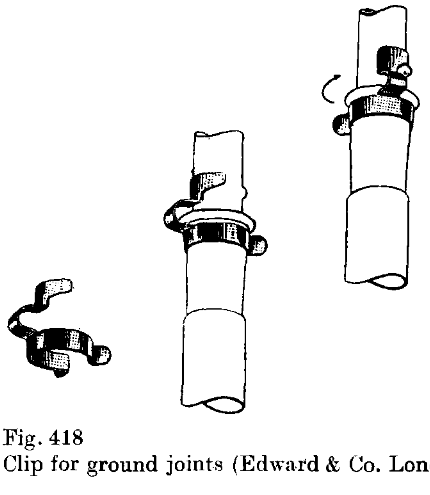


Fig. 418
Clip for ground joints (Edward & Co. London)

be secured by hooks and springs. Small joints usually have fused-on hooks; larger joints may be fastened with metal clamps (Fig. 415). A clip for securing ball joints is shown in Fig. 416 and one for plane joints in Fig. 417. The clip for ground joints which is manufactured by Messrs. W. Edwards & Co, London, (Fig. 418) is easily detachable.

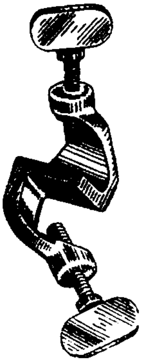


Fig. 419
Boss, 14 mm

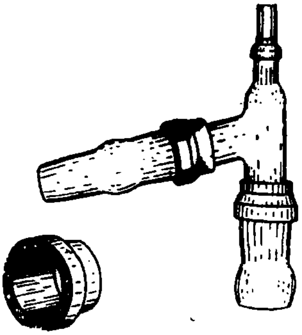


Fig. 420
Rubber joint collars

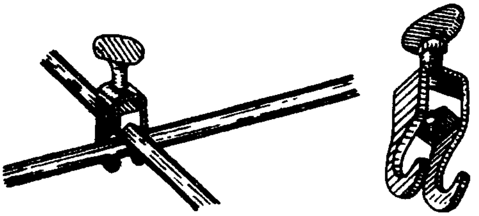


Fig. 421
"Specco" hook-clamp

Rubber collars can be used for fastening ground joints and are manufactured for the sizes NS 12 to NS 29 (Fig. 420); they can be employed at temperatures up to 130 °C [6]. Their main advantages are that the use of joint grease is unnecessary and that strains are uniformly distributed around the circumference.

Bosses must be carefully machined so that, when the screws are tightened, the object connected is not forced out of position. If this happens, strains will ensue which may lead to the breakage of glass parts, usually after they have been heated in the course of distillation. A reliable form of boss is shown in Fig. 419. The "Specco" hook clamp (Fig. 421) is intended specially for the construction of frameworks. The double three-point bearing ensures a tight hold free from movement. The standardized Geru system consisting of a variety of components allows the construction of apparatus ranging from simple devices to large pilot plants [7].

For supporting components that have to be adjusted exactly to a certain level, such as flask heaters, levelling bottles etc., the variable height support due to Mannchen (Fig. 422) is convenient, as it allows the position to be regulated to within a millimetre. Ring clamps (Fig. 423) are better than the customary jaw clamps for

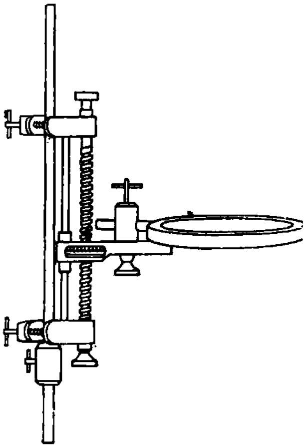


Fig. 422
Variable height support (Mannchen-Riedel)

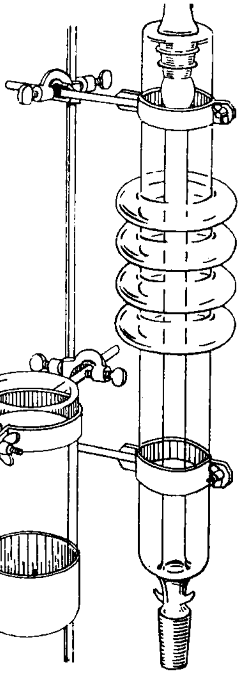


Fig. 423
Ring clamps

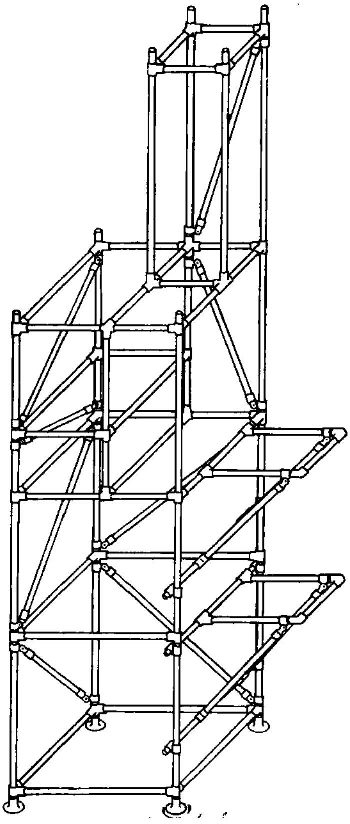


Fig. 424
Framework for a 200 l distillation plant. Galvanized tubes with galvanized coupling sleeves

holding columns and other cylindrical parts. A systematic survey of supports for and the suspension of, chemical apparatus has been given by Schwarz [5].

Pilot plant and semi-technical distillation apparatus made of glass requires special connections, clamps and frameworks. It may suffice here to refer the reader to the catalogues of the glassware manufacturers. Some firms even send crews for the assembly of apparatus. As an example Fig. 424 shows a framework of galvanized tubes joined by means of sockets with Imbus screws.

9.4 Sealing ground joints

In most cases the problem of ensuring that ground joints and taps are leak-proof needs attention. The substances to be distilled have widely different solvent powers for joint greases, so that preliminary tests may be necessary to find the most suitable lubricant. Some data on the subject are given in Table 79.

The experience obtained with silicone greases is not yet sufficient to allow a definite judgment. There is some danger that components of the grease will enter the column and affect the wetting of the packing, and it is difficult to remove the white, powdery filler which remains when the silicone itself has been leached out.

As a general rule it can be said that taps and stop-cocks should be lubricated with a softer grease than ground joints. Lithelen (Table 79) contains lithium soaps and undergoes little change in consistency with temperature. It can therefore be used for greasing taps at temperatures from below 0° up to 150 °C. A review on the preparation of special laboratory greases has been compiled by Brooke [8]. The various lubricants

Table 79

Greases for ground joints and taps

Type of grease	Maximum operating temp. (°C)	Composition or manufacturer	Application
Ramsay grease	25	6 pts. vaseline 1 pt. paraffin wax 6 pts. Para rubber	General work
High vacuum grease P	25	E. Leybold's Nachf., Cologne, Germany	High-vacuum work
High vacuum grease R	30		
Lithelen	150		
Kapsenberg grease		1 pt. soluble starch 1 pt. glycerin	For powerful grease solvents, such as diethylether or chloroparaffins
BZ 6564; BZ 6563		E. Merck, Darmstadt, Germany	
Sirupy phosphoric acid			
Graphite		As graphite powder or a mixture of graphite and paraffin wax, or as colloidal graphite suspension in water	High-temperature distillation

have been extensively discussed by Wagner [9]. Bernhauer [10], Wittenberger [11], Wolf [12] and Friedrichs [13] have given detailed instructions for the handling of ground glass joints and glass taps, with particular consideration of how ground joints that have seized should be treated.

In molecular distillation it is essential to use a thoroughly degassed lubricant with a low vapour pressure, for instance the high-vacuum greases P and R. Ground joints with a mercury seal (Fig. 425), though providing an entirely tight seal, should be employed only in exceptional cases, owing to the poisonous nature of mercury; the cup is better filled with vacuum oil or grease.

An ungreased joint — even one having the finest ground surfaces — will never be entirely vacuum-tight or, conversely, will not prevent the escape of some vapour. Greasing is carried out by coating the upper half of the cone with a uniform layer of the lubricant in question. This is best done with a smooth wooden spatula; greasing with the finger gives a uniform coating, but has the disadvantage that dirt or moisture may be introduced into the lubricant. Another method, particularly suitable for Ramsay or Apiezon grease, is to warm the cone gently over a hot-plate (not an open gas flame) until the lubricant flows, after which it is distributed by rotating the cone. It is then inserted into the socket and pressed in with a turning motion until the joint appears uniform and transparent. If this does not happen at once the process should be repeated after rewarming the joint.

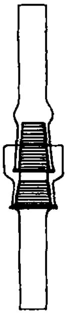


Fig. 425
Joint with mercury seal

If a joint starts to leak during a distillation owing to solution or decomposition of the lubricant, it may be possible to seal the leak by applying a suitable cement around the edge. A grade of picein — melting point 80° or 105 °C — is most used. Sealing wax may be employed as a substitute; its disadvantage is that it tends to become brittle. A cement that can be used up to 250 °C is a mixture of glycerin and litharge, which sets hard. Picein and sealing wax should not be melted in a gas flame; the proper method is to heat the place to be sealed with a Bunsen burner to about 100 °C, and then to apply and spread out the cement by means of a spatula heated to the same temperature. Finally a small flame is passed over the surface for a short time so as to make the cement flow and penetrate into the crevices of the joint.

A different approach for ground joints is the use of Teflon sleeves. This gives the joints a tight fit and does not allow them to seize. The French firm Gâchot supply those pieces, called "Rodets", in sizes suited for the commonly used joints. In chap. 3.1 it was pointed out that precision ground joints may also do without grease. In pilot and semi-technical plants Teflon rings and sleeves are preferably used for sealing ball and flat joints.

9.5 Starting up distillation apparatus

When the apparatus has been assembled the charge is put into the still pot. It should be filled to at most two-thirds of its nominal volume, or to one-half in vacuum distillation. Boiling chips are added to the contents. The volume of charge should be measured at the same temperature as the distillate fractions to be collected later, and this temperature may be relatively high if the fractions are solid at room temperature. Poisonous substances and those with a high vapour pressure are best forced by gas pressure from a bottle into the still pot, which should then immediately be stoppered. In order to ensure good wetting of the packing it is customary to pour the charge in through the condenser if possible. If it is essential for the apparatus to be completely free from moisture it can be dried by blowing in hot air with the jacket heater in operation.

Stress should again be laid on the importance of a thorough cleaning of the packing material before it is put into the column. It is not sufficient to rinse it a few times, say with carbon tetrachloride or trichloroethylene. The adhering layer can be removed by a treatment with hot benzene (poisonous; use fume cupboard) followed by a rinse with trichloroethylene [14].

For vacuum distillation, a preliminary test for leakage is necessary. The apparatus is evacuated; when the required pressure has been reached the vacuum pump is stopped and the rate of increase of pressure is observed (section 5.4.1). A further test for tightness is performed when the column is in operation and the thermal load has been established. The still pot heater is switched on only when the desired pressure is attained, and the column jacket heater as soon as vapour evolution starts. The cooling water should be turned on before the heaters are put into operation; during the initial period its rate of flow should be checked at intervals since it usually tends to vary somewhat at the start with the expansion of tap washers. When the vapour has reached the column head the load is adjusted to the required value (section 4.10.7) unless the column is to be flooded (section 4.10.8) to wet the packing. The apparatus is then allowed to run for at least half an hour at total reflux, so as to allow the initial boiling point to be accurately determined, and only then is it adjusted to the required reflux ratio (section 4.10.4).

As mentioned before, a few *boiling chips* are added to the still pot in order to promote regular ebullition. Generally speaking the use of boiling capillaries cannot be recommended, since their presence makes it difficult to determine the effective distillation pressure and air sometimes gives rise to polymerization. The "boiling chips" may be small pieces of earthenware (flower pots) or pumice, platinum tetrahedra and in some cases even bits of wood. For alkaline materials, tin dust may be employed. It should be noted that boiling stones lose their activity if a vacuum distillation is interrupted and air is admitted. Their action is connected with the small bubbles of air clinging to their surface; if the vacuum is interrupted it is therefore necessary to add fresh boiling chips [15].

If *foaming* occurs to a troublesome extent at the beginning of distillation, an attempt may be made to reduce it by the addition of an anti-foaming agent [16]. Silicone oils have recently been used with success for this purpose. If the material to be distilled is highly viscous it is advisable to keep the still pot contents in constant motion with a magnetic stirrer or the stirrer due to Hübner [17].

9.6 Safety measures

In laboratory practice it is frequently necessary to distil combustible, poisonous or explosive substances; in vacuum distillation there is the danger that vessels may collapse. It is therefore essential to observe certain safety measures [18]. Data on combustible gases and vapours which are of importance from the point of view of laboratory safety have been collected by Dittmar [19]. In every case it should be decided whether or not an explosion-proof electric installation is required.

Very *poisonous materials* should always be handled and distilled in the well-ventilated room or in a fume cupboard. Explosive substances such as ether should be distilled only in a room especially designed for such operations unless work in the open air is preferred. If the charge contains poisonous gases in solution, the condenser should be connected to a tube leading to the atmosphere or to a fume cupboard. When distilling substances which injure the skin the operator should wear rubber gloves and goggles since it is difficult to avoid contact with traces of such materials; it may also be advisable to wear protective clothing.

Vacuum distillations require special precautions. Safety spectacles or, rather, a face shield should be worn for work at reduced pressures. Heaters give some protection from flask and column. In addition, glass-wool sheaths may be applied to the other parts for insulation and protection. If this is not possible for experimental reasons, for instance because the separation process should be visible throughout its course a wire gauze or plane glass screen must be placed in front of the apparatus.

Buffer vessels can be fitted into wooden boxes lined with glass wool or completely encased in a wire gauze cage. If the vacuum pumps have a belt transmission, the latter must be provided with an effective guard. The safety measures that are nesessary in a high-pressure laboratory and in work with toxic substances are considered in detail by Craig and Dew [20].

References

Chapter 1 — Introduction

[1] Rechenberg, C. V., Einfache und fraktionierte Destillation in Theorie und Praxis, Schimmel u. Co. AG, Miltitz 1923

[2] Young, S., Distillation Principles and Practice, MacMillan, London 1922

[3] Thormann, K., Destillieren und Rektifizieren, Verlag Spamer, Leipzig 1928

[4] Badger, W. L., and McCabe, W. L., Elements of Chemical Engineering, McGraw-Hill, New York and London 1911

[5] McCabe, W. L., and Thiele, E. W., Ind. Eng. Chem. 17 (1925) 605

[6] Jantzen, E., Dechema Monograph, Vol. 5 (1932) No. 48; Angew. Chem. 36 (1923), 592

[7] Kirschbaum, E., Distillation and Rectification, Chemical Publishing Co. Inc., New York, 1948

[8] Gyula, N., Lepárlás (Distillation), Muszaki Könyvkiadó, Budapest 1955

[9] Jacobs, J., Destillier- und Rektifizieranlagen, R. Oldenbourg-Verlag, München 1950

[10] Robinson, C. S., and Gilliland, E. R., Elements of Fractional Distillation, McGraw-Hill, New York 1950

[10a] Perry, J. H., Chemical Engineers Handbook, McGraw-Hill, New York, 3rd Ed. 1953

[11] Schultze, G. R., and Stage, H., Die Kolonnendestillation im Laboratorium, VDI-Forschungsheft 424, VDI-Verlag, Berlin 1944

[12] Thormann, K., Dechema-Erfahrungsaustausch, Laboratoriumstechnik, Arbeitsmethoden und Geräte, Destillieren und Rektifizieren, Dechema, Frankfurt/Main, September 1950

[13] Thormann, K., Dechema-Erfahrungsaustausch, Techn. Apparate und Anlagen, Trennen flüssiger Mischungen, Destillieren, Betriebstechnik, Dechema, Frankfurt/Main, August 1952

[14] Stage, H., and Schultze, G. R., Die grundlegenden Arbeiten über Theorie, Apparate sowie Verfahren der Destillation und Rektifikation, VDI-Verlag, Berlin 1944

[15] Rose, A. and E., Distillation Literature Index and Abstracts 1941—1945, 1946—1952, Applied Science Laboratories, State College, Pennsylvania 1953

[16] ZIC Referatedienst Chemische Verfahrenstechnik, ed. by Zentralstelle für Information der chemischen Industrie, Berlin 1972ff.
Fortschritte der Verfahrenstechnik, ed. by Ingenieurwissenschaftliche Abteilung der Farbenfabriken Bayer AG, Leverkusen, Verlag Chemie GmbH, Weinheim/Bergstr. 1952ff.; from Vol. 9 (1971ff.) ed. by Verfahrenstechnische Gesellschaft im VDI, VDI-Verlag, Düsseldorf
Verfahrenstechnische Berichte (Vorankündigungsblätter, Karteiblätter und halbjährliche Sach-, Autoren- und Firmenregister), ed. by Ingenieurwissenschaftliche Abteilung der Farbenfabriken Bayer AG, Leverkusen, Verlag Chemie GmbH, Weinheim/Bergstr.

