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EXPERIMENTAL TECHNIQUES IN LOW-TEMPERATURE PHYSICS

BY
GUY K. WHITE

THIRD EDITION

prefer the texts of E. F. Burton, H. Grayson Smith, and J. O. Wilhelm (*Phenomena at the temperature of liquid helium*, Reinhold, 1940), L. C. Jackson (*Low temperature physics*, Methuen, 2nd edn, 1948), or C. F. Squire (*Low temperature physics*, McGraw-Hill, 1953).

I would like to acknowledge my debt of gratitude to the late Sir Francis Simon for his kindness and patience when I started the study of low-temperature physics; he asked me, as one of his students, to design and build a Linde helium liquefier. I hope this book is rather more successful than my first effort at solving the problems of helium liquefaction.

In preparing this book I have been helped considerably by various friends who have read and criticized individual chapters: these include my colleagues Drs. T. H. K. Barron, J. S. Dugdale, D. K. C. MacDonald, F. D. Manchester, and S. B. Woods of the Division of Pure Physics (National Research Council), Dr. J. A. Morrison of the Division of Pure Chemistry (National Research Council), Dr. H. Preston-Thomas of the Division of Applied Physics (National Research Council), and Dr. R. P. Hudson of the National Bureau of Standards in Washington.

As will appear throughout the text many publishers and learned societies have kindly granted permission for the reproduction of figures which originally appeared in their books and periodicals. The facilities and the co-operation of such sections of the National Research Council as the Central Drafting Office, Duplication, and the Typing Pool have been of great assistance.

Finally, I am happy to thank Dr. M. T. Elford for his help in the proof-reading of this book.

G. K. W.

Ottawa, Canada July 1957

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CHAPTER I

PRODUCTION OF LOW TEMPERATURES

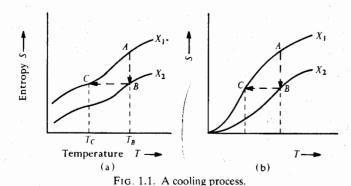
1. Isentropic cooling

Introduction

SINCE the entropy or degree of disorder of a system at constant volume or constant pressure is a monotonically increasing function of temperature, any process of cooling may be regarded as one of ordering or entropy reduction. In the words of Simon, a refrigerator is a form of 'entropy-squeezer'. This 'squeezing' is possible since entropy S is a function of other variable parameters as well as temperature, e.g. S = S(T, X) where the parameter X is a physical property of the system which can be varied within limits so as to change the entropy.

Figure 1.1a shows that when X is altered isothermally from X_1 to X_2 the entropy is reduced. By further varying X from X_2 to X_1 under isentropic conditions, a lowering in temperature from a temperature T_B to temperature T_C is achieved; an isentropic change is adiabatic since $\Delta S = \int dQ/T$. The process is a reversible one and therefore by the second law of thermodynamics is the most efficient means of cooling, in terms of the external work required. From Fig. 1.1a it would seem possible, in principle at least, to cool the system to the absolute zero of temperature by a limited number of such steps as $A \rightarrow B \rightarrow C$. However, if the situation is as depicted in Fig. 1.1b, this is no longer the case; that 1b is correct, rather than 1a, is implied by the third law of thermodynamics, which in the form due to Simon (1930, 1956) states: 'at absolute zero the entropy differences disappear between all those states of a system which are in internal thermodynamic equilibrium'.

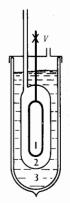
The equivalence of this statement to the alternative statement that 'it is impossible by any procedure, no matter how idealized to reduce the temperature of any system to the absolute zero in a finite number of operations', has been demonstrated by Guggenheim and is strongly suggested by Fig. 1.1b. However, we still have a means of lowering the temperature—even if not to



absolute zero—at our disposal and in practice such methods have been widely used. Associating the parameter X with the pressure p applied to a gas or with the magnetic field H applied to an assembly of magnetic dipoles, the principles of gas cooling by isothermal compression and adiabatic expansion, and of magnetic cooling by isothermal magnetization and adiabatic demagnetization are exemplified.

Examples

In the single-expansion helium liquefier (Simon 1932) shown schematically in Fig. 1.2, helium gas is compressed isothermally into chamber 1 to a pressure of 100 atm; a temperature of about 15 K is maintained, heat being transferred through the medium of helium exchange gas in the space 2 to a bath of liquid hydrogen boiling under reduced pressure in the dewar vessel 3. Thus the initial temperature $T_B \approx 15 \text{ K}$; in practice T_B may be lowered to 10 K by reducing the pressure above the evaporating hydrogen to well below its triple-point pressure. Then the exchange gas is removed from 2 and the compressed helium in chamber 1 is expanded through the valve V to a pressure of 1 atm, so that the gas remaining in the chamber is adiabatically cooled to the final temperature T_C (equal to the liquefaction temperature); a substantial fraction of the chamber is left filled with liquid helium. The importance of the metal chamber 1 having a heat capacity small in relation to the gas is paramount, and is easily realized with helium gas at about 10 K, but would not be the case for compressed air at 200 K, for the heat capacity of the containing pressure vessel at this higher temperature would be considerable.



F1G. 1.2. Schematic diagram of the Simon expansion liquefier.

The desorption helium liquefier first discovered by Simon in 1926 and developed further by Mendelssohn (1931) is very similar. In this the inner container is partially filled with activated charcoal and the process $A \rightarrow B$ of Fig. 1.1 is simply the isothermal adsorption of helium gas to a pressure of 1–5 atm on the charcoal, the heat of adsorption being removed via exchange gas to the liquid-hydrogen bath. This is followed by an adiabatic desorption or pumping away of the adsorbed helium gas during which the temperature of the remaining gas, charcoal, and the container fall toward or to the liquefaction temperature.