[17] Walsh, T. J., Ind. Eng. Chem. from 1956

[18] Orlicek, A. G., and Pöll, H., Hilfsbuch für Mineralöltechniker, Vol. I: Die Eigenschaften von Kohlenwasserstoffen, Mineralölprodukten und Hilfsstoffen, Springer-Verlag, Vienna 1951

[19] Sigwart, K., Destillation und Rektifikation, in: Ullmanns Encyklopädie der technischen Chemie, Vol. 1, Urban & Schwarzenberg, München/Berlin 1951, pp. 429—470

[20] Kortüm, G., and Buchholz-Meisenheimer, H., Die Theorie der Destillation und Extraktion von Flüssigkeiten, Springer-Verlag, Berlin/Göttingen/Heidelberg 1952

[21] Bosnjaković, Fr., Technische Thermodynamik, Vol. 1 (6th Ed.) and Vol. 2 (5th Ed.), Theodor Steinkopff Verlag, Dresden 1972/1971

[22] Gattermann, L., and Wieland, H., Die Praxis des organischen Chemikers, 41st Ed., Walter de Gruyter & Co., Berlin 1962

[23] Wittenberger, W., Chemische Laboratoriumstechnik, 6th Ed., Springer-Verlag, Vienna New York 1963

[24] Weygand, C., and Hilgetag, G., Organisch-chemische Experimentierkunst, 4th Ed., Johann Ambrosius Barth, Leipzig 1970

[25] Bernhauer, K., Einführung in die organisch-chemische Laboratoriumstechnik, Springer-Verlag, Vienna 1947

[26] Carney, Th. P., Laboratory Fractional Distillation, MacMillan, New York 1949

[27] Rosengart, M. J., Die Technik der Destillation und Rektifikation im Laboratorium, VEB Verlag Technik, Berlin 1954 (translated from Russian)

[28] Rose, A. and E., et al., Technique of Organic Chemistry, Vol. IV, Distillation, Interscience Publishers, New York 1951

[29] Weber, U. von, Gewinnung ätherischer Öle durch Destillation, in: Gildemeister, E., and Hoffmann, Fr., Die ätherischen Öle (revised by W. Treibs), Akademie-Verlag, Berlin 1966

[30] Sigwart, K., Destillieren und Rektifizieren, in: Houben-Weyl, Methoden der organischen Chemie (ed. by E. Müller), Vol. I/1, Georg Thieme Verlag, Stuttgart 1958

[31] Zuiderweg, F. J., Laboratory Manual of Batch Distillation, Interscience Publishers, New York 1957

[32] Coulson, E. A., and Herington, E. F. G., Laboratory Distillation Practice, Georg Newnes, London 1958

[33] Bukala, M., Majewski, J., and Rodzinski, W., Fraktionierte Destillation im Laboratorium, Państwowe Wydawnictwo Naukowe, Warsaw 1958

[34] Industrial and Engineering Chemistry, Chemical and Process Engineering, VDI-Zeitschrift, Chemische Technik

[35] Hoppe, K., Künne, H., und Bendix, H., Fortschritte in der Destillation, Rektifikation, Sorption und Extraktion, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1970

[36] Treybal, E. R., Masstransfer Operations (International Student Edition), 2nd Ed., McGraw-Hill, New York 1968
Geiseler, G., et al., Ausgewählte physikalische Methoden der organischen Chemie, Akademie-Verlag, Berlin 1963
Keil, B., et al., Laboratoriumstechnik der organischen Chemie (ed. by H. Fürst), Akademie-Verlag, Berlin 1961
Wiberg, K. B., Laboratory Technique in Organic Chemistry, McGraw-Hill, New York 1960

[37] Organikum — Organisch-Chemisches Grundpraktikum, 15th Ed., VEB Deutscher Verlag der Wissenschaften, Berlin 1977
Anorganikum — Lehr- und Praktikumsbuch der anorganischen Chemie (ed. by L. Kolditz), 8th Ed., VEB Deutscher Verlag der Wissenschaften, Berlin 1978

[38] Röck, H., Destillation im Laboratorium — Extraktive und azeotrope Destillation, Dr. Dietrich Steinkopff Verlag, Darmstadt 1960

[39] Stage, H., and Bose, K., Die Belastungsverhältnisse in Füllkörpersäulen unter Destillationsbedingungen, Springer-Verlag, Berlin/Göttingen/Heidelberg 1962
Müller, E., and Stage, H., Experimentelle Vermessung von Dampf-Flüssigkeits-Phasengleichgewichten, Springer-Verlag, Berlin/Göttingen/Heidelberg 1961

[40] Hála, E., Pick, J., Fried, V., and Vilim, O., Vapour-Liquid Equilibrium, 2nd Ed., Pergamon Press Ltd., London 1968

[41] Hála, E., Wichterle, I., Polák, J., and Boublik, T., Vapour-Liquid Equilibrium Data at Normal Pressures, Pergamon Press Ltd., London 1969
Wichterle, F., Linek, J., and Hála, E., Vapour-Liquid Data Bibliography, Elsevier Scientific Publishing Company, Amsterdam/Oxford/New York 1973, Supplement I, 1976; Supplement II, 1979

[42] Cf. References Chap. 4 [105]
Ogorodnikov, C. K., Lesteva, T. M., and Kogan, V. B., Handbook of azeotropic mixtures, Khimiya, Leningrad 1971 (in Russian)

[43] Billet, R., Grundlagen der thermischen Flüssigkeitszerlegung, Bibliographisches Institut, Mannheim 1961
Billet, R., Verdampfer-Technik, Bibliographisches Institut, Mannheim 1965

[43a] Billet, R., Industrielle Destillation, Verlag Chemie GmbH, Weinheim/Bergstr. 1973

[44] Billet, R., Optimierung in der Rektifiziertechnik, unter besonderer Berücksichtigung der Vakuumrektifikation, Bibliographisches Institut, Mannheim 1967

[45] Oliver, E. D., Diffusional Separation Processes: Theory, Design and Evaluation, John Wiley and Sons, New York 1966

[46] Pratt, H. R. C., Countercurrent Separation Processes, Elsevier Publishing Company, Amsterdam 1967

[47] Krell, E., Frey, H.-P., Gawalek, G., and Werner, G., Einführung in die Trennverfahren, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1975

[48] Hoppe, K., and Mittelstrass, M., Grundlagen der Dimensionierung von Kolonnenböden, Theodor Steinkopff Verlag, Dresden 1967

[49] Jungnickel, H., and Otto, E., Tiefe Temperaturen in der Verfahrenstechnik (Vol. 11 of the series „Beiträge zur Verfahrenstechnik"), VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1972

[50] Frank, W., and Kutsche, D., Die schonende Destillation, Otto Krausskopf-Verlag, GmbH, Mainz 1969

[51] Olevskiy, V. M., and Ruchinskiy, V. R., Rektification of temperature-sensitive substances , Khimiya, Moscow 1972

[52] Holló, J., Kurucz, E., and Boródi, A., The Applications of Molecular Distillation, Akadémiai Kiadó, Budapest 1971

[53] Schuberth, H., Thermodynamische Grundlagen der Destillation und Extraktion, Vol. I, VEB Deutscher Verlag der Wissenschaften, Berlin 1972

[54] Brauer, H., and Mewes, D., Stoffaustausch, einschl. chemischer Reaktionen, Verlag Sauerländer AG, Aarau and Frankfurt/Main 1971
Brauer, H., Grundlagen der Einphasen- und Mehrphasenströmung, Verlag Sauerländer AG, Aarau and Frankfurt/Main 1971

[55] Holland, C. D., Multicomponent Distillation, Prentice-Hall International, Englewood Cliffs 1963

[56] Chemie-Ing.-Techn. 42 (1970) 14, 945—957; Chem. Techn. 22 (1970), 117—120

[56a] Third International Symposium on Distillation 1979, I. Chem. Symposium Series 56, 1043 pages

[57] Billet, R., CZ-Chemie-Techn. 3 (1974) 10, 353—361

[58] Sharov, V. T., and Serafimov, L. A., Physico-chemical Fundamentals of Distillation and Rectification, Khimiya, Leningrad 1975

[59] Hirata, M., Ohe, S., and Nagahama, K., Computer aided data book of vapor-liquid equilibria, Elsevier Scientific Company, Tokyo/Amsterdam/Oxford/New York 1975 (cf. also Chem.-Ing.-Techn. 48 (1976) 7, 634

[60] Fratzscher, W., Picht, H. P., and Bittrich, H. J., Chem. Techn. 29 (1977) 7, 361 to 367

[61] Stichlmair, J., Grundlagen der Dimensionierung des Gas/Flüssigkeit-Kontaktapparates Bodenkolonne, Verlag Chemie, Weinheim 1979

[62] Sattler, K., Thermische Trennverfahren, Vogel-Verlag, Würzburg 1977

[62a] Kafarov, V. V., Grundlagen der Stoffübertragung, translated from Russian, revised and edited by Hartmann, K. and Reher, E. O., Akademie-Verlag, Berlin 1977

[63] Wünsch, G., Haufe, S. and Köpsel, R., Chem. Techn. 31 (1979) 6, 286—291

[64] Kaibel, G., Mayer, H.-H. and Seid, B., Chem.-Ing.-Techn. 50 (1978) 8, 586—592

[65] Winter/Merte/Herz, Recent Development in Boiling and Condensation, Verlag Chemie, Weinheim, New York, 1977

[66] Gmehling, J. and Onken, U., Vapour-Liquid-Equilibrium Data Collection, in Chemistry Data Series, DECHEMA, Vol. I
Part 1: Aqueous Organic Systems,
2a: Organic Hydroxy Compounds: Alcohols (1978)
2b: Gmehling, J., Onken, U. and Arlt, W.
Organic Hydroxy Compounds: Alcohols and Phenols (1978)
3+4: Aldehydes and Ketones (1979)
Gmehling, J. and Onken, U., Chem.-Ing.-Techn. **51** (1979) **2**, 127
[67] Weiß, S., Chem. Techn. **31** (1979) 9, 459–463

Chapter 2 — A Review of the History of Laboratory Distillation

[1] Schelenz, H., Zur Geschichte der pharmazeutisch-chemischen Destilliergeräte. Beilage zum Bericht April 1911, Verlag Schimmel und Co. AG, Miltitz
[2] Gildemeister, E., Die ätherischen Öle, Verlag Schimmel und Co. AG, Miltitz 1928
[3] Rechenberg, C. von, Einfache und fraktionierte Destillation in Theorie und Praxis, Verlag Schimmel und Co. AG, Miltitz 1923
[4] Underwood, A. J. V., Trans. Instn. chem. Engr. **13** (1935), 34
[5] Forbes, R. J., Short history of the art of distillation, Verlag E. J. Büll, Leiden 1948
[6] Forbes, R. J., and Dijksterhuis, E. J., A History of Science and Technology, Vol. I: Ancient Times to the Seventeenth Century; Vol. II: The Eighteenth and Nineteenth Centuries. Pelican Books No. A 498 and A 499, Penguin Books Ltd., Harmondsworth Middlesex 1963
[7] Schneider, W., Lexikon alchemistisch-pharmazeutischer Symbole, Verlag Chemie GmbH, Weinheim/Bergstr. 1962
[8] Lippmann, E. O. von, Entstehung und Ausbreitung der Alchemie, Vols. 1 and 2, Verlag Julius Springer, Berlin 1919, 1931; Vol. 3, Verlag Chemie GmbH, Weinheim/Bergstr. 1953
[9] Lippmann, E. O. von, Abhandlungen und Vorträge zur Geschichte der Naturwissenschaften 1 (1906), 2 (1913), Verlag Chemie GmbH, Weinheim/Bergstr.
[10] Lippmann, E. O. von, Beiträge zur Geschichte der Naturwissenschaften und der Technik 1 (1923), 2 (1953), Verlag Chemie GmbH, Weinheim/Bergstr.
[11] Stage, F., Angew. Chem., Ed. B **19** (1947), 181
[12] Kreis, H., Liebigs Ann. Chem. **224** (1884), 259
Young, S., J. Chem. Soc. [London] **75** (1889), 679
Friedrichs, J., Z. angew. Chem. **32** (1919), 340
[13] Glas-Instrumenten-Techn. **14** (1970), 196
[14] Krell, E., Glas-Instrumenten-Techn. **11** (1967) 1–5, Beilage 1–20
[15] Strube, W., Der historische Weg der Chemie, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1976
[16] Bittel, A., Chem.-Ing.-Techn. **31** (1959) 6, 365–378

Chapter 3 — Standardization and Data on Concentrations

[1] DDR-Standards und Fachbereichsstandards der DDR, Ed.: Amt für Standardisierung der Deutschen Demokratischen Republik, Berlin 1968
[2] Verzeichnis der DIN-Normblätter, Stand vom 28. 2. 72, Beuth-Vertrieb GmbH, Berlin (West)
[3] Telle, W., Chemische Laboratoriumsgeräte, 2nd Ed., VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1969
[4] Friedrichs, F., Die Glashütte **76** (1949), 3–6
[5] Fliedner, K., Glasapparatetechnik **5** (1958), 33–37; Suppl. of Chem. Techn. 10 (1958)
[6] Kuehnhanss, G., et al., Chem. Techn. **9** (1957) 407–409
[7] TGL 10192–10200, 11641–11644, 12023–12032, 20277, DIN drafts 28800–28808

[7a] Hampel, B., Chemiker-Ztg. **95** (1971) 7, 316–325

[8] Krell, E., Chem. Techn. **6** (1954), 452–455

[9] Padelt, E., and Laporte, H., Einheiten und Größenarten der Naturwissenschaften, 2nd Ed., VEB Fachbuchverlag, Leipzig 1967
Fischer, R., Padelt, E., and Schindler, H., Physikalisch-technische Einheiten — richtig angewendet, 7nth Ed., VEB Verlag Technik, Berlin 1979

[10] Förster, H., Einheiten, Größen, Gleichungen und ihre praktische Anwendung, VEB, Fachbuchverlag, Leipzig 1968

[11] Haeder, W., and Gärtner, E., Die gesetzlichen Einheiten in der Technik, Verlag Beuth-Vertrieb, Berlin 1970

[12] Krell, E., Chem. Techn. **7** (1955), 30–32

[13] Lessels, A. G., Chem. Engng. **63** (1956), 208–210

[14] Orlicek, A. F., Pöll, H., and Walenda, H., Hilfsbuch für Mineralöltechniker, Vol. 1: Die Eigenschaften von Kohlenwasserstoffen, Mineralölprodukten und Hilfsstoffen, Springer-Verlag, Vienna 1951

[15] Baehr, H., Chemie-Ing.-Techn. **23** (1953), 676

[16] Kramer, M. T., Glas-Instrumenten-Techn. **15** (1971), 251–254; **17** (1973), 43–48, 137–139

[17] Späth, W., Chem.-Ing.-Techn. **50** (1978) 6, 446–448
Späth, W., Zahl-Maß-Bild, A. W. Gentner Verlag KG, Stuttgart 1977

Chapter 4 — Physical Fundamentals of the Separation Process

[1] Sigwart, K., Destillation und Rektifikation, in: Ullmanns Encyklopädie der technischen Chemie, Vol. 1, Urban & Schwarzenberg, München/Berlin 1951, p. 429/470

[2] TGL 21120

[3] Kuhn, W., Helv. chim. Acta **25** (1942), 252–295
Kuhn, W., and Ryffel, K., Helv. chim. Acta **26** (1943), 1693–1721

[3a] Niselson, L. A., Tretyakova, K. V., and Yamko, M. A., Zh. prikl. chim. **46** (1973) 7, 1613–1614

[3b] Graczyk, J., Nukleonika **1** (1973) 1, 25–33

[4] Meier, W., and Huber, M., Chemie-Ing.-Techn. **39** (1969), 797–800

[4a] Bemer, G. G. and Zuiderweg, F. J., Chem. Engng. Sci. **33** (1978) 12, 1637–1643

[4b] Farid, M. M. and Gunn, D. J., Chem. Engng. Sci. **34** (1979) 4, 579–592

[5] Huber, M., and Hiltenbrunner, R., Chem. Engng. Sci. **21** (1966), 819–832

[6] Kafarov, V. V., Dorokhov, J. N., and Shestopavlov, V. V., Hydrodynamic Parameters of Packed Columns, Proceedings, Part 4, Distillation 1969, Brighton/England, Abstract: Chemie-Ing.-Techn. **42** (1970) 14, 953

[7] Jonas, Chr., Chem. Techn. **26** (1974) 12, 87–91

[8] Zuiderweg, F. J., and Harmens, A., Chem. Engng. Sci. **9** (1958) 2/3, 89–103
Medina, A. G., McDermott, C. and Ashton, N., Chem. Engng. Sci. 33 (1978) **11**, 1489 to 1493

[8a] Gomez, R. A., and Strumillo, Cz., Inżynieria chemiczna 2 (1975) **5**, 267–281

[8b] Bauer, H., Chemie-Ing.-Techn. **48** (1976) 10, 891

[8c] Ponter, A. B., Trauffler, P., and Vijayan, S., I & EC Process Des. Devel. **15** (1976) 1, 196–199

[9] Krell, E., Chem. Techn. **16** (1964) 10, 591–600

[9a] Kolev, N., Chem.-Ing.-Techn. **48** (1976) 12, 1105–1112

[10] Titov, A. A., and Zelvenskiy, Ya. D., khim, prom. (1974) 9, 690–693

[11] Krell, E., Plaste und Kautschuk **14** (1967) 4, 251–254

[11a] Kwasniak, J., Verfahrenstechnik 8 (1974) 11, 315–322

[11b] Yilmaz, T., and Brauer, H., Chemie-Ing.-Techn. **45** (1973) 14, 928–934

[11c] Künne, H.-J., Chem. Techn. **25** (1973) 9, 533–538

[11d] Dietz, H., Reinemann, G., and Comel, M., Chem. Techn. **25** (1973) 3, 143–148

[11e] Godau, H.-S., Chem. Techn. **26** (1974) 9, 561–564

[11f] Billet, R., CZ-Chem.-Techn. **3** (1974), 9–12

[11g] Adolphi, H.-V., Chem. Techn. **26** (1974) 10, 643–645

[11h] Antonov, Y. E., Safin, R. Sh., and Reut, V. J., teoret. osnovy khim. tekhnol. **9** (1975) 1, 140–142

[11i] Grabbert, G., Wünsch, G., Straßberger, L., and Meyer, B., Chem. Techn. **26** (1974) 8, 457–458

[11k] Marschall, E., Chem.-Ing.-Techn. **47** (1975), 879

[11l] Wünsch, G., Chem. Techn. **27** (1975) 12, 717–723

[11m] Krell, E., and Heinrich, W., Chem. Techn. **29** (1977) 11, 615–618

[11n] Heinrich, W., Thesis TH „Carl Schorlemmer", Leuna-Merseburg 1975

[11o] Weiß, S., and Schmidt, E., Chem. Techn. **26** (1974), 476

[11p] Schmidt, E., Thesis TH „Carl Schorlemmer", Leuna-Merseburg 1975

[11q] Vorontsov, E. G., J. of Appl. Chem. USSR, N. Y. **51** (1978) 4, Pt. 1, 754–759

[12] Staudinger, H., Anleitung zur organischen qualitativen Analyse, 6th Ed., Springer-Verlag, Berlin/Göttingen/Heidelberg 1955, pp. 12–13

[13] Stage, H., Erdöl und Kohle **3** (1950), 478–490

[14] Hildebrand, J. H., and Rotariu, S. J., Analytic. Chem. **24** (1952), 770–773

[15] Mauser, H., and Kortüm, G., Z. Naturforsch. **10a**/4 (1955), 317–322

[16] Mannchen, W., Einführung in die Thermodynamik der Mischphasen, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1965

[17] Schuberth, H., Thermodynamische Grundlagen der Destillation und Extraktion, Vol. I, VEB Deutscher Verlag der Wissenschaften, Berlin 1972

[17a] Bittrich, H.-J., Gratzscher, W., Lempe, D. and Picht, H.-P., Chem. Techn. **31** (1979) 9, 468–472

[18] Dreisbach, R. R., Pressure-Volume-Temperature Relationship of Organic Compounds, 3rd Ed., Handbook Publ., Inc., Sandursky, Ohio 1952

[19] Dreisbach, R. R., Physical Properties of Chemical Substances, The Dow Chemical Company, Midland, Michigan 1951–1953

[20] Stull, D. R., Ind. Engng. Chem. **39** (1947), 517/550 and 1684

[21] Stage, H., Fette u. Seifen **53** (1951), 677–682

[22] Stage, H., Fette u. Seifen **55** (1953), 217–224

[23] Stage, H., Müller, E., and Faldix, P., Erdöl u. Kohle **6** (1953), 375–380

[24] Stage, H., Müller, E., and Faldix, P., Chem. Techn. **6** (1954), 31/36

[25] Jordan, T. E., Vapor Pressure of Organic Compounds, 2nd Ed., Interscience Publishers New York 1954

[26] Riddick, J. A., and Toops jr., E. E., Organic Solvents, Physical Properties and Methods of Purification, Interscience Publishers, New York 1955

[27] Sage, B. H., and Lacey, W. N., Some Properties of the Lighter Hydrocarbons, Hydrogen Sulfide and Carbondioxide, American Petroleum Institute, New York 1955

[28] Glaser, F., and Rüland, H., Chemie-Ing.-Techn. **29** (1957), 772–775

[29] Jaeckel, R., Destillation und Sublimation in Fein- und Hochvakuum, in: Houben-Weyl, Methoden der organischen Chemie (ed. by Eugen Müller), Vol. I/1, Georg Thieme Verlag, Stuttgart 1958

[30] Kienitz, H., Bestimmung des Dampfdruckes, in: Houben-Weyl, Methoden der organischen Chemie (ed. by Eugen Müller), Vol. III/1, Georg Thieme Verlag, Stuttgart 1958, pp. 255–324

[31] Milazzo, G., Chemie-Ing.-Techn. **28** (1956), 646–654

[32] Swiętosławski, W., Ebulliometric Measurements, Reinhold, New York 1945
Swiętosławski, W., and Anderson, J. R., in: A. Weissberger: Physical Methods of Organic Chemistry, Vol. I, Interscience Publishers, New York **1949**, p. 107

[33] Weber, U. von, J. prakt. Chem. **1**/4 (1955), 318–323

[34] Eblin, P., J. chem. Educat. **27** (1950), 67

[35] Herrington, E. F., and Martin, J. F., Trans. Faraday Soc. **49**/2 (1953), 154–162

[36] Natelson, S., and Zuckermann, J. L., Ind. Engng. Chem., analyt. Edit. **17** (1945), 739–740

[37] Gould, C., jr., Holtmann, G., and Niemann, C., Analyt. Chem. **19** (1947), 204—206

[38] Wiberley, F. J., Siegfriedt, R. K., and Benedetti-Pichler, A. A., Mikrochem. verein. Microchim. Acta **38** (1951), 417—475

[39] Nesmeyanov, A. N., Atomic Energy (Russian) **3** (1957), 1013—1025, Kernenergie 1 (1958), 579—587

[40] Skliarenko, S. Y., J. phys. Chem. (Russian) **32** (1958), 1916—1921

[41] Henning, F., and Stock, A., Z. Physik **5** (1921), 226

[42] Smith and Menzies, Z. physik. Chem. **75** (1911), 501

[43] Eucken, A., and Suhrmann, R., Physikalisch-chemische Praktikumsaufgaben, 7th Ed., Akademische Verlagsgesellschaft Geest & Portig KG, Leipzig 1968, pp. 100—106

[44] Kortüm, G., Moegling, D., Woerner, F., Chemie-Ing.-Techn. **22** (1950), 453—457

[45] Schlünder, E. U., Chemie-Ing.-Techn. **35** (1963) 7, 482—487

[46] Röck, H., Z. physik. Chem., N. F. **4** (1955), 242—245

[47] Péter, M., Magyar Kémiai Folyóirat **10** (1953), 295—300, Abstract in: Chem. Techn. **6** (1954), 307

[47a] Kollár, G., and Nagy, É., Chem. Techn. **23** (1971) 1, 35—36

[47b] Smith, G., Winnick, J., Abrams, D. S., and Prausnitz, J. M., Canad. J. chem. Engng. **54** (1976), 337—343

[48] Pearson, D. E., J. chem. Educat. **28** (1951), 60—62

[49] English, W. D., J. Amer, chem. Soc. **74** (1952), 2927—2928

[50] Dühring, U., Wiedem. Ann. **11** (1880), 163; **52** (1894), 556

[51] Rechenberg, G. von, Einfache und fraktionierte Destillation in Theorie und Praxis, Verlag Schimmel & Co. AG, Miltitz 1923

[52] Jantzen, E., and Erdmann, W., Fette u. Seifen **54** (1952), 197—201

[53] Kirejev, V. A., J. appl. Chem. (Russian) **7** (1934)

[54] Antoine, C., C. R. hebd. Séances Acad. Sci. **107** (1888), 681, 863, 1143/45

[55] Thomson, G. W., Chem. Rev. **38** (1946), 1—39

[56] Riedel, L., Chemie-Ing.-Techn. **26** (1954), 83—89

[57] Reckhard, H., Erdöl u. Kohle **116** (1958), 234—241; Chemiker-Ztg. **84** (1960), 33—36

[58] Wichterle, I., and Linek, J., Die Antoinschen Dampfdruck-Konstanten reiner Verbindungen, Verlag Academia, Prague 1971 (in English)

[59] Berechnung thermodynamischer Stoffwerte von Gasen und Flüssigkeiten, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1966, pp. 77—89

[60] Othmer, D. F., and Yu, E.-S., Ind. Engng. Chem. **60** (1968) 1, 22—35

[60a] Zia, T., and Thodos, G., Canad. J. chem. Engng. **52** (1974) 5, 630—635

[60b] Gomez-Nieto, M. and Thodos, G., AIChEJ. **23** (1977) 6, 904—913

[60c] Zia, T. and Thodos, G., Chem. Engng. J. **16** (1978), 41—49

[60d] Gomez-Nieto, M. and Thodos, G., Ind. and Engng. Chem., Fundam. 17 (1978) 1, 45—51

[60e] Westmeier, S. and Picht, H.-P., Chem. Techn. 31 (1979) 2, 86—88

[60f] Waseda, J., Jacob, K. T., Tsuchiya, Y. and Tamaki, S., Z. f. Nat. forsch. TlA 33 (1978) 8, 940—945

[61] Schwab, G. M., Z. f. angew. Chem. **43** (1930), 155—156

[62] Stange, R., Chem. Techn. **5** (1953), 78—79,

[63] Othmer, D. F., Maurer, P. W., Molinary, C. J., Kowalski, R. C., Ind. Engng. Chem. **49** (1957), 125—137

[64] Wittenberger, W., Chemiker-Ztg. **76** (1952), 371—373

[65] Bergholm, A., Svensk kem. Tidskr. **60** (1948), 96

[66] Hoffmann, W., and Florin, F., Z. Ver. dtsch. Ing., Beih. Verfahrenstechn., (1943), 47—51

[67] Cox, E. R., Ind. Engng. Chem. **15** (1932), 592—593

[68] Davis, D. S., Ind. Engng. Chem. **17** (1925), 435

[69] Calingart, G., and Davis, D. S., Ind. Engng. Chem. **17** (1925), 1287

[70] Faldix, P., and Stage, H., Chem. Techn. **5** (1953), 526—528, 718—719

[71] Stage, H., and Juilfs, J., Chemiker-Ztg. **77** (1953), 511, 538, 575; **78** (1954), 43, 112, 182, 217

[72] Thormann, K., Destillieren und Rektifizieren, Spamer-Verlag, Leipzig 1928

[73] Matz, W., Die Thermodynamik des Wärme- und Stoffaustausches in der Verfahrenstechnik, Vols. 1 and 2, Dr. Dietrich Steinkopff Verlag, Darmstadt 1949/1953

[74] Kortüm, G., and Buchholz-Meisenheimer, H., Die Theorie der Destillation und Extraktion von Flüssigkeiten, Springer-Verlag, Berlin/Göttingen/Heidelberg 1952

[75] Bosnjaković, Fr., Technische Thermodynamik, Part II, 5th Ed., Verlag Theodor Steinkopff, Dresden 1971

[76] Florin, F., Brennstoff-Chem. **33** (1952), 161–166

[77] McCabe, W. L., and Thiele, E. W., Ind. Engng. Chem., ind. Ed. **17** (1925), 605

[78] Hála, E., Pick, J., Fried, V., and Vilim, O., (2nd English Ed.:) Vapour-Liquid Equilibrium, Pergamon Press, London 1968

Wichterle, F., et al., Vapour-Liquid Data Bibliography, Elsevier Scientific Publishing Company, Amsterdam/Oxford/New York 1973, Supplement I, 1976

[79] N. N., Chemie-Ing.-Techn. **11** (1969) 12, 735–736

[80] Wilson, G. M., J. Amer. chem. Soc. **86** (1964), 127

[81] Donth, E. J., and Weichmann, R., Chem. Techn. **20** (1968) 2, 93–95

[82] Krug, K., Haberland, D., and Bittrich, H.-J., Chem. Techn. **23** (1971) 7, 410–415

[83] Renon, H., and Prausnitz, J. M., American Institute of Chemical Engineers Journal **14** (1968), 135

[83a] Onken, U., and Gmehling, J., Chemie-Ing.-Techn. **49** (1977) 5, 404–411

[83b] Wichterle, I., Fluid Phase Equilibria **1** (1977) 2, 161–172

[83c] Prausnitz, J. M., Ber. Bunsenges. phys. Chem. **81** (1977) 10, 900–908

Oellrich, L., Plöcker, U., Prausnitz, J. M., and Knapp, H., Chem.-Ing.-Techn. **49** (1977) 12, 955–965

Plöcker, U., Knapp, H., and Prausnitz, J. M., Ind. and Engng. Chem., Process Des. Dev. **17** (1978) 3, 324–332

Anderson, T. F., and Prausnitz, J. M., Ind. and Engng. Chem., Process Des. Dev. **17** (1978) 4, 552–561

[83d] Drahos, J., Wichterle, I., and Hala, E., Fluid Phase Equilibria **1** (1977/78) 3, 173–184

Wichterle, I., Fluid Phase Equilibria **1** (1977/78) 3, 225–245

[83e] Onken, U., Chem.-Ing.-Techn. **50** (1978) 10, 760–766

[83f] Bittrich, H.-J., Chem. Techn. **31** (1979) 2, 104–105

[83g] Hauthal, H., Chem. Techn. **31** (1979) 1, 37–41

[84] Rosengart, M. J., Die Technik der Destillation und Rektifikation im Laboratorium, VEB Verlag Technik, Berlin 1954 (Transl. from Russian)

[85] Orlicek, A. F., and Pöll, H., Hilfsbuch für Mineralöltechniker, Vols. I and II, Springer-Verlag, Vienna 1951/1955

[86] Voorwijk, J. F., Chem. Engng. **63** (1956), 201–202

[87] Hollo, J., and Lengyel, T., Ind. Engng. Chem. **51** (1959), 957–960; Collect. Czechoslov. chem. Comm. **23** (1958), 1735–1743

Hollo, J., Periodica polytechn. [Budapest]; chem. Ingenieurwes. **2** (1958), 113–128; Fette, Seifen, Anstrichmittel **62** (1960) 10, 913–918

[88] Umstätter, H., and Flaschka, H., Erdöl u. Kohle **1** (1948), 151–157

[89] Williams, R. A., and Henley, E. J., Chem. Engng. J. **1** (1970) 2, 145–151

[89a] Halá, E., Chem. Techn. 26 (1974) 8, 492–493

[89b] Lu, B. C.-J., and Polak, J., Advances Cryogenic Engng. **20** (1975) F-1, 204–217

[90] Melpolder, F. W., and Headington, C. E., Ind. Engng. Chem. **39** (1947), 763–766

Rose, A., and Biles, R., Chem. Engng. Progr. **51** (1955), 138–140

[91] Rose, E., Ind. Engng. Chem. **33** (1941), 596

[92] Hawkins, J. E., and Brent, J. A., Ind. Engng. Chem. **43** (1951), 2611–2621

[93] Zypkina, O. Ya., J. appl. Chem. (Russian) **28** (1955), 185–192

[94] Kortüm, G., Chemiker-Ztg. **74** (1950), 151–154

[95] Carlson, H. C., and Colburn, A. P., Ind. Engng. Chem. **34** (1942), 581

[96] Orlicek, A. F., Österr. Chemiker-Ztg. **50** (1949), 86

[97] Laar, J. J. van, and Lorenz, R., Z. anorg. Chem. **145** (1925), 239; Z. phys. Chem. **72** (1910), 723; **83** (1913), 599

[98] Margules, M., Wiener Sitz. Ber. **104** (1895), 1243

[98a] Grewer, Th., and Schmidt, A., Chemie-Ing.-Techn. **45** (1973) 17, 1063–1066

[99] Landolt, H., and Börnstein, R., Physikalisch-chemische Tabellen, 6th Ed., Springer-Verlag, Berlin/Göttingen/Heidelberg 1950/55

[100] Perry, J. H., Chemical Engineers' Handbook, 4th Ed., McGraw-Hill Book Company, New York 1963, pp. 1942ff.

[101] Yu Chin, Distillation Equilibrium Data, 2nd Ed., Reinhold, New York 1956

[102] Chu Wang, Levy and Paul, Vapour Liquid Equilibrium Data, Edwards, T. W., Ann Arbor, Mich. 1956

[103] Kirschbaum, E., Destillier- und Rektifiziertechnik, 4th Ed., Springer-Verlag, Berlin/Heidelberg/New York 1969

[103a] Hübner, W., and Schlünder, E. U., Chemie-Ing.-Techn. **45** (1973) 5, 247–253

[103b] Vogelpohl, A., and Ceretto, R., Chemie-Ing.-Techn. **44** (1972) 15, 936–938

[104] Jacobs, J., Destillier-Rektifizier-Anlagen, R. Oldenbourg Verlag, München 1950

[105] Kogan, V. B., and Fridmann, V. F., Handbuch der Dampf-Flüssigkeits-Gleichgewichte, VEB Deutscher Verlag der Wissenschaften, Berlin 1960 (Transl. from Russian)

[106] Halá, E., Wichterle, I., Polák, J., and Boublík, T., Vapour-Liquid Equilibrium Data at Normal Pressure, Pergamon Press, London 1969

[106a] The Institution of Chemical Engineers, London, runs a data service, PPDS (Physical Property Data Service), which covers also liquid-vapour equilibrium data

[107] Kortüm, G., and Freier, H.-J., Chemie-Ing.-Techn. **26** (1954), 670–675

[108] Weber, U. von, Z. phys. Chem., N.F. **38** (1963) 3/4, 129–139

[109] Gelbin, D., Chem. Techn. **15** (1963) 1, 6–9

[110] Stage, H., Müller, E., and Gemmeker, L., Chemiker-Ztg./Chem. Apparatur **85** (1961), 11

[111] Othmer, D. F., Ind. Engng. Chem., ind. Edit. **20** (1928), 743

[112] Stage, H., and Fischer, W. G., Glas-Instrumenten-Techn. **12** (1968) 11, 1167–1173

[113] Gillespie, D. C., Ind. Engng. Chem., analyt. Edit. **18** (1946), 575

[114] Röck, H., and Sieg, L., Z. physik. Chem., N.F. **3** (1955), 355–364; Chemie-Ing.-Techn. **28** (1956), 133

[115] Kortüm, G., and Biedersee, H. von, Chemie-Ing.-Techn. **42** (1970) 8, 552–560

[116] Schmidt, R., Werner, G., and Schuberth, H., Z. phys. Chem. **242** (1969), 381–390

[116a] Rafflenbeul, L., and Hartmann, H., Chem. Techn. **7** (1978) 4, 145–148

[117] Wichterle, I., and Halá, E., Ind. Engng. Chem. Fundamentals **2** (1963) 2, 155–157

[118] Neumann, A., and Walch, W., Chemie-Ing.-Techn. **40** (1968) 5, 241–244

[118a] Stage, H., and Fischer, W. G., Verfahrenstechnik **7** (1973) 6, 1–3

[118b] Schmidt, A. P., Chem.-Ing.-Techn. **50** (1978), 537–538

[119] Kumarkrishna Rao, V. N., Swami, D. R., and Narasingarao, M., Amer. Ind. chem. Eng. **3** (1957), 191–197

[120] Jost, W., Röck, H., Schröder, W., Sieg, W., and Wagner, H. G., Z. physik. Chem., N.F. **10** (1957), 133–136;
Schröder, W., Chemie-Ing.-Techn. **30** (1958), 523–525

[120a] Slocum, E. W., I & EC Fundam. **14** (1975), 126–128

[120b] Gransø, L., and Fredenslund, A., Ber. Bunsenges. phys. Chem. **81** (1977) 10, 1088 to 1093

[120c] Gransø, L., Fredenslund, A., and Mollerup, J., Fluid Phase Equilibria **1** (1977), 13–26

[121] Lydersen, A. L., and Hammer, E. A., Chem. Engng. Sci. **7** (1958), 241–245

[122] Junghans, W., and Weber, U. von, J. prakt. Chem. **4/2** (1955), 265–273

[123] Mai, K. L., and Babb, A. L., Ind. Engng. Chem. **47** (1955), 1749–1757

[124] Zelvenskiy, Y. D., and Shalygin, V. A., J. phys. Chem. (Russian) XXXI, **7** (1957), 1501–1509

[124a] Trybuła, St., and Bandrowski, J., Inżyneria chemiczna **5** (1975), 679–695

[125] Redlich, O., and Kister, A. T., Ind. Engng. Chem. **40** (1948), 341–348

[126] Herington, E. F. G., Nature [London] **161** (1947), 610–611
Hamer, D. F. O., et al., Ind. Engng. Chem. **42** (1950), 120
Haase, R., and Jost, W., Z. phys. Chem., N.F. **9** (1956), 300–301
Tierney, J. W., Ind. Engng. Chem. **50** (1958), 707–710

[127] Herington, E. F. G., J. appl. Chem. **2** (1952), 11–23

[128] Bittrich, H.-J., Chem. Techn. **14** (1962) 9, 527–533

[129] Tao, L. C., Ind. Engng. Chem., Fundamentals **1** (1962) 2, 119–123

[130] Kolling, H., Chemie-Ing.-Techn. **24** (1952), 405–411

[131] Bowman, J. R., and Cichelli, M. T., Ind. Engng. Chem. **41** (1949), 1985

[132] Junge, C., Chem. Techn. **8** (1956), 579–588

[133] Anschütz, R., Chem. Techn. **9** (1957), 516–519

[134] Fisher, G. T., Ind. Engng. Chem., Process Des. and Devel. **2** (1963), 284–288

[135] Billet, R., Chemie-Ing.-Techn. **30** (1958), 513–515

[136] Thum, O., Chemie-Ing.-Techn. **29** (1957), 675–678

[137] Neretnicks, I., Ericson, I., and Eriksson, S., Brit. chem. Engng. **14** (1969) 12, 1711–1712

[138] Weber, U. von, Chem. Techn. **2** (1950), 241–246

[139] Vogelpohl, A., Chemie-Ing.-Techn. **43** (1971) 20, 1116–1121

[139a] Domenech, S., Guiglion, C., and Enjalbert, M., Chem. Engng. Sci. **29** (1974) 7, 1519 to 1528, 1529–1535

[140] Billet, R., Chemie-Ing.-Techn. **30** (1958), 407–416

[140a] Wilcox, W. R., Ind. Engng. Chem., Fundamentals **3** (1964) 1, 81–83

[141] Thormann, K., Chem. Techn. **2** (1950), 255–256

[142] Cavers, S. D., Ind. Engng. Chem., Fundamentals **4** (1965) 2, 229–230

[143] Pohl, K., Chemie-Ing.-Techn. **28** (1956), 562–564

[144] Horvath, P. J., and Schubert, R. F., Chem. Engng. **10** (1958)

[145] Flatt, R., Chimia [Zurich] **9** (1955), 232–237

[146] Stage, H., and Schultze, Gg. R., Oel u. Kohle **5/6** (1944), 90–95

[147] Zuiderweg, F. J., Laboratory of Batch Distillation, Interscience Publishers, New York 1957

[148] Schäfer, W., Angew. Chem., Part B **19** (1947), 251–253

[149] Fischer, W., Chemie-Ing.-Techn. **23** (1951), 116

[150] Matz, W., Angew. Chem., Part B **19** (1947), 131–134

[151] Hilberath, F., Oel u. Kohle **39** (1943), 875–886

[152] Bragg, L. B., and Lewis, J. W., Wld. Petroleum Rep. **14** (1943), 61

[152a] Strangio, V. A., and Treybal, R. E., Ind. Engng. Chem., Process Des. and Devel. **13** (1974) 3, 279–285

[153] Rose, A. and E., et al., Distillation, Interscience Publishers, New York 1951

[154] Rose, A., Ind. Engng. Chem. **33** (1941), 594

[155] Fenske, M. R., Tongberg, S. O., and Quiggle, D., Ind. Engng. Chem. **26** (1934), 1169

[156] Richter, H., Oel u. Kohle **40** (1944), 282–288

[157] Pohl, H., Erdöl u. Kohle **5** (1952), 291–294

[158] Zuiderweg, F. I., Chemie-Ing.-Techn. **25** (1953), 297–308

[159] Sizmann, R., Chemie-Ing.-Techn. **33** (1961), 659–668

[160] Manning, R. E., and Cannon, M. R., Ind. Engng. Chem. **49** (1957), 346–349

[161] Stuke, B., Chemie-Ing.-Techn. **25** (1953), 677–682

[162] Heise, F., Hiller, G., and Wagner, H. Gg., Chemie-Ing.-Techn. **41** (1969) 20, 1100

[162a] Käuter, A., and Wagner, H. Gg., Chemie-Ing.-Techn. **42** (1970), 1127; **46** (1974). 997

[162b] Borchardt, E., and Wagner, H. Gg., Chemie-Ing.-Techn. **43** (1971), 956–962: **48** (1976), 725

[163] Chilton, T. H., and Colburn, A. P., Ind. Engng. Chem., ind. Edit. **27** (1935), 255–260, 904

[164] Carney, Th. P., Laboratory Fractional Distillation, MacMillan, New York 1949

[165] Danatos, S., and Osburn, J. O., Chem. Engng. **65** (1958), 147–150

[166] Arkenbout, G. J., and Smit, W. M., Separation Sci. **2** (5) (1967), 575–596

[167] Merkel, F., Arch. Wärmewirtsch. Dampfkesselwes. **10** (1929), 13–17

[168] Weber, U. von, in: Gildemeister, E., and Hofmann, Fr., Die ätherischen Öle (revised by W. Treibs), Vol. I, Akademie-Verlag, Berlin 1966

[169] Robinson, C. S., and Gilliland, E. R., Elements of Fractional Distillation, 6th Ed. McGraw-Hill Book Company, New York 1950, pp. 476–478

[170] Weber, U. von, Chem. Techn. **2** (1950), 241–246

[171] Kolling, H., Chemie-Ing.-Techn. **22** (1952), 405–411

[172] Kohrt, H. U., Angew. Chem., Part B **20** (1948), 117–124

[173] Hausen, H., Z. angew. Physik **4** (1952), 41–51

[174] Wijk, W. R. van, and Thijssen, H. A. C., Chem. Engng. Sci. **1** (1952), 121–123; **3** (1954), 145–152

[175] Lwow, S. W., Ber. Akad. Wiss. UdSSR **57** (1947), 375–378

[175a] Mostafa, H. A., Chemie-Ing.-Techn. **47** (1975) 2, 63

[175b] Chien, H. H. J., Chem. Engng. Sci. **8** (1973) 11, 1967–1974

[175c] Serov, V. V., Abramenko, V. P., and Zykov, D. D., Int. chem. Engng. **13** (1973) 3, 514–516

[175d] Wagner, H., and Blaß, E., Chemie-Ing.-Techn. **48** (1967) 3, 220–227

[176] Krell, E., Chem. Techn. **4** (1952), 200–207

[176a] Faldix, P., and Stage, H., Chemie-Ing.-Techn. **41** (1969) 23, 1265–1269

[176b] Müller, W., Chem. Techn. **26** (1974) 1, 16–20

[176c] Billet, R., verfahrenstechnik **8** (1974) 3, 65–72

[176d] Jobst, W., Köllner, H., and Balke, M., Chem. Techn. **31** (1979) 1, 19–22

[177] Thormann, K., Dechema-Erfahrungsaustausch, Techn. Apparate und Anlagen, Trennen flüssiger Mischungen, Destillieren, Betriebstechnik, Dechema, Frankfurt/Main, August 1952

[178] Ellis, S. R. M., and Freshwater, D. C., Perfum. essent. Oil Rec. **45** (1954), 380–386

[179] Colburn, A. P., Trans. Amer. Inst. chem. Engr. **37** (1941), 805

[180] Underwood, A. J. V., Chem. Engng. Progr. **44** (1948), 603

[181] Fenske, M. R., Ind. Engng. Chem. **24** (1932), 482

[182] Harbert, W. D., Ind. Engng. Chem. **37** (1945), 1162

[183] Bruijn, P. J., Meded. Landbouwhogeschool, Wageningen **61** (9) (1961), 1–94

[183a] Wagner, H., Chemie-Ing.-Techn. **48** (1976) 8, 705–708; 9, 790–792; 10, 875–878 11, 1059–1062; 12, 1195–1198; **49** (1977) 1, 45–48

[184] Underwood, A. J. V., Trans. Instn. chem. Engr. [London] **10** (1932), 112–152

[185] Murch, D. P., Ind. Engng. Chem. **45** (1953), 2616–2621

[186] Mullin, J. W., Ind. Chemist. **33** (1957) 390, 408–417

[186a] Groenhof, H. C., Chem. Engng. J. **14** (1977) 3, 181–191; 193–201
Groenhof, H. C., and Stemerding, St., Chem.-Ing.-Techn. **49** (1977) 10, 835

[187] Kirschbaum, E., Angew. Chem., Part B **19** (1947), 13–14; Chemie-Ing.-Techn. **28** (1956), 639–644

[188] Kasanski, B. A., J. org. chem. (Russian) **12** (1942), 112

[189] Bushmakin, Y. N., and Lyslova, R. V., J. appl. Chem. (Russian) **25** (1952), 303–312

[190] Perktold, F., Angew. Chem., Part B **19** (1947), 184–185

[191] David, A., Dechema-Monogr. **23** (1954), 126–175

[192] Myles, M., et al., Ind. Engng. Chem. **43** (1951), 1452–1456

[193] Allenby, O. C. W., and L'Heureux, C., Analytic. Chem. **22** (1950), 1340

[194] Haldenwanger, K., Chemie-Ing.-Techn. **23** (1951), 437–440

[195] Zuiderweg, F. J. (edit.) Recommended Test Mixtures for Distillation Columns, The Institution of Chemical Engineers, London 1969

[196] Brandt, H., and Röck, H., Chemie-Ing.-Techn. **29** (1957), 397–402

[197] Feldmann, J., et al., Ind. Engng. Chem. **45** (1953), 214

[198] Zelvenskiy, Y. D., and Shalgin, B. A., Chem. Ind. (Russian) **6** (1962), 38 (424)–41 (427)

[199] Schultze, Gf. R., and Stage, H., Oel u. Kohle **40** (1944), 68

[200] Collins, F. C., and Lantz, V., Ind. Engng. Chem., analyt. Edit. **18** (1946), 673–677

[201] Naumann, K., and Leibnitz, E., Chem. Techn. **8** (1956), 458–471

[202] Obolonzev, R. D., and Frost, A. V., Petroleum Econ. (Russian) **25** (1947), 35–45

[203] Struck, R. T., and Kinney, C. R., Ind. Engng. Chem. **42** (1950), 77–82

[204] Weber, U. von, Personal communication.

[205] Zuiderweg, F. H., Chem. Engng. Sci. **1** (1952), 174–193

[206] Kirschbaum, E., Busch, W., and Billet, B., Chemie-Ing.-Techn. **28** (1956), 475–480

[207] Szapiro, S., Zeszyty naukowe Politechn. Łodzkiej, Chem. **2** (1955), 33–37

[208] Brauer, H., Chemie-Ing.-Techn. **29** (1957), 520–530, 785–790

[209] Zelvenskiy, Y. D., Titov, A. A., and Shalgin, B. A., Chem. Ind. (Russian) **2** (1963), 36 (116)–42 (122)

[210] Weygand, C., and Hilgetag, G., Organisch-chemische Experimentierkunst, 4th Ed., Johann Ambrosius Barth, Leipzig 1970

[211] Bernhauer, K., Einführung in die organisch-chemische Laboratoriumstechnik, Springer-Verlag, Vienna 1947

[212] Pestemer, M., Angew. Chem. **63** (1951), 118–122

[213] Brandt, P. L., Perkins, R. B., and Halverson, L. K., Oil Gas J. **7** (1946)

[214] Lentz, H., Chemie-Ing.-Techn. **41** (1969) 15, 855–861

[214a] Leung, L. S., Hutton, B. E. T., and Nicklin, D. J., Ind. Engng. Chem., Fundamentals **14** (1975) 1, 63–67

[214b] Kafarov, V. V., Blyakhman, L. F., and Planovsky, A. N., teoret. osnovy khim. tekhnol. **10** (1976) 3, 331–339

[215] Stage, F., Angew. Chem., Part B **19** (1947), 182

[216] Schultze, Gg. R., and Stage, H., Über die Wirksamkeit der neuen Normalkolonne des „Ausschusses für Laboratoriumsdestillation", Fiat-Report No. 1133 of 23 Dec. 1947

[217] Sigwart, K., Destillation und Rektifikation, in: Ullmanns Encyklopädie der technischen Chemie, Vol. 1, Urban & Schwarzenberg, München/Berlin 1951, pp. 429–470

[218] Thormann, K., Dechema-Erfahrungsaustausch, Laboratoriumstechnik, Arbeitsmethoden und Geräte, Destillieren und Rektifizieren, Dechema, Frankfurt/Main, September 1950

[219] Mach, E., VDI-Forschungsheft 375 Nov./Dec. 1935

[220] Barth, W., Chemie-Ing.-Techn. **23** (1951), 289–293; 26 (1954), 29–34

[221] Leva, M., Flow through Packings and Beds, Part I, New York 1957

[222] Kast, W., Chemie-Ing. Techn. **36** (1964) 5, 464–468

[223] Teutsch, T., Chemie-Ing.-Techn. **36** (1964) 5, 496–523

[224] Gelbe, H., Chemie-Ing.-Techn. **40** (1968), 528–530

[225] Glaser, H., Chemie-Ing.-Techn. **41** (1969) 7, 444–450

[226] Heckmann, C. J., and Krell, E., Chem. Techn. **5** (1953), 609–704

[227] Neumann, F., Chemie-Ing.-Techn. **33** (1961), 439–442

[228] Reed, T. M., and Fenske, M. R., Ind. Engng. Chem. **42** (1950), 654–660

[229] Stage, H., From a prospectus on Labodest distillation apparatus from standard components, drawing No. 741, 98, 156
Stage, H., and Bose, K., Chemie-Ing.-Techn. **27** (1955), 439

[230] Umholtz, C. L., and Winkle, M. van, Petroleum Refiner **34** (1955), 114–117

[231] Schumacher, R., Erdöl u. Kohle **2** (1949), 501–508

[231a] Schumacher, R., Verfahrenstechnik **10** (1976) 11, 727–732

[232] Borchert, R., and Jubitz, W., Infrarotstrahler zur Erwärmung, Trocknung und Aushärtung, SVT Vol. 5, VEB Verlag Technik, Berlin 1951

[233] Junge, C., Chem. Techn. **6** (1954), 37–38

[234] Grosse-Oetringhaus, H., Erdöl u. Kohle **1** (1948), 273–280

[235] Reid, R. C., and Sherwood, T. K., The Properties of Gases and Liquids, 2nd Ed., McGraw-Hill Book Company, New York 1966

[236] Hecht, G., et al., Berechnung thermodynamischer Stoffwerte von Gasen und Flüssigkeiten, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1966

[237] Stage, H., Fette u. Seifen **55** (1953), 284–290

[238] Kharbanda, O. M. P., Nomograms for Chemical Engineers, Heywood & Company, London 1958

[239] Orlicek, A. F., and Pöll, H., Hilfsbuch für Mineralöltechniker, Vols. I and II, Springer-Verlag, Vienna 1951/55

[240] Häussler, W., Technik **9** (1954), 51–52

[241] Cole, P. J., Analyt. chem. **22** (1950), 946–947

[242] Krell, E., Chem. Techn. 4 (1952), 200–207

[243] Meier-Grolman, F. W., and Wesolofsky, F., Oel u. Kohle **39** (1941), 297–300

[244] Beck, R., Chemie-Ing.-Techn. **44** (1972) 8, 596–598

[244a] Savkovič-Stefanovič, J., Simonovič, D., and Popovič, G., Chem.-Ing.-Techn. 49 (1977), 825–826

[245] Gemmeker, L., and Stage, H., Glas-Instrumenten-Techn. 7 (1963) 1, 18–23

[246] Kaplick, K., and Schubert, M., Datenverarbeitung in der Verfahrenstechnik — Digitale Rechenautomaten, Vol. 6 of the series Beiträge zur Verfahrenstechnik, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1969

[247] Wagner, M., Analogrechner in der Verfahrenstechnik, Vol. 10 of the series Beiträge zur Verfahrenstechnik, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1972

[248] Adler, H., Elektronische Analogrechner, 3rd Ed., VEB Deutscher Verlag der Wissenschaften, Berlin 1970

[249] Savas, E. S., Computer Control of Industrial Processes, McGraw-Hill Book Company, New York/Toronto/London 1965

[250] Roth, H., Chem. Techn. **20** (1968) 2, 77–82

[251] Schubring, A., Chemie-Ing.-Techn. **32** (1960) 3, 223–227

[251a] Chien, H. H. J., AIChEJ **24** (1978) 4, 606–613

[251b] Rose, L. M., Chimia, Aarau **33** (1979) 2, 59–65

[252] Sealey, C. J., Chem. Engng. Sci. **25** (1970), 561–568

[253] Leibnitz, E., and Schuhler, C., Z. physik. Chem. **217** (1961), 217–229
Schuhler, C., Z. physik. Chem. **217** (1961), 263–270

[254] Nagel, O., Smits, H., Wolf, D., and Günzler, H., Chemie-Ing.-Techn. **41** (1969) 17, 983–987

[255] Pilhofer, Th., Chemie-Ing.-Techn. **42** (1970) 1, 509–515
Johnson, M. L., and Lupfer, D. E., Chem. Engng. Progr. **62** (1966) 6, 75–79

[256] Wang, I. C., and Henke, G. E., Hydrocarb. Process. **45** (1966) 8, 155

[257] Sargent, R. W. H., and Murtagh, B. A., Trans. Instn. chem. Engr. **47** (1969), 85

[258] Stainthorp, F. P., et al., in: Piric, J. M.: Efficient Computer Methods for the Practising Chemical Engineer, London 1967, pp. 181–189

[259] Blatt, E., and Fleissner, H., Glas-Instrumenten-Techn. **15** (1971), Sonderheft, 1333 to 1337

[260] Brauer, H., and Mewes, D., Chemie-Ing.-Techn. 44 (1972) 1/2, 93–96

[261] Bitter, R. C., Chemie-Ing.-Techn. **40** (1968) 13, 651–656

[262] Wagner, H., and Blass, E., Chemie-Ing.-Techn. **45** (1973), 63–67

[263] Reichelt, W., and Blass, E., Chemie-Ing.-Techn. **43** (1971) 17, 949–956
Reichelt, W., Chemie-Ing.-Techn. **43** (1971) 22, 1196–1203; **44** (1972) 18, 1068–1071

[264] Köhler, R., and Schober, G., Chem. Techn. **25** (1973) 12, 718–721; **26** (1974) 8, 482 to 483, and 12, 747–750

[265] Kirbach, V., Frenzel, L., and Strankmüller, H., Chem. Techn. **25** (1973) 12, 721–722

[266] Morozova, L. V., and Platonov, V. M., Theor. Found. chem. Engng. 8 (1974), 453–458

[267] Grosshennig, P., Thesis TU München 1976

[268] Blaß, E., and Kurtz, R., Verfahrenstechnik **10** (1976) 11, 721–724

[269] Achwal, S. K., and Stepanek, J. B., chem. Engng. J. **12** (1976) 1, 69–75

[270] Zech, J. B., and Mersmann, A. B., Chem.-Ing.-Techn. **50** (1978) 7, 549

[271] Ponter, A. B., Peier, W., and Fabre, S., Chem.-Ing.-Techn. **50** (1978) 6, 444–446

[272] Fabre, S., Ponter, A. B., and Huber, M., Ind. and Engng. Chem., Process Des. Dev. 18 (1979) 2, 266–269

[273] Gohrke, E., and Kleemann, G., Chem. Techn. **29** (1977) 11, 604–607

[274] Weiß, S., and Kirbach, V., Chem. Techn. **30** (1978) 11, 562–565

Chapter 5 — Separating Process

[1] Stage, H., and Gemmeker, L., Chem. Labor Betrieb **15** (1964) 5, 177—188; 6, 232—242; 7, 290—298; 8, 325—338

[1a] Stage, H., CZ-Chemie-Technik **1** (1972), 263—272

[2] Bodenheimer, W., Nature [London] **173** (1954), 124

[3] Jantzen, E., and Witgert, H., Fette u. Seifen **46** (1939), 563

[3a] Fischer, W. G., GIT Fachz. Lab. **18** (1974) 7, 689—691

[3b] Bertele, E., and Humbel, F. A., GIT Fachz. Lab. **17** (1973) 6, 667—674

[4] Babcock, M. J., Analytic. Chem. **21** (1949), 632—633

[5] Shrader, S. A., and Ritzer, J. E., Chem. Fabrik **12** (1935), 173

[6] Klenk, E., Hoppe-Seyler's Z. physiol. Chem. **242** (1936), 250

[7] Fischer, W. S., Chemiker-Ztg. **94** (1970) 5, 157—161; Glas-Instrumenten-Techn. **13** (1969), 535—540

[8] Winters, J. C., and Dinerstein, R. A., Analytic. Chem. **27** (1953), 546—550
Nerheim, A. G., and Dinerstein, R. A., Analytic. Chem. **28** (1956), 1029—1033

[9] Spiegelberg, C., Thesis F.U. Berlin 1956

[10] Gould jr., C. W., Holzmann, G., and Niemann, C., Analytic. Chem. **20** (1948), 361

[11] Breger, J. A., Analytic. Chem. **20** (1948), 980

[12] Paschke, R. F., et al., J. Amer. Oil Chemists' Soc. **31** (1954), 5—7

[13] Pfeil, E., Angew. Chem. **54** (1941), 161—184

[14] Eigenberger, E., Mikrochemie **26** (1939), 204

[15] Clasen, H., Chemie-Ing.-Techn. **28** (1956), 45—48

[15a] Bock, R., Methoden der Analytischen Chemie, eine Einführung, Band 1: Trennungsmethoden, Verlag Chemie, Weinheim/Bergstr. 1974

[16] Stage, H., Fette u. Seifen **55** (1953), 217—224

[17] Günther, G., Kühnhanns, K., and Hüttig, E., Chem. Techn. **7** (1955), 656—662

[18] Profft, E., and Buchmann, G., Chem. Techn. **8** (1956), 417—418
Buchmann, G., Chem. Techn. **14** (1962) 10, 617—620; 12, 741—744

[19] Fürst, H., and Schwetlick, K., Chem. Techn. **8** (1956), 458—471

[20] Olechnowitz, A. F., Thesis Halle—Wittenberg 1956

[21] Fiebach, K., Thesis Leipzig 1957

[22] Gutwasser, H., and Müller, K., Chem. Techn. **21** (1969) 11, 756—759
Gutwasser, H., Chem. Techn. **22** (1970) 8, 467—471

[23] Mair, B. J., et al., Analytic. Chem. **30** (1958), 1814—1817

[24] Naumann, K., and Leibnitz, E., Chem. Techn. **8** (1956), 458—471

[25] Oldroyd, D. M., and Goldblatt, L. A., Ind. Engng. Chem., analytic. Edit. **18** (1946), 761—763

[26] Petrocelli, J. A., Puzniak, T. J., and Clark, R. O., Analytic. Chem. **36** (1964), 1008—1011

[27] Prospectus "Aerograph Research Notes 1965", Wilkens Instrument and Research AG, Basle/Switzerland

[28] Stage, H., CZ-Chemie-Technik **2** (1973) 1, 35—40

[29] Hampel, B., Chemiker-Ztg. **95** (1971) 7, 316—325

[30] Rieger, H., Chem. Techn. **22** (1970) 1, 36—40

[30a] Winkelsesser, G., CAV (1976) **5**, 122—130

[30b] Pietzsch, W., and Rautenberg, K.-H., Chem. Techn. **31** (1979) 3, 135—137

[31] Carpenter, J. K., and Helwig, R. W., Ind. Engng. Chem. **42** (1950), 571—578

[32] Jordan, D. G., Chemical Pilot Plant Practice, Interscience Publishers, New York 1955

[33] Dietz, H., and Kardos, J., Chem. Techn. **19** (1967) 12, 713—719

[34] Billet, R., Chemie-Ing.-Techn. **42** (1970) 14, 910—917

[35] Kullmann, W. W., Pharmaz. Ind. **15** (1953), 159—162

[36] Job, C., and Zellner, H., Pharmaz. Ind. **17** (1955), 161—163. Manufacturer: Schott u. Gen., Mainz

[36a] Prospectus "Quickfit, Single-stage water distillation apparatus". Throughput 3.5 to 4 l/h of distilled water

[36b] Schulze, F.-W., Petrick, H.-J., Cammenga, H. K., and Baer, K., GIT Fachz. Lab. **22** (1978) 6, 475–483

[37] Schpolski, E. W., Atomphysik, Part 1, 12th Ed., Part 2, 9th Ed., VEB Deutscher Verlag der Wissenschaften, Berlin 1974

[38] Brodsky, A. E., Isotopenchemie, ed. by J. Mühlenpfordt, Akademie-Verlag, Berlin 1959 (Transl. from Russian)

[39] Brunnée, K., and Voshage, H., Massenspektrometrie — Physikalische und apparative Grundlagen sowie Anwendungen, Verlag Karl Thiemig, München 1964
Birkenfeld, H., Haase, G., and Zahn, H., Massenspektrometrische Isotopenanalyse, 2nd Ed., VEB Deutscher Verlag der Wissenschaften, Berlin 1969
Wetzel, K., Hübner, H., Hübner, G., and Maass, I., Anwendung stabiler Isotope in Forschung und Technik, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1963

[40] Conn, A. L., and Wolf, J. E., Ind. Engng. Chem. 50 (1958), 1231–1234, DBP No. 944848, granted 28 June, 1956

[41] Mercea, V., Isotopenpraxis **2** (1966) 8, 313–322

[42] Müller, G., Mauersberger, K., and Sprinz, H., Analyse stabiler Isotope durch spezielle Methoden, Akademie-Verlag, Berlin 1969

[43] Baertschi, P., Kuhn, W., and Kuhn, H., Nature [London] **171** (1953), 1018

[44] Sellers, E. S., and Augood, D. R., Trans. Instn. chem. Engr. 34 (1956), 53–78

[45] Timmerhaus, K. D., Weitzel, D. H., and Flynn, T. M., Chem. Engng. Progr. **54** (1958), 35–46

[46] Weisser, R. H., Techn. Rundschau Sulzer **40** (1958), 71–73

[47] Shavoronkov, N. M., and Sakodynskiy, K. I., Kernenergie **4** (1961) 12, 893–904

[48] Clusius, K., and Meyer, H., Helv. chim. Acta **36**/7 (1953), 2045–2055

[49] Groth, W., Ihle, H., and Murrenhoff, A., Angew. Chem. **68** (1956), 644–648

[50] Clusius, K., and Schleich, K., Helv. chim. Acta **42** (1959), 232–239
McInteer, B. B., and Potter, R. M., Ind. Engng. Chem. Proc. 4 (1965) 1, 35–42

[51] Devyatikh, G. G., Sorin, A. D., and Nikolaev, N. Y., J. appl. Chem. (Russian) **31** (1958), 368–375

[52] Sevrugova, N. N., Uvarov, O. V., and Shavoronkov, N. M., Atomic Energy (Russian) **4** (1956), 113–117

[53] Kistemaker, J., Bigeleisen, J. B., and Nier, A. O., Proceedings of the International Symposium on Isotope Separation (Amsterdam, April 23–27, 1957), North-Holland Publishing Company, Amsterdam 1958

[54] Yagodin, G. A., Uvarov, O. V., and Shavoronkov, N. M., Ber. Akad. Wiss. UdSSR **111** (1956), 384–387

[55] Clusius, K., and Schleich, K., Helv. chim. Acta **41** (1958), 1342–1358

[56] Kirshenbaum, J., Physical Properties and Analysis of Heavy Water, McGraw-Hill Book Company, New York 1951

[57] Urey, H. C., J. chem. Soc. [London] 1947, 562

[58] Benedict, M., Survey of Heavy Water Production Processes, Conference, Switzerland, 30 June, 1955

[59] Kuhn, W., Chemie-Ing.-Techn. **25** (1953), 12–18; **29** (1957), 6–16
Kuhn, W., Baertschi, P., and Thürkauf, M., Chimia [Zurich] 8 (1954), 109–122, 145–156
Kuhn, W., Helv. chim. Acta **35** (1952), 1684–1736
Kuhn, W., Helv. chim. Acta **37** (1954), 1407–1422

[59a] Lumb, P. B., Nuclear Engng. **21** (1976) 244, 64–69

[60] Baertschi, P., and Kuhn, W., Final Concentration of Heavy Water by Rectification, Conference, Switzerland, 8 July, 1955

[61] Becker, E. W., Angew. Chem. **68** (1956), 6–13
Huber, M., Die Rektifikation als Spezialfall der Theorie der Isotopentrennung, Sulzer-Verfahrenstechnik, Achema 1961

[62] Hänny, J., Hartmann, F., and Hiltbrunner, R., Techn. Rundschau Sulzer **4** (1961), 21–26

[63] Dixon, O. G., J. Soc. chem. Ind. **68** (1949), 88–91
[64] Krell, E., Chemie-Ing.-Techn. **32** (1960), 233–240
[65] Uvarov, O. V., Sokolski, V. A., and Shavoronkov, N. M., Chem. Ind. (Russian) 7 (1956), 20–21
[66] Dostrovsky, J., Llewellyn, D. R., and Vromen, B. H., J. chem. Soc. **4** (1952), 3509–3524
[67] Jackson, R. F., and Pigford, R. L., Ind. Engng. Chem. **48** (1956), 1020–1026
[68] Rosen, A. M., Ber. Akad. Wiss. UdSSR **107**/2 (1956), 295
[69] London, H., Separation of Isotopes, George Newnes Ltd., London 1961
Cohen, K., Theory of Isotopic Separations, McGraw-Hill Book Company, New York 1951
[70] Staschewski, D., Chemie-Ing.-Techn. **40** (1968), 748; **43** (1971), 14, 810–816
Chem. Techn. 4 (1975), 269–280
Production of Oxygen-18 and Oxygen-17 by Countercurrent Distillation of Reactor Grade Heavy Water, in Panel Proceedings Series: "Stable Isotopes in the Life Sciences", IAEA Vienna 1977 43 (1971), 14, 810–816
[71] Surowiec, A. J., Ind. Engng. Chem. **52** (1960) 9, 798
Gupta, D., and Ray, S. N., Ind. Engng. Chem. Proc. **1** (1962), 255–262
Petyluk, F. B., Platanov, V. M., and Girsanov, I. V., Ind. Engng. Chem. **5** (1965) 7, 309–317
[72] Baertschi, P., and Kuhn, W., Helv. chim. Acta **40** (1957), 1084–1103
[73] Stage, H., Chemische Arbeitsgemeinschaft Verfahrenstechnik, Jan./Feb. 1970, 44–54.
[73a] Schwab, H., Chemie-Ing.-Techn. **44** (1972) 11, 704–707
[74] Gelbin, D., Chem. Techn. **21** (1969) 6, 329–334
[75] Cannon, N. R., Ind. Engng. Chem. **53** (1961), 629
[76] McWhirter, I. R., and Lloyd, W., Chem. Engng. Progr. **59** (1963) 6, 58
[77] Burstin, H., and Winkler, J., Chemiker-Ztg. **22** (1931), 212
[78] Kolling, H., and Tramm, H., Chemie-Ing.-Techn. **21** (1949), 9
[79] Capitani, C., and Miöani, E., Ind. chimica **36** (1954), 671–684
[80] Stage, H., Dechema-Monogr. **15** (1950), 156–170
[81] Sigwart, K., Destillieren und Rektifizieren, in: Houben-Weyl, Methoden der organischen Chemie, ed. by E. Müller, Vol. I/1, Georg Thieme Verlag, Stuttgart 1957
[82] Hausen, H., and Schlatterer, R., Chemie-Ing.-Techn. **21** (1949), 453–460
Kirschbaum, E., and Lipphardt, G., Chemie-Ing.-Techn. **29** (1957), 393–397
[83] Otto, W., Chem. Techn. **14** (1962) 4, 228–231
[84] Kirschbaum, E., Destillier- und Rektifiziertechnik, 4th Ed., Springer-Verlag, Berlin/Heidelberg/New York 1969
[85] Fabuss, B., Z. Ver. ung. Chemiker 8 (1953), 323–324
[86] Fischer, V., Ann. Physik **6** (1947), 139–152
[87] Herrmann, E., Chemiker-Ztg. **80** (1956), 102–104, 131–134, 169–173
[88] Tröster, E., Chemie-Ing.-Techn. **32** (1960) 8, 525–531
[88a] Wondrak, G. A. M., Ber. Bunsenges. **81** (1977) 10, 1033–1036
Chem.-Ing.-Techn. **46** (1974) 65 (Synopsis)
[89] Junge, C., Chem. Techn. **6** (1954), 37–38
[90] Trenne, H., Erdöl u. Kohle **2** (1951), 63–66
[91] Kuhn, W., Helv. chim. Acta **25** (1952), 252–295
[92] Weber, U. von, Chem. Techn. **2** (1950), 241–246
[93] Voigt, G., Kernenergie **2** (1959), 14–39
[93a] Blass, E., Chemie-Ing.-Techn. **45** (1973) 13, 865–872
[93b] Wondrak, A. M., and Kohler, F., Chemie-Ing.-Techn. **46** (1974) 1, 37
[93c] Anderle, F., Frey, H., and Lerch, G., Kerntechn. **19** (1977) 11, 483–487
[93d] Blaß, E., and Sauer, H., Chem.-Ing.-Techn. **50** (1978), 525–532
[94] Podbielniak, W. J., Ind. Engng. Chem., analytic. Edit. **3** (1931), 177; **5** (1933), 119
[95] Grosse-Oetringhaus, H., Erdöl u. Kohle **2** (1949), 286–299
[96] Wustrow, W., Z. analyt. Chem. **108** (1937), 305
[97] Stokes, Ch. S., and Hauptschein, M., Analytic. Chem. **24** (1952), 1526
Drawin, H. W., Vakuum-Techn. (1961), 2

[98] Lerer, E., and Kuss, E., Z. physik. Chem., Sec. A, Vol. 163 (1933), 73

[99] Miller, G. H., Operations with Gases in Technique of Organic Chemistry, Vol. III, Part II, Chap. V, Interscience Publishers, New York 1957

[100] Müller, G., and Gnauck, G., Reinste Gase, VEB Deutscher Verlag der Wissenschaften, Berlin 1965

[101] Koch, H., and Hilberath, F., Brennstoff-Chem. 21 (1940), 197–203
Hammerich, Th., Erdöl u. Kohle 5 (1952), 361–366

[102] Gemmeker, W., and Stage, H., Glas-Instrumenten-Techn. 6 (1962) 10, 372–376

[103] Klein, E., and Walz, H., Glas-Instrumenten-Techn. 11 (1967) 5, 405–411

[104] Podbielniak, W. J., and Preston, S. T., Petroleum Engr. 5 (1955), 205–211

[105] Manufacturer: Ernst Haage, Mülheim/Ruhr

[106] Simons, G., Ind. Engng. Chem., analytic. Edit. 10 (1938), 648

[107] Podbielniak, W. J., Apparatus and Methods for Precise Fractional Distillation Analyses, American Chemical Society, Atlantic City Meeting 1941

[108] Rose, A. and E., et al., Distillation, Interscience Publishers, New York 1951

[109] Preston, W., et al., Freiberger Forschungshefte 5, Akademie-Verlag, Berlin 1953, pp. 231–238

[110] Stage, H., Destillieren und Rektifizieren, Sec. 19, in: Fortschritte der Verfahrenstechnik 1952/53, Verlag Chemie GmbH, Weinheim/Bergstr. 1954

[111] Bernhauer, K., Einführung in die organisch-chemische Laboratoriumstechnik, Springer-Verlag, Vienna 1947

[112] Gemmeker, L., and Stage, H., Glas-Instrumenten-Techn. 6 (1962) 11, 455–458

[113] Holland-Merten, E. L., Tabellenbuch der Vakuumverfahrenstechnik in der Grundstoffindustrie, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1968

[114] Jaeckel, R., Kleinste Drücke, ihre Messung und Erzeugung, in: Technische Physik in Einzeldarstellungen, Springer-Verlag, Berlin/Göttingen/Heidelberg 1950
Leybold, Vakuum-Taschenbuch, ed. by K. Diels and R. Jaeckel, Springer-Verlag, Berlin/Göttingen/Heidelberg 1962
Keunecke, E., Chemiker-Ztg. 81 (1957), 239–244
Yarwood, J., Hochvakuumtechnik, 3rd Ed., Rudolf A. Lang Verlag, Berlin 1955 (Transl. from English)
Pupp, W., Vakuumtechnik, Grundlagen und Anwendungen, Thiemig-Taschenbuch, Vol. 43, Verlag Karl Thiemig, München 1973

[115] Müller, L., Freiberger Forschungshefte, Edit. B 6, Akademie-Verlag, Berlin 1954, pp. 81–115; Freiberger Forschungshefte 11, Akademie-Verlag, Berlin 1957, p. 575

[116] Spendlove, M. J., Vakuum-Techn. 6 (1957), 15–18 and 36–44

[117] Horsley, W., J. appl. Chem. 8 (1958), 13; Chemie-Ing.-Techn. 30 (1958), 736

[118] Parker, S. G., and Wilson, O. W., Ind. Engng. Chem. Proc. 4 (1965) 4, 365–368

[118a] Bezobrazov, E. G., et al., khim. prom. (1974) 4, 301–302

[118b] Schmücker, H., and Grigull, U., Heat Transfer in Boiling, Academic Press, 1977, pp. 361–387

[119] Laporte, H., Hochvakuum, VEB Wilhelm Knapp Verlag, Halle 1951

[120] Echols jr., L. S., and Gelus, E., Analytic. Chem. 19 (1947), 668

[121] Ulusoy, E., and Sakaloz, T., Theoretische Grundlagen der Isotherm-Destillation (Mitt. I–III), Revue de la faculté des sciences de l'université d'Istanbul, Série C, Tome XXIII/XXIV, Fasc. 3–4 (1958/59)

[122] Frank, W., and Kutsche, D., Die schonende Destillation, Otto Krausskopf-Verlag GmbH, Mainz 1969

[123] Billet, R., and Raichle, L., Chemie-Ing.-Techn. 39 (1967) 3, 133–137

[124] Gelbe, H., Chemie-Ing.-Techn. 40 (1968) 11, 528–530

[125] Harries, W., Chemie-Ing.-Techn. 21 (1949), 139–142

[126] Mönch, G. C., Hochvakuumtechnik, Rudolf A. Lang Verlag, Pößneck 1950; Neues und Bewährtes aus der Hochvakuumtechnik, 2nd corr. Reprint, VEB Verlag Technik, Berlin 1961

[127] Holland-Merten, E. L., *Die Vakuum-Pumpen in der Verfahrenstechnik*, VEB Wilhelm Knapp Verlag, Halle 1950

[128] Ardenne, M. von, Technik **13** (1958), 275–285

[128a] Prospectus "Quickfit-Wiegand Glas-Dampfstrahlpumpen", QVF Glastechnik GmbH, Wiesbaden

[129] Kienel, G., Glas-Instrumenten-Techn. **10** (1966) 9, 761–770

[130] Krell, E., Chem. Techn. **2** (1950), 252–255; **4** (1952), 443–450

[131] Wittka, F., Angew. Chem. **53** (1940), 557

[132] Gemmeker, L., and Stage, H., Glas-Instrumenten-Techn. **8** (1964) 6, 413–428; 7, 503–508
Stage, H., *Chemieanlagen + Verfahren* (1972), No. 2

[132a] Wilhelm, G., and Miß, H., Chem. Techn. **8** (1979) 8, 377–383

[133] Utzinger, G. E., Chem. Techn. **7/8** (1943), 61

[134] Janosfia, P., Dechema-Monogr. **55** (1965)

[135] Fürst, H., and Schimke, D., Chem. Techn. **22** (1970) 9, 553–555

[136] Dieter, K., *Chemiker-Ztg.* **94** (1970) 12, 445–451

[137] Billet, R., Chemie-Ing.-Techn. **29** (1957), 733–742

[138] Egli, R., Glas-Instrumenten-Techn. **11** (1967) 6, 509–515

[138a] Kramer, M. T., GIT Fachz. Lab. **18** (1974) 7, 862–868

[138b] Sorbe, G., GIT Fachz. Lab. **21** (1977) 14, 1315

[139] Burrows, G., Molecular Distillation, Oxford-Clarendon Press, Oxford 1960
Holó, J., et al., The Applications of Molecular Distillation, Akademiai Kiadó, Budapest 1971

[140] Ridgway-Watt, P., Chem. and Ind., 27 May, 1961, 680–692

[140a] Habendorff, R., CZ-Chem.-Techn. **2** (1973), 21–24

[141] Hickmann, K. C. D., and Trevoy, T. J., Chemie-Ing.-Techn. **25** (1953), 672–676

[142] Langmuir, S., Phys. Rev. **8** (1916), 176

[143] Burrows, G., J. appl. Chem. **7** (1957), 375–384

[144] Jaeckel, R., Erdöl u. Kohle **4** (1951), 1761

[145] Perry, E. S., Methods in Enzymol. **3** (1957), 383–391
Jaeckel, R., and Oetjen, G.-W., Chemie-Ing.-Techn. **21** (1949), 169–176
Jaeckel, R., et al., Vakuumtechnik und Molekulardestillation, in: Fortschritte der Verfahrenstechnik, Vol. 2, 1954/55, pp. 29–43; Vol. 3, 1956/57, pp. 62–73, Verlag Chemie GmbH, Weinheim/Bergstr. 1954/57
Jaeckel, R., Destillation und Sublimation im Fein- und Hochvakuum, in: Houben-Weyl, Methoden der organischen Chemie, ed. by E. Müller, Vol. I/1, Georg Thieme Verlag, Stuttgart 1958

[146] Frank, W., Glas-Instrumenten-Techn. **9** (1956) 11, 777–782

[147] Utzinger, G. E., Chemie-Ing.-Techn. **26** (1954), 129–131

[148] Melpolder, F. W., et al., Analytic. Chem. **27** (1955), 974–977

[149] Malyusov, V. A., et al., Chem. Ind. (Russian) **5** (1958), 36–42

[150] Malyusov, V. A., Umnik, N. N., and Shavoronkov, N. M., Chem. Ind. (Russian) July/Aug. (1958), 296–302; Collect. Czechoslov. chem. Commun. **23** (1958), 1720–1726

[151] Hickman, K. C. D., Ind. Engng. Chem. **39** (1947), 686–694

[152] Hickman, K. C. D., Ind. Engng. Chem., analyt. Edit. **29** (1937), 968

[153] Hickman, K. C. D., U.S. Patent No. 2117802 of 17 May, 1938, and No. 2210928 of 13 Aug., 1940

[154] Embree, N. D., Ind. Engng. Chem. **29** (1937), 975

[155] Gorriz, A. M., et al., An. Real. Soc. espan. Fisica Quim., Ser. B **48** (1952), 825–850; Ser. B **49** (1953), 19–22, 107–114, 579–586

[156] Fawcett, E. W., Kolloid-Z. **86** (1939), 34–91

[157] Masch, L.-W., Chemie-Ing.-Techn. **22** (1950), 141–146

[158] Hickman, K. C. D., Ind. Engng. Chem. **48** (1956), 496–499

[159] Carney, T. P., Laboratory Fractional Distillation, MacMillan, New York 1949

[160] Malyusov, V. A., Malafoev, N. A., and Shavoronkov, N. M., J. phys. Chem. (Russian) **32** (1958) 10, 2403–2409
[161] Schneider, K. W., Erdöl u. Kohle **4** (1951), 4–9
[162] Simons, J. H., Ind. Engng. Chem., analyt. Edit. **10** (1938), 30
[163] Uyeha, H., and Hagihara, Y., J. chem. Engng. Japan **3** (1970) 1, 13–17
[164] Bewilogua, L., Verges, P., and Vinzelberg, H., Isotopenpraxis **9** (1973) 3, 97–100
[165] Liedel, K. H., Glas in der Chemie — Laborgeräte, Großapparate, Rohrleitungen, Otto Krausskopf-Verlag GmbH, Mainz 1973
[166] Stage, H., and Fischer, W. G., GIT Fachz. Lab. **23** (1979) 8, 724–731
[167] Matwiyoff, N. A., et al., The Stable Isotopes (ICONS) Research and Development Program at the Los Alamos Scientific Laboratory, in Proceedings Series "Isotope and Radiation Techniques in Soil Physics and Irrigation Studies", IAEA, Vienna 1977
Asatiani, P. Ya., et al., Industrial Pilot Plant for the Production of Oxygen-18, in Panel Proceedings Series: "Stable Isotopes in the Life Sciences", IAEA, Vienna 1977
[168] Block, U., Schoenemakers, H., and Wolf, D., Verf. tech. 12 (1978) 10, 678–681

Chapter 6 — Selective Separating Processes

[1] Findlay, A., Die Phasenregel und ihre Anwendungen, Verlag Chemie GmbH, Weinheim/Bergstr. 1958 (transl. from English)
[2] Badger, W. L., and McCabe, W. L., Elemente der Chemie-Ingenieur-Technik, Springer-Verlag, Berlin 1932 (transl. from English)
[3] Stage, H., Fette u. Seifen **55** (1953), 513–516
[4] Stage, H., Erdöl u. Kohle **3** (1950), 478–490
[5] Hoffmann, E. J., Azeotropic and Extractive Distillation, John Wiley & Sons, London 1965
[6] DRP No. 767162 Kl. 12r, of 27 Nov., 1936, issued 3 Dec., 1951
[7] Sizmann, R., and Stuke, B., Chemie-Ing.-Techn. **27** (1955), 669–675
[8] Algermissen, J., Chemie-Ing.-Techn. **30** (1958), 502–510
[9] Merkel, H., Chemie-Ing.-Techn. **24** (1952), 511–512
[10] Stage, H., Bünger, R., and Jonas, A., Fette u. Seifen **55** (1953), 580–583
[11] Pozzi and Escot, Bull. Soc. chim. France **31** (1904), 932
[12] Pfeil, E., Angew. Chem. **54** (1941), 161–184
[13] Bernhauer, K., Einführung in die organisch-chemische Laboratoriumstechnik, Springer, Verlag, Vienna 1947
[14] Thormann, K., Chem. Fabrik **13** (1940), 3–9
[15] Weber, U. von, Gewinnung ätherischer Öle durch Destillation, in: Gildemeister, E., and Hoffmann, Fr., Die ätherischen Öle (revised by W. Treibs), Akademie-Verlag, Berlin 1966
[16] Rigamonti, R., Chemiker-Ztg. **80** (1956), 628–631
[16a] Prenosil, J. E., Chem. Engng. J. 12 (1976) 1, 59–68
[16b] Berkes, R., Blickle, T., and Ujhidy, A., Chem. Techn. **31** (1979) 2, 69–72
[17] Röck, H., Destillation im Laboratorium, Extraktive und azeotrope Destillation, Dr. Dietrich Steinkopff Verlag, Darmstadt 1960
[18] Kümmerle, K., Chemie-Ing.-Techn. **32** (1960), 513–517
[19] Gerster, J. A., Chem. Engng. Progr. **65** (1969) 9, 43
[19a] Müller, E., Verfahrenstechnik 8 (1974) 3, 88–93
[19b] Helms, G., and John, P., inform. chimie (1976) 161, 105–109
[19c] Schober, G., Orschel, K.-D., Sichting, H., Sasse, H., Köhler, R., and Kleinschmidt, G., Chem. Techn. **31** (1979), 73–75
[20] Lecat, M., Tables azéotropiques, Azéotropes binaires orthobares, 2nd Ed., Brussels 1949 (published by the author)
[21] Ogorodnikov, C. K., Lesteva, T. M., and Kogan, V. B., Azeotropic Mixtures (Russian), Khimiya, Leningrad 1971

[22] Stuke, B., Chemie-Ing.-Techn. **25** (1953), 133–136

[23] Coulson, E. A., and Herrington, E. F., J. Chem. Soc. [London] 1947, 597–607

[24] Kuhn, W., and Massini, P., Helv. chim. Acta 33 (1950), 737
Kuhn, W., and Kuhn, H. J., Helv. chim. Acta **40** (1957), 2433–2454

[25] Enüstün, B. V., Commun. Fac. Sci. Univ. Ankara, Ser. B 5 (1951), 1–21

[26] Litvinov, N. D., J. phys. Chem. (Russian) 27 (1953), 476–490

[27] Swiętosławski, W., Przemysł. chem. 7 (1951), 363–370; Bull. Soc. chim. belges **62** (1953), 10–20; Bull. Acad. polon. Sci., Cl. III, Vol. I, 1–2, 1953
Swiętosławski, W., Physikalische Chemie des Steinkohlenteers, N. J. Hoffmann Verlag, Köln 1954
Swiętosławski, W., Azeotropie und Polyazeotropie, Vol. 1, Państwowe Wydawnictwo Naukowe, Warsaw 1957

[28] Lecat, M., Azéotropisme et Distillation, in: Grignard, Traité de Chimie Organique I, Paris 1935

[28a] Othmer, D. F., Verfahrenstechnik 8 (1974) 3, 94–99; 4, 118–123

[29] Schuberth, H., Thermodynamische Grundlagen der Destillation und Extraktion, Vol. I, VEB Deutscher Verlag der Wissenschaften, Berlin 1972

[29a] Avetyan, V. S., Mashkona, V. F., Petlyuk, F. B., and Serafimov, L. A., Theor. Found. chem. Engng. 8 (1974), 253–258

[29b] Svoboda, V., Vonková, J., Holub, R. and Pick, J., Coll. Czech. chem. Com. **42** (1977) 9, 2607–2614

[30] Zieborak, K., Prace Głównego Inst. Chem. przemysłowej, (1951), 1–44

[31] Orszagh, A., Przemysł. chem. **9** (32) (1953), 333–336

[31a] Avetyan, V. S., Karp, L. E., Petlyuk, F. B. and Serafimov, L. A., Russ. J. of phys. Chem., London **52** (1978) 10, 1425–1427

[31b] Tamir, A. and Wisniak, J., Chem. Engng. Sci. **33** (1978) 6, 657–672

[32] Malesinski, I. W., Bull. Acad. polon. Sci., Sér. Sci. chim., geol., geogr. **6** (1958), 105–109

[33] Stecki, J., Bull. Acad. polon. Sci., Sér. Sci. chim., geol., geogr. **6** (1958), 47–53,

[34] Berg, L., et al., Hydrocarbon Processing **45** (1966), 103; Ind. Engng. Chem. **37** (1945) 585; 38 (1946), 1249
Berg, L., Chem. Engng. Progr. **65** (1969) 9, 52–57

[35] Rose, A. and E., et al., Distillation, Interscience Publishers, New York 1951

[35a] Sharov, V. T., and Serafimov, L. A., Physico-chemical Fundamentals of Distillation and Rectification (Russian), Khimiya, Leningrad 1975

[35b] Schlünder, E. U., Chem.-Ing.-Techn. 50 (1978) **10**, 749–754

[36] Franck, H. G., Angew. Chem. **63** (1951), 260–263

[37] Coulson, E. A., and Jones, J. J., J. Soc. chem. Ind. **65** (1946), 163–175

[38] Dummett, G. A., Petroleum [London] **18** (1955), 41–45

[39] Hunsmann, W., and Simmrock, K. H., Chemie-Ing.-Techn. **38** (1966) 10, 1053–1059

[39a] Petlyuk, F. B., and Avetyan, V. S., teoret. osnovy khim. tekhnol. **7** (1973) 3, 307–312

[39b] Naka, Y., Komatsu, T., Hashimoto, I., and Takamatsu, E., Int. chem. Engng. **16** (1976) 2, 272–279

[39c] Susarev, M. P., and Toikka, A. M., J. phys. Chem. (Russian) **50** (1976) 3, 458–460

[39d] Kudryavtseva, L., Toome, M., and Eisen, O., Chem. Techn. **29** (1977) 11, 622–624

[40] Lino, M., et al., J. chem. Engng. Japan **4** (1971) 1, 33–36

[41] Mair, B. J., Glasgow, A. R., and Rossini, F. D., J. Res. Nat. Bur. Standards **27** (1941), 39

[42] Mair, B. J., et al., Analyt. Chem. **30** (1958), 393–400

[43] Feldman, J., and Orchin, M., Amer. Pat. No. 2583554, of 9 Feb., 1950, issued 29 Jan., 1952

[44] Schubert, H., Chem. Techn. **21** (1969) 1, 28–34, 51

[45] Sheinker, Y. N., and Peresleni, Y. M., J. phys. Chem. (Russian) **26** (1952), 1103–1109

[46] Ruether, J. A., and Lu, B. C. Y., Canad. J. chem. Engng. **50** (1972) 2, 266–270

[47] Nutting, H. S., and Horsley, L. H., Ind. Engng. Chem., analyt. Edit. **19** (1947), 602–603

[48] Joffe, J., Ind. Engng. Chem. **47** (1955), 2533–2535

[49] Malesinski, W., Bull. Acad. polon. Sci., Cl. III 4 (1956), 371–379

[49a] Bril, Zh. A., Mozzhukin, A. S., Petlyuk, F. B., and Serafimov, L. A., teoret. osnovy khim. tekhnol. **9** (1975) 6, 811–821

[50] Kortüm, G., and Buchholz-Meisenheimer, H., Die Theorie der Destillation und Extraktion von Flüssigkeiten, Springer-Verlag, Berlin/Göttingen/Heidelberg 1952

[51] Horsley, L. H., Azeotropic Data, Vol. I and II, American Chemical Society, Washington 1952/1962; Advances in Chem., Series No. 6 and 35

[52] Ewell, R. H., Harrison, J. M., and Berg, L., Ind. Engng. Chem. **36** (1944), 871

[52a] Eduljee, G. H., and Tiwari, K. K., Chem. Engng. Sci. **31** (1976) 7, 535–540

[53] Marschner, R. F., and Cropper, W. P., Ind. Engng. Chem. **38** (1946), 262–268

[54] Horsley, L. H., Analytic. Chem. **19** (1947), 603

[55] Meissner, H. P., and Greenfeld, S. H., Ind. Chemist **40** (1948), 438–442

[56] Novikova, K. Y., and Natradse, A. G., Chem. Ind. (Russian) 2 (1958), 102–105

[56a] Marinichev, A. N. and Susarev, M. P., Zh. prikl. khim. **51** (1978) 10, 2221–2225

[57] Skolnik, H., Ind. Engng. Chem. **40** (1948), 442

[58] Nakanisi, K., Ichinose, S., and Skirai, H., Ind. Engng. Chem., Fundamentals 7 (1968) 3, 381–387

[58a] Brandani, V., Ind. Engng. Chem., Fundamentals **13** (1974) 2, 154–156

[58b] Martin, G. Q., Hydrocarbon Process. **54** (1975) 11, 241–246

[58c] Bril, Zh. A., Mozzhukhin, A. S., Petlyuk, F. B. and Serafimov, L. A., teoret. osnovy khim. tekhnol. **11** (1977) 6, 811–817

[58d] Timofeev, V. S., Babich, S. V., Tikhonova, N. K., Anton, N. D. and Serafimov, L. A., khim. prom. (1977) 9, 665–669

[59] Kuhn, W., Helv. chim. Acta **37** (1954), 1585–1605

[60] Szapiro, S., Przemysł. chem. **12** (35) (1956), 106–110

[61] Kortüm, G., and Bittel, A., Chemie-Ing.-Techn. 28 (1956), 40–44, 282–284

[61a] Hunsmann, W., Chemie-Ing.-Techn. **33** (1961) 8, 537–540

[61b] Hegener, B., Hesse, D., and Wolf, D., Chemie-Ing.-Techn. **45** (1973) 14, 942–945

[61c] Morozova, L. V., and Platonov, V. M., Theor. Found. chem. Engng. 8 (1974), 453–458

[62] Houdry Process Corp., Amer. Pat. No. 2776936 of 25 June, 1953, issued 8 Jan., 1957

[62a] Lehmann, P., Oehler, R., Hennig, R. and Ulbrecht, H., Chem. Techn. 30 (1978) 8, 403–406
Hennig, R., Ulbrecht, H. and Lehmann, P., Wiss. Z. d. TH Leuna-Merseburg 21 (1979) 2, 185–195

[63] Grewer, Th., Chemie-Ing.-Techn. **43** (1971), 655–658

[63a] Pavlov, S. Yu., Skorikova, V. V., and Borkova, S. B., Theor. Found. chem. Engng. **6** (1972) 3, 425–428

[64] Stage, H., Erdöl u. Kohle **3** (1950), 478–490

[65] Scheibel, E. G., Chem. Engng. Progr. **44** (1948), 927–931

[65a] Garber, Yu. N., and Mironenko, V. F., teoret. osnovy khim. tekhnol. 8 (1974) 6, 846–852

[66] Kogan, V. B., J. phys. Chem. (Russian) **29** (1953), 1470–1476

[67] Kafarov, V. V., and Gordiyevski, L. A., J. appl. Chem. (Russian) **29** (1956), *176–183*

[68] Kogan, V. B., Chem. Ind. (Russian) **6** (1957), 356–361

[69] Röck, H., Chemie-Ing.-Techn. **28** (1956), 489–495
Horsley, L. H., Analytic. Chem. **19** (1947), 508–600; 21 (1949), 831

[70] Porter, R. S., and Johnson, J. F., Ing. Engng. Chem. **52** (1960) 8, 691–694

[71] Hildebrand, Solubilities, 2nd Ed., New York 1936

[72] Brit. Pat. No. 613867, issued 2 Dec., 1948

[73] Amer. Pat. No. 2549586 of 7 Nov., 1945, issued 17 April, 1951
Griswold, J., et al., Ind. Engng. Chem. **38** (1946), 65–70

[74] Amer. Pat. No. 2610704 of 3 July, 1947, issued 16 Sep., 1952, Amer. Pat. No. 2588063 of 30 Sep., 1947, issued 4 March, 1952, Amer. Pat. No. 2371342 of 13 March, 1945, issued 13 March, 1945

[75] Garner, F. H., Ellis, S. R. M., and Granville, W. H., J. Inst. Petroleum **42** (1956), 148–154

[76] Null, H. W., and Palmer, D. A., Chem. Engng. Progr. **65** (1969) 9, 47

[77] Gelbin, D., Chem. Techn. **11** (1959), 70—73

[78] Nagel, O. and Sinn, R., Chemie-Ing.-Techn. **39** (1967) 5/6, 275—282

[79] Kortüm, G., and Faltusz, E., Chemie-Ing.-Techn. **33** (1961), 599—606

[80] Garwin, L., and Hutchinson, K. E., Ind. Engng. Chem. **42** (1950), 727—730

[81] Daubach, E., Final Examination Paper, Marburg 1948

[82] Jost, W., Chemie-Ing.-Techn. **23** (1951), 64

[83] Tursi, R. R., and Thompson, R., Chem. Engng. Progr. 47 (1951), 304—308

[84] Novella, E. C., and Tarasso, J. M., An. Real. Soc. espan. Fisica Quim., Ser. B 48 (1952), 441—448

[85] Schier, K. H., Thesis, Halle—Wittenberg 1959

[85a] Olefir, L. I., Knyshenko, M. I. and Priima, L. K., khim. prom. (1978) 2, 123—124

[86] Belck, L., Chemie-Ing.-Techn. **23** (1951), 90—91

[87] Bogart, M. J. P., and Brunjes, A. S., Chem. Engng. Progr. 44 (1948), 95

[88] Rieder, R. M., and Thompson, A. R., Ind. Engng. Chem. **42** (1950), 379

[89] Guyer, A., Guyer jr., A., and Karth Johnson, B., Helv. chim. Acta **38** (1955), 946—954

[90] Miró, A. R., de la Gándara, J. L. O., and Gonzáles, J. R. A., An. Real. Soc. espan. Fisica Quim., Ser. B **53** (1957), 171—184, 185—194

[91] Furter, W. F., Chem. Engng. (1968), June, CE 173-Ce 177

[91a] Furter, W. F., Canad. J. chem. Engng. **55** (1977) 3, 229—239

[92] Schreiber, E., Schüttau, E., Rant, D., and Schuberth, H., Z. physik. Chem. [Leipzig] **247** (1971) 1/2, 23—40

[92a] Schubert, H. and van Nhu, N., Z. phys. Chem., Leipzig, **258** (1977) 1, 106—112

[93] Fuchs, O., and Roth, F. H., Chem. Fabrik **11** (1938), 401—406

[94] Ino, M., et al., J. chem. Engng. Japan 4 (1971) 1, 22—26

[94a] Saraev, B. A., Pavlov, A. Yu., Bolkhova, L. A. et al., Khim. prom. (1975) 11, 815—819

[95] Jaques, D., and Furter, W. F., Canad. J. chem. Engng. **50** (1972) 4, 502—505

[96] Furter, W. F., and Meranda, D., GVC/AI Che-J., Joint Meet. 2 (1974) D 1—3, 1—10

[97] Sada, E., Kito, Sh., Yamaji, H., and Kimura, M., J. appl. Chem. Biotechnol. **24** (1974) 4/5, 229—238

Chapter 7 — Constructional Materials and Apparatus

[1] Liedel, K. H., Glas in der Chemie — Laborgeräte, Großapparate, Rohrleitungen. Otto Krausskopf-Verlag GmbH, Mainz 1973

[2] Mönch, G. Ch., Hochvakuumtechnik, Rudolf A. Lang Verlag, Pößneck 1950

[3] Eitel, W., et al., Glastechnische Tabellen, Springer-Verlag, Berlin 1932

[4] VVB Westglas, Ilmenau, Technik 8 (1953), 675—680

[5] Rieger, H., Silikattechnik 4 (1953), 339—342; Chem. Techn. **22** (1970) 1, 36—40

[6] Pomeroy, H. H., Analytic. Chem. **24** (1952), 1076

[7] Kammel, H., Silikattechnik 2 (1951), 227—231

[8] Krell, E., Chem. Techn. 4 (1952), 200—207

[9] Catalogues of Glassware Manufacturers
Friedrichs, F., Das Glas im chemischen Laboratorium, 3rd Ed., Springer-Verlag, Berlin/Göttingen/Heidelberg 1960
Telle, W., ABC der Laboratoriumsgeräte, VEB Fachbuchverlag Leipzig 1953
Telle, W., Chemische Laboratoriumsgeräte, 2nd Ed., VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1969

[10] Stage, H., Erdöl u. Kohle **3** (1950), 377—383

[11] Krell, E., Chem. Techn. 4 (1952), 443—450

[12] Kinza, V., Registered design (GDR), No. 10175

[13] Wolf, F. W. D., Glas-Instrumenten-Techn. 4 (1960), 43—52, 126—131, 343—349

[14] Heckmann, C. J., Chem. Techn. **24** (1972) 9, 533—536; **25** (1973) 1, 20—23

[14a] Reichelt, W., Chemie-Ing.-Techn. **45** (1973) 1, 25—29

[14b] Handl, R., Chem.-Ing.-Techn. **50** (1978) 1, 45

[15] Malewski, W., Chemie-Ing.-Techn. **42** (1970) 6, 385–390

[16] Sigwart, K., Destillation und Rektifikation, in: Ullmanns Encyklopädie der technischen Chemie, Vol. 1, Urban & Schwarzenberg, München/Berlin 1951

[17] Ray, J. D., Rev. sci. **28** (1957), 200–201

[18] Carney, Th. P., Laboratory Fractional Distillation, MacMillan, New York 1949

[19] Thormann, K., Dechema-Erfahrungsaustausch, Arbeitsmethoden und Geräte, Destillieren und Rektifizieren, Dechema, Frankfurt/Main, Sep. 1950

[20] Fenske, M. R., Amer. Pat. No. 2037316 of 4 April, 1936

[21] Rose, A. and E., et al., Technique of Organic Chemistry, Vol. IV, Interscience Publishers, New York 1951

[22] Kuhn, W., Chemie-Ing.-Techn. **25** (1953), 12–18
Kuhn, W., et al., Chimia [Zurich] **8** (1954), 109–122

[23] Craig, L. C., Ind. Engng. Chem., analytic. Edit. **8** (1936), 219; **9** (1937), 441

[24] Kuhn, W., Helv. chim. Acta **25** (1942), 252–295

[25] Kuhn, W., and Ryffel, K., Helv. chim. Acta **26** (1943), 1693 to 1721
Jost, W., Angew. Chem., Part B **20** (1948), 231
Coenen, A., Thesis, T. H. Aachen 1941
Mair, B. J., and Willingham, Ch. B., J. Res. Nat. Bur. Standards **22** (1937), 519–527

[26] Westhaver, C. J., Ind. Engng. Chem. **34** (1942), 126

[27] Donnell, C. K., and Kennedy, R. M., Ind. Engng. Chem. **42** (1950), 2327–2332

[28] Jantzen, E., and Wieckhorst, O., Chemie-Ing.-Techn. **26** (1954), 392–396

[29] Koch, R., and Feind, K., Chemie-Ing.-Techn. **30** (1958), 577–584

[30] Beck, F., Chemie-Ing.-Techn. **35** (1963), 837–844

[31] Fischer, W. G., Glas-Instrumenten-Techn. **13** (1969) 5, 535–540; **14** (1970) 8, 933–936; **15** (1971) 7, 753–759; **15** (1971) 8, 832–838
Chemiker-Ztg. **94** (1970) 5, 157–161
Fette, Seifen, Anstrichmittel **72** (1970), 444–454
Fette, Seifen, Anstrichmittel **75** (1973), 131–133
Chemie-Labor Betrieb **27** (1976) 2, 42–46

[32] Macura, H., and Grosse-Oetringhaus, H., Brennstoff-Chem. **19** (1938), 437–439

[33] Manning. R. E., and Cannon, M. R., Ind. Engng. Chem. **49** (1957), 346–349

[34] Hoppe, K., and Mittelstrass, M., Grundlagen der Dimensionierung von Kolonnenböden (Technische Fortschrittsberichte, Vol. 61), Verlag Theodor Steinkopff, Dresden 1967

[35] Stage, H., Glas-Instrumenten-Techn. **13** (1969) 12, 1285–1299
Stage, H., Chemieanlagen und -verfahren (1970), No. 1/2

[35a] Hutla, V., and Strnal, M., Chem. Techn. **28** (1976), 545–547

[36] Keesom, W. H., et al., Physica **1** (1934), 1109–1114

[37] Bruun, J. G., and Schicktanz, S. T., J. Res. Nat. Bur. Standards **7** (1931), 851–882

[38] Stage, F., Angew. Chem., Part B **19** (1947), 182

[39] Stage , H., DBP No. 862598 of 4 July, 1950, granted 20 Nov., 1952
Kirschbaum, E., Chemie-Ing.-Techn. **25** (1953), 73–80

[40] Fritz, P. W., Glas-Instrumenten-Techn. **11** (1967) 3, 161–162; Registered design (FRG) No. 1957085

[41] Oldershaw, C. F., Ind. Engng. Chem., analytic. Edit. **13** (1941), 265–268

[42] Hilberath, F., Oel u. Kohle **39/40** (1943), 875–880

[43] Wijk, W. R. van, and Thissen, H. A. C., Chem. Engng. Sci. **3** (1954), 153–160

[44] Umholtz, C. L., and Winkle, M. van, Petroleum Refiner **34** (1955), 114–117

[45] Jones, P. D., and Winkle, M. van, Ind. Engng. Chem. **49** (1957), 232–238

[46] Developed in the Research Laboratory of Messrs. C. F. Bram and Co.; Manufacturer: Messrs. Emil Greiner and Co.

[47] McGure, G. V., and Maddox, R. N., Ind. Engng. Chem. Proc. **6** (1971) 1, 9

[48] Wagner, C. D., Lukens jr., H. R., and Hughes, R. R., Nucleonics **14** (1956), 78–83

[49] Newitt, D. M., Dombrowski, N., and Knelman, F. H., Trans Instn. Chem. Engr. **32** (1954), 244–261

[50] Melikyan, R. A., J. appl. Chem. (Russian) **31** (1958), 550–558

[51] Widmer, G., Helv. chim. Acta **7** (1924), 194–196
[52] Golodets, A., Chem. Ind. (Russian) **35** (1912), 102–108, 141–145
[53] Lecky, H. S., and Ewell, R. H., Ind. Engng. Chem., analyt. Edit. **14** (1942), 503–547
[54] Stallcup, W. D., et al., Ind. Engng. Chem., analyt. Edit. **14** (1942), 503–547
[55] Bower jr., J. R., and Cooke, L. M., Ind. Engng. Chem. **15** (1943), 290–293
[56] Podbielniak, W. J., Ind. Engng. Chem. **13** (1941), 639–645
[57] Brezina, V., Glas- Instrumenten-Techn. **14** (1970) 5, 493–494
[58] Stedman, D. F., Trans. Amer. Inst. chem. Engr. **33** (1937), 153–161
[59] Koch, H., and Raay, H. van, Chemie-Ing.-Techn. **8** (1950), 172
[60] Bragg, L. B., Ind. Engng. Chem. **45** (1953), 1676
[61] DRP, according to prospectus from Messrs. Ernst Haage, Mülheim/Ruhr
[62] Ellis, S. R. M., and Varjavandi, J., Chem. Process Engng. **39** (1958), 239
[63] Juchheim, G., Glas-Instrumenten-Techn. **10** (1966) 10, 914–917
[64] Sperandio, A., Richard, M., and Huber, M., Chemie-Ing.-Techn. **37** (1965) 3, 322–328
Zogg, M., Chemie-Ing.-Techn. **45** (1973) 2, 67
[64a] Sulzer techn. Rdsch. **59** (1977) 3, 138
[64b] Bonio, P., Chem.-Ing.-Techn. **49** (1977) 11, 895–897
Meier, W., Hunkeler, R. and Stöcker, W.-D., Chem.-Ing.-Techn. **51** (1979) 2, 119–122
[64c] Meier, W., Sulzer techn. Rdsch. **61** (1979) 2, 49–61
[65] Timofeev, A. V., and Aerov, M. E., Chem. Ind. (Russian) 5 (1965), 381–383
[65a] Kwasniak, J., Verfahrenstechnik 8 (1974) 11, 315–318
[65b] Endřst, M., Cervenka, J., and Kólar, V., Coll. Czech. chem. Com. **41** (1976) 9, 2676–2681
[65c] Timofeev, A. V., Aerov, M. E., and Gursky, M. M., khim. prom. (1977) 2, 140–142
[66] Shavoronkov, N. M., and Malyusov, V. A., Chem. Techn. **24** (1972) 7, 397–401
[66a] Billet, R., Maćkowiak, J. and Suder, St., Chem.-Ing.-Techn. **50** (1978) 7, 550–551
[67] Zuiderweg, F. I., Chem. Engng. Sci. **1** (1952), 164–174, 184–194
[68] Podbielniak, W. J., DRP No. 595250 Kl. 12a of 18 Aug., 1931, granted 6 April, 1934.
[69] Benner, F. C., Dinardo, A., and Tobin, D. J., Ind. Engng. Chem. **43** (1951), 722–727
[70] Byron, E. S., Bowman, J. R., and Coull, J., Ind. Engng. Chem. **43** (1951), 1002–1010
[71] Willingham, C. B., Sedlak, V. A., Rossini, F. D., and Esthaver, J. W., Ind. Engng. Chem., ind. Edit. **39** (1947), 706–712
[72] Jost, W., Chemie-Ing.-Techn. **25** (1953), 356
Jost, W., Rektifikation unter extremen Bedingungen, in: Dechema-Monogr. **22** (1954), 30–72
[73] Jost, W., Sieg, L., and Brandt, H., Chemie-Ing.-Techn. **25** (1953), 291–292
[74] Gelperin, N. Y., and Khatsenko, M. S., J. appl. Chem. (Russian) **25** (1952), 610–615
[75] Murray, K. E., J. Amer. chem. Soc. **28** (1951), 235
[76] Irlin, A. L., and Bruns, B. P., J. analyt. Chem. (Russian) **5** (1950), 44–47
[77] Höher, G., Untersuchungen über die Trennfähigkeit einer Labor-Rektifikationskolonne mit rotierender Wendel als Austauschfläche, Examination paper, Ingenieurschule für Chemie, Leipzig 1958
[78] Neumann, F., Chemie-Ing.-Techn. **33** (1961) 7, 485–491
[78a] Mamin, V. N., et al., khim.-farm. Zh. 8 (1974) 3, 51–55
[79] Toeldte, W., Seifen-Öle-Fette-Wachse **74** (1948), 126
[80] N. N., Glas-Instrumenten-Techn. **10** (1966) 4, 259–260
[81] Kramer, M. T., Glas-Instrumenten-Techn. **15** (1971) 8, 856–860
[82] Brezina, V., Glas-Instrumenten-Techn. **10** (1966) 3, 162–172
[83] Friedrichs, F., Z. angew. Chem. **33** (1920), 29–32
[84] Friedrichs, J., and v. Kruska, H., Chem. Fabrik **7** (1934), 284–287
[85] Mach, F., and Herrmann, R., Chem. Fabrik **6** (1933), 211–213
[86] Eichhorn, E., Untersuchung der Wirkung von Laboratoriumskühlern, Examination paper, Ilmenau 1955
[87] Gemmeker, L., and Stage, H., Glas-Instrumenten-Techn. **6** (1962) 3, 69–78; 4, 114–119; 5, 169–174; 6, 206–208; 9, 327–328; 10, 372–376; 12, 494–497
[88] Krell, E., Chem. Techn. **5** (1953), 581–587

[89] Schneider, K. W., and Schmid, Ch., Erdöl u. Kohle **2** (1949), 508—510

[89a] Kloss, H.-J., CZ-Chem.-Techn. **3** (1974), 89—93

[90] Kramer, M. T., Glas-Instrumenten-Techn. **16** (1972) 4, 445—448; 5, 571—574; 8, 943—946

[91] Prospectus from Normag, Hofheim/Ts., List No. 10; Chemie-Ing.-Techn. **26** (1954) 231

[92] Schulz, E. O., Glasinstrumentenkunde, Wagner u. Sohn, Weimar 1937

[93] Hübner, G., Chemiker-Ztg. **83** (1959), 581—583

[94] Lloyd, L. E., and Hornbacher, H. G., Analytic. Chem. **19** (1947), 120—122

[95] Collins, F. C., and Lantz, V., Ind. Engng. Chem., analyt. Edit. **18** (1946), 673—677

[96] Kieselbach, K., Analytic. Chem. **19** (1947), 815

[97] Stage, H., and Gemmeker, L., Glas-Instrumenten-Techn. **6** (1962) 12, 494—497

[98] N. N., Glas-Instrumenten-Techn. **10** (1966) 3, 178—179

[99] Stage, H., and Gemmeker, L., Glas-Instrumenten-Techn. **7** (1963) 11, 608—614; 12, 687—704; **8** (1964) 6, 413—428; 7, 503—508

[100] Manufacturer: Glaswerk Schott und Gen., Mainz

[101] Rock, E. J., and Jantz, G. F., Analytic. Chem. **22** (1950). 626

[102] Grassmann, W., and Deffner, C., Chemiker-Ztg. **76** (1952), 623

[103] Schram, E., Analytic. Chem. **25** (1953), 1424

[104] Stage, H., and Gemmeker, L., Glas-Instrumenten-Techn. **7** (1963) 11, 608—614; 12, 687—704; **8** (1964) 6, 413—428; 7, 503—508
Stage, H., Glas-Instrumenten-Techn. **14** (1970) 3, 213—220; 4, 337—349

[105] Hübner, G., Chemiker-Ztg. **76** (1952), 67

[106] Manufacturer: Edmund Bühler, Tübingen

[107] Manufacturer: Dr. Hofmann and Roth, Stuttgart-Hedelfingen; cf. also Krell, E., Chem. Techn. **7** (1955), 599—608

[108] Manufacturer: W. C. Heraeus GmbH, Hanau

[109] Borchert, R., and Jubitz, W., Infrarotstrahler zur Erwärmung, Trocknung und Aushärtung, VEB Verlag Technik. Berlin 1951

[110] Klees, K. F., Chem. Rdsch. [Solothurn] **7** (1954), 358—359

[111] Schulze, H., Chemie-Ing.-Techn. **23** (1951), 565—569

[112] Weber, U. von, Chem. Techn. **1** (1949), 159—160

[113] Zampachova, L., Chem. průmysl. (Czech) **7/32** (1957), 408—413

[114] Kolling, H., and Tramm, H., Chemie-Ing.-Techn. **21** (1949), 9—14

[115] Manufacturer: Bronwill Scientific Ind., New York

[116] Kortüm, G., and Bittel, A., Chemie-Ing.-Techn. **28** (1952), 40—44

[117] Rose, A. and E., et al., Technique of Organic Chemistry, Vol. IV, Interscience Publishers, New York 1951

[118] Manufacturer: W. C. Heraeus GmbH, Hanau, Electrothermal Engineering Ltd., London, and VEB Asbestdraht, Berlin

[118a] Sellin, J., chemie-anlagen + verfahren **4** (1975), 87—91; see also [66a]

[119] Exclusive right of sale for "Calorex": Heraeus-Wittmann GmbH, Heidelberg

[120] Leva, M., Tower Packings and Packed Tower Design, 2nd Ed., The United States Stoneware Company, Akron/Ohio 1953

[121] Kerényi, E., and Schultheiß, I., Proc. and Conf. on Appl. Phys. Chem., Veszprém, Aug. 2—5, 1971, Akademiai Kiado, Budapest 1971, Vol. 2, pp. 67—74

[121a] Reichelt, W., Chemie-Ing.-Techn. **45** (1973), 2, 53—57

[122] Manufacturer: Podbielniak Inc., Chicago 11

[123] Braun, R., Chemie-Ing.-Techn. **33** (1961), 350—352

[124] Dixon, O. G., J. Soc. chem. Ind. **68** (1949), 88, 119, 299

[125] Huber, M., and Sperandio, A., Chemie-Ing.-Techn. **36** (1964) 3, 221—227

[125a] Zelvenskii, Ya. D., Kovalenko, A. E., Mukhina, T. V., and Panfilov, V. I., khim. prom. (1977) 10, 783—786

[126] Ellis, S. R. M., and Varjavandi, J., Chem. Process Engng. **7** (1958), 239—243

[127] Unpublished measuring results of the Institut für Apparatebau und Verfahrenstechnik, TH Karlsruhe (personal communication)

[128] MacMahon, H. O., Ind. Engng. Chem., ind. Edit. **39** (1947), 712–718

[129] Manufacturer: The United States Stoneware Company, Akron/Ohio

[130] Manufacturer: Hydronil Ltd., Chemical Plant Division, Fenton/England

[131] Kirschbaum, E., Z. Ver. Dtsch. Ing. **98** (1956), 1801–1802
Alt, C., Meier, A., and Richter, G., Chemie-Ing.-Techn. **27** (1955), 502–506

[132] Manufacturer: Vereinigte Füllkörperfabrik GmbH u. Co., Baumbach/Westerwald

[133] Fuchs, O., Chemie-Ing.-Techn. **23** (1951), 537–540

[134] Forsythe, W. L., et al., Ind. Engng. Chem. **39** (1947), 714

[135] Wolf, F., and Günther, W., Dechema-Monogr. **29** (1957), 364–377

[136] Krell, E., Chem. Techn. **16** (1964) 10, 591–600

[137] Krell, E., Plaste und Kautschuk **14** (1976) 4, 251–254

[138] Teller, A. J., Chem. Engng. Progr. **50** (1954) 2, 65–71; Ind. Engng. Chem. **50** (1958) 8, 1201–1206

[139] N. N., Chem. Engng. **80** (1973) 19, 88

[140] Egberongbe, S. A., Process Engng. (1973) 2, 82–83, 85

[141] Stürmann, H., Leistungssteigerung von Füllkörperkolonnen durch neue Wandformen. Thesis, Hamburg 1937

[142] Krell, E., Patent (GDR) No. 63761. Kl. 12a5, granted 20 Sep., 1968, "Column with reduced wall flow"

[143] Laukner, E., Wichmann, H., and Stäbler, U., Chem. Techn. **28** (1976) 12, 718–721

[144] Ponter, A. B., Shaver, C., and Trauffler, P., Chemie-Ing.-Techn. **48** (1976) 7, 635–636

[145] Ponter, A. B., Taymour, N., and Dankyi, S. O., Chemie-Ing.-Techn. **48** (1976) 7, 635–638

Chapter 8 — Automatic Devices; Measuring and Control Equipment

[1] Rolfson, F. B., et al., Analytic. Chem. **20** (1948), 1014–1019

[2] Bayerl, V., and Quarg, M., *Taschenbuch des Chemietechnologen*, 3rd Ed., VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1968

[3] Kanterman, L. B., et al., Chem. Technol. Brennstoffe Öle (Russian) **3** (1958), 57–60

[4] Salzer, F., Chemie-Ing.-Techn. **31** (1959), 405–409

[5] Jirmann, R., Glas-Instrumenten-Techn. **14** (1970) 1, 11–12

[6] Stage, H., CZ-Chemie-Techn. **1** (1972), 263–272

[7] Zappe, D., Heckmann, M., Gutwasser, H., and Dornbusch, E., Heckmann-Mitt. No. 5 (1968)

[8] Ulusoy, E., Chemiker-Ztg. **79** (1955), 46–48

[9] Stage, H., Gemmeker, L., Fischer, G., and Richter, R., Glas-Instrumenten-Techn. **5** (1961), 138–145 and 204–211

[10] Fischer, W. G., and Weyand, H., Glas-Instrumenten-Techn. **14** (1970) 1, 23–26

[11] Krell, E., Chem. Techn. **9** (1957), 266–274

[12] Kortüm, G., and Bittel, A., Chemie-Ing.-Techn. **28** (1956), 40–44

[12a] Koukol, H., Kupka, H. J., and Henning, G., GIT Fachz. Lab. **19** (1975), Special Number Labormedizin, 493–497

[13] Brandt, H., and Röck, H., Chemie-Ing.-Techn. **25** (1953), 511–514
Brandt, H., Röck, H., and Langers, F., Chemie-Ing.-Techn. **29** (1957), 86–91

[14] Abegg, H., Chimia [Zurich] **6** (1952), 258–267

[15] Laporte, H., Messung, Erzeugung und Konstanthaltung hoher bis tiefer Temperaturen. VEB Fachbuchverlag Leipzig 1961

[16] Kössler, I., and Vodehnal, J., Chem. Průmysl. (Czech) **7** (32) (1957), 292–297

[17] Kadlec, M., Chem. Listy (Czech) **51** (1957), 987–990

[17a] Stage, H., CZ-Chemie-Technik **5** (1973), 203–208

[17b] Mitteilung der Fischer Labortechnik in GIT Fachz. Lab. **21** (1977) 4, 392

[18] Vanvor, H., Glas-Instrumenten-Techn. **8** (1964), 415

[19] Telle, W., Chemische Laboratoriumsgeräte, 2nd Ed., VEB Fachbuchverlag Leipzig 1969

[20] Piatti, L., and Marti, W., Chemie-Ing.-Techn. **28** (1956), 473—475

[21] Manufacturer: Siemens AG, Erlangen — Dr. Neumann GmbH, München 80

[22] Löffler, H. J., and Henrici, H., Chemie-Ing.-Techn. **30** (1958), 718
Soble, A. B., Chem. Engng. Progr. **56** (1957), 444—451

[23] Manufacturer: VEB Thermometerwerk, Geraberg

[24] Manufacturer: Juchheim KG, Solingen

[25] Kleinteich, R., Glas-Instrumenten-Techn. **3** (1959), 89—93

[26] Walter, M., Relaisbuch, Franck'sche Verlagshandlung, Stuttgart 1951

[27] Fischer, W., Glas-Instrumenten-Techn. **14** (1970) 5, 513—516

[28] Thormann, K., Dechema-Erfahrungsaustausch, Arbeitsmethoden und Geräte, Destillieren und Rektifizieren, Dechema, Frankfurt/Main, Sep. 1950

[29] Hutla, V., Chem. Listy (Czech) **51** (1957), 1964—1965

[30] Jaeckel, R., Dechema-Erfahrungsaustausch, Vakuumtechnik, Dechema, Frankfurt/Main 1956

[31] Leck, J. H., Pressure Measurement in Vacuum Systems, The Institute of Physics, London 1957

[32] Nickel, E., Gas- und Wasserfach, Beilage Bau und Betrieb **6** (1954), No. 5 (Edit. Gas)

[33] Farquarson, J., and Kermicle, H. A., Rev. sci. Instr. **28** (1957), 324—325

[34] Dosch, R., Glas-Instrumenten-Techn. **4** (1960), 9—17

[35] Holland-Merten, E. L., Tabellenbuch der Vakuumverfahrenstechnik in der Grundstoffindustrie, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1964

[36] Hohlschütter, H. W., and Kämpf, G., Angew. Chem. **66** (1956), 355

[36a] Manufacturer: Airflor-Lufttechnik GmbH. Rheinbach

[37] Crompton, R. W., and Elford, M. T., J. sci. Instr. **34** (1957), 405—407

[38] Störzbach, W., Glas-Instrumenten-Techn. **14** (1970) 1, 36—37

[39] Krell, E., Chem. Techn. **3** (1951), 333—336

[40] Gilmont, R., Ind. Engng. Chem., analyt. Edit. **18** (1946), 633—636

[41] Manufacturer: Dr. Friedrichs—Dr. Matschke KG Normschliff-Glasgeräte, Wertheim/Main

[42] Young, C. G., et al., Canad. J. Technol. **29** (1951), 447—450

[43] Krell, E., Chem. Techn. **10** (1958), 327

[44] Coulson, E. A., and Warne, R. J., J. sci. Instr. **21** (1944), 122—123

[45] Mönch, G. C., Hochvakuumtechnik, Rudolf A. Lang Verlag, Pößneck 1950; Neues und Bewährtes aus der Hochvakuumtechnik, VEB Wilhelm Knapp Verlag, Halle 1959

[46] Hoch, H., Vakuum-Techn. **16** (1966) 1/2, 8—13

[47] Steckelmacher, W., J. sci. Instr. **1** (1951), 10—19

[48] Gaede, W., Z. techn. Physik **15** (1934), 664

[49] Jaeckel, R., Kleinste Drücke, ihre Messung und Erzeugung, in: Technische Physik in Einzeldarstellungen, Springer-Verlag, Berlin/Göttingen/Heidelberg 1950
Laporte, H., Hochvakuum, seine Erzeugung, Messung und Anwendung im Laboratorium, VEB Wilhelm Knapp Verlag, Halle 1951; Vakuummessungen, VEB Verlag Technik, Berlin 1955
Yarwood, J., Hochvakuumtechnik, Rudolf A. Lang Verlag, Berlin 1955
Leybold, Vakuum-Taschenbuch, ed. by K. Diels and R. Jaeckel, 2nd Ed., Springer-Verlag, Berlin/Göttingen/Heidelberg 1962
Frank, W., and Kutsche, D., Die schonende Destillation, Otto Krausskopf-Verlag GmbH, Mainz 1969

[50] Müller, B., Glas-Instrumenten-Techn. **14** (1970) 7, 798—807

[51] Ebert, H., Kompressionsvakuummeter, Friedr. Vieweg + Sohn GmbH, Braunschweig 1951

[52] Peche, G., Glas-Instrumenten-Techn. **7** (1963) 1, 4—7, 48—49

[53] Manufacturer: Rudolf Brand, Wertheim/M., Glashütte

[54] Nisbet, J. S., J. sci. Instr. **26** (1949), 271—273

[55] Melpolder, F. W., Ind. Engng. Chem. **39** (1957), 617

[56] Fischer, H. E., Analytic. Chem. **20** (1948), 982

[57] Gemmeker, L., and Stage, H., Glas-Instrumenten-Techn. **6** (1962) 12, 494–497; **7** (1963) 1, 18–23

[58] Stage, H., Chemie-Ing.-Techn. **22** (1950), 374–375
Stage, H., GIT Fachz. Lab. **19** (1975) 3, 182

[58a] Fieberg, D., CAV (1977) **3**, 64–65

[59] Houben-Weyl, Methoden der organischen Chemie, ed. by E. Müller, Physikalische Methoden, Part 1 and 2, Georg Thieme Verlag, Stuttgart 1955

[60] Müller, R. H., and Zenchelsky, S. T., Analytic. Chem. **24** (1952), 844–847

[61] Thomas, G. R., et al., Analytic. Chem. **22** (1950), 1221–1223

[62] Latchum, J. W., Amer. Pat. No. 2529030 of 7 Nov., 1950

[63] Nebe, W., Riegler, H., and Menzel, W., Jenaer Rundschau 18 (1973), Special Issue, 87–89

[64] Kegeles, G., and Sober, H. A., Analytic. Chem. **24** (1952), 654–660

[65] Oehme, F., Chemische Analyse durch Messung von Dielektrizitäts-Konstanten, Verlag VEB Laborchemie, Apolda 1953
Oehme, F., Dielektrische Meßmethoden, 2nd Ed., Verlag Chemie GmbH, Weinheim/Bergstr. 1962

[66] Slevogt, K. E., Dechema-Monogr. **14** (1950), 97–120; 17 (1951), 95–107

[67] Grant, R. A., J. appl. Chem. 8 (1958), 136; Chemie-Ing.-Techn. 30 (1958), 738

[68] Felloni, L., and Tantillo, E., Ann. Chimica **47** (1957), 751–758

[68a] Lertes, E., and Niel, F., GIT Fachz. Lab. **23** (1979) 5, 376

[69] Clasen, H., Chemie-Ing.-Techn. **28** (1956), 45–48; **29** (1957), 110–111

[70] Linford, A., Ind. Chemist. **34** (1958) 403, 481–488

[71] Fritzsche, R. W., Petroleum Processing **7** (1952), 1138–1143

[72] Koch, O., Chemie-Ing.-Techn. **30** (1958), 181–187
Kienitz, H., Chemie-Ing.-Techn. **32** (1960) 10, 641–650

[73] Siggia, S., Continuous Analysis of Chemical Process Systems, John Wiley & Sons, London 1959

[74] Chemie-Ing.-Techn. **36** (1964) 9A, 1455–1457

[75] Herforth, L., and Koch, H., Praktikum der angewandten Radioaktivität, 2nd Ed., VEB Deutscher Verlag der Wissenschaften, Berlin 1972

[75a] Zelvenskij, Ya. D., Malinov, S. A., and Shalyzin, V. A., teoret. osnovy khim. tekhnol. **10** (1976) 2, 184–189

[76] Bernhauer, K., Einführung in die organisch-chemische Laboratoriumstechnik. Springer-Verlag, Vienna 1947

[77] Wittenberger, W., Chemische Laboratoriumstechnik, 6th Ed., Springer-Verlag, Berlin/Göttingen/Heidelberg 1963

[78] Müller, G., and Gnauck, G., Reinste Gase, VEB Deutscher Verlag der Wissenschaften, Berlin 1965

[79] Hinzpeter, G., Vakuum-Techn. **11** (1962), 2

[80] Manufacturer: Fischer, Labor- u. Verfahrenstechnik, Bonn—Bad Godesberg
Schulze, F.-W., Hammerschmidt, H., and Cammenga, H.-K., GIT Fachz. Lab. **21** (1977) 12, 1033

[81] Dammer, H. J., Glas-Instrumenten-Techn. **15** (1971) 2, 115–116

[82] Hänel, R., Chem. Techn. **15** (1963) 3, 176–177

[83] Pinkava, J., and Wichterle, O., Collect. Czechoslov. chem. Commun. **20** (1955), 697–707
Pinkava, J., and Kaláb, V., Collect. Czechoslov. chem. Commun. **20** (1955), 707–712

[84] Pinkava, J., Laboratory technique of continuous chemical processes (Czech). Nakladatelství technické Literatury (SNTL), Prague 1958

[85] Schmidt, W., Chem. Techn. **10** (1958), 131–134

[86] Heusch, R., Fette, Seifen, Anstrichmittel **72** (1970) 11, 969–977

[86a] Engler, J., and Kühnlenz, H., Chem. Techn. **31** (1979) 5, 251–254

[87] Pohlenz, W., Pumpen für Flüssigkeiten, VEB Verlag Technik, Berlin 1970
[88] Liedel, K. H., Glas in der Chemie — Laborgeräte, Großapparate, Rohrleitungen, Otto Krausskopf-Verlag GmbH, Mainz 1973

Chapter 9 — Arrangement of a Distillation Laboratory; Starting Up Distillation Apparatus

[1] Behre, A., Chemisch-physikalische Laboratorien und ihre neuzeitlichen Einrichtungen, Akademische Verlagsgesellschaft Geest & Portig, Leipzig 1950
[2] Colemann, H. S., et al., Laboratory Design, Reinhold, New York 1952
[3] Schramm, W., Chemische und biologische Laboratorien, 3rd Ed. Verlag Chemie GmbH, Weinheim/Bergstr. 1969
[4] Kincannon, C. B., and Baker, M. O., Analytic. Chem. **29** (1957), 1189—1193
[5] Schwarz, H., Stative, Aufhängung von Apparaturen, in: Houben-Weyl, Methoden der organischen Chemie (ed. by E. Müller), Vol. I/1, Georg Thieme Verlag, Stuttgart 1958
[6] Manufacturer: Ernst Haage, Mülheim/Ruhr
[7] Manufacturer: Geru, Geroldwill, Switzerland
[8] Brooke, M., J. chem. Educat. **28** (1951), 602—603
[9] Wagner, G., Österr. Chemiker-Ztg. **43** (1940), 229
[10] Bernhauer, K., Einführung in die organisch-chemische Laboratoriumstechnik, Springer-Verlag, Vienna 1947
[11] Wittenberger, W., Chemische Laboratoriumstechnik, 7th Ed., Springer-Verlag, Berlin/Heidelberg/New York 1973
[12] Wolf, F. W. D., Glas-Instrumenten-Techn. **4** (1960), 34—52, 126—131
[13] Friedrichs, F., Das Glas im chemischen Laboratorium, 3rd Ed., Springer-Verlag, Berlin/Göttingen/Heidelberg 1960
[14] Brauer, H., Chemie-Ing.-Techn. **29** (1957), 520—530
[15] Greinacher, H., Ausgewählte Aufgaben und Probleme aus der Experimentalphysik (§ 28: Der Siedeverzug), Springer-Verlag, Vienna 1953
[16] Amer. Pat. No. 2580880, issued 1 Jan., 1952; No. 2580922, issued 1 Jan., 1952
[17] Hübner, G., Chemiker-Ztg. **75** (1951), 229—230
[18] The General Safety Committee of the Manufacturing Chemists' Association, Guide for Safety in the Chemical Laboratory, Van Nostrand, New York 1954
[19] Dittmar, P., Erdöl u. Kohle **11** (1958), 25—30
[20] Craig, L. E., and Dew, J. E., Ind. Engng. Chem. **51** (1959), 1249—1252
[21] Kulbe, B., Hoppe, K., Kunze, R., and Noack, J., Chem. Techn. **29** (1977) 11, 600—603

Subject index