The suggestion that a process of ordering by a magnetic field could be applied to an assembly of weakly interacting magnetic dipoles, as in a paramagnetic salt, and that a subsequent adiabatic demagnetization would cause cooling, was made independently in 1926 by Debye and Giauque. Within a few years Giauque and MacDougall (1933), de Haas, Wiersma, and Kramers (1933), and Kurti and Simon (1935) verified this experimentally; Fig. 1.3 illustrates the process schematically. A pill of a paramagnetic salt (gadolinium sulphate in Giauque's early experiments) is magnetized in a field of one tesla at a temperature of about 1 K, the heat of magnetization being transferred through helium exchange gas to the pumped liquid helium in the surrounding dewar vessel. After removal of the exchange gas, the magnetic field is reduced and the temperature of the salt pill falls. There is a further analogy with the expansion liquefier in that for appreciable cooling to occur, the lattice vibrational specific heat at 1 K of the

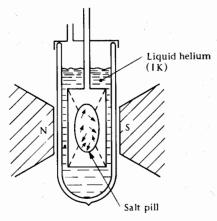


Fig. 1.3. Schematic diagram of the magnetic cooling process.

salt pill must be small in comparison with the 'magnetic heat capacity', i.e. with the thermal energy of the disoriented magnetic ions; if this were not so, the reduction in the entropy on magnetization would be small in comparison with the total entropy of the crystal lattice.

2. Isenthalpic cooling

Introduction

The discovery, in 1862, by Joule and Thomson that a gas undergoes a temperature change when it expands slowly through a porous plug, has been widely applied to gas refrigeration. The cooling on adiabatic expansion discussed in § 1 is a property of the perfect gas—in which attractive or repulsive forces are zero—and occurs for real gases at all temperatures by virtue of their performing 'external' work. However, the Joule—Thomson effect for any real gas depends both in magnitude and sign on the temperature and is zero for a perfect gas at all temperatures. This effect is sometimes called an 'internal work' process because the temperature change is determined by the change in energy of gas when the average separation between the gas molecules is increased.

In the Joule-Thomson process a gas undergoes a continuous throttling or expansion as it is driven by a constant pressure p_1 on one side of the expansion valve (or porous plug) and expands to a

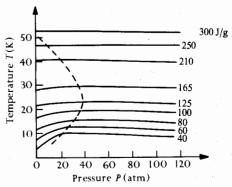


Fig. 1.4. Isenthalpic curves of helium.

lower pressure p_2 on the other. Considering a fixed mass of gas passing the valve, it can easily be shown that the total heat or enthalpy H = U + pV is unchanged in passing from state 1 (pressure p_1) to state 2 (pressure p_2); U is the internal energy per unit mass and V is the volume.

Since dH = 0 such a process is called isenthalpic.

Performing such a throttling experiment for helium we should obtain a set of values of T_2 —the temperature after expansion—lying on a smooth curve. If T_1 —the temperature before expansion—is below the so-called inversion temperature, such curves have a maximum as seen in Fig. 1.4. The locus of the maxima encloses a region within which the differential Joule—Thomson coefficient

$$\mu = \left(\frac{\partial T}{\partial p}\right)_{H}$$

is positive and hence a cooling results on expansion. We may show:

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT,$$

therefore

$$\left(\frac{\partial T}{\partial p}\right)_{\mathbf{H}} = -\left(\frac{\partial H}{\partial p}\right)_{\mathbf{T}} / \left(\frac{\partial H}{\partial T}\right)_{\mathbf{p}}$$
$$= -\frac{1}{C_{\mathbf{p}}} \left(\frac{\partial H}{\partial p}\right)_{\mathbf{T}}$$

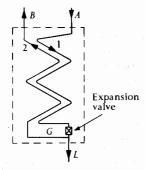


Fig. 1.5

or, since

$$dH = dU + p \ dV + V \ dp = T \ dS + V \ dp,$$

$$\left(\frac{\partial T}{\partial p}\right)_{H} = -\frac{1}{C_{p}} \left\{ T \left(\frac{\partial S}{\partial p}\right)_{T} + V \right\}$$

$$= \frac{1}{C_{p}} \left\{ T \left(\frac{\partial V}{\partial T}\right)_{p} - V \right\}$$

and this vanishes for the perfect gas since pV = RT.

This isenthalpic process is important as it forms the final stage for nearly all 'circulation' liquefiers ('circulation' liquefiers exclude the Simon expansion and desorption liquefiers). Such a final stage, including expansion valve and heat interchanger, is shown schematically in Fig. 1.5, where compressed gas at pressure p_A , temperature T_A , and enthalpy H_A per gram enters at A. After expansion the gas (state p_B , T_B , H_B) leaves through the interchanger at B and liquid L (state p_L , T_L , H_L) collects at L.

If the liquefaction efficiency is denoted by \mathscr{E} , then since the process is isenthalpic

$$H_{\rm A} = \mathscr{E}H_{\rm L} + (1 - \mathscr{E})H_{\rm B},$$

therefore the efficiency $\mathscr{E} = (H_{\rm B} - H_{\rm A})/(H_{\rm B} - H_{\rm L})$.

Heat interchanger

So far the heat interchanger has not been mentioned, but it plays a vital role in determining the liquefaction efficiency as it determines T_B and therefore the enthalpy H_B . The exchanger efficiency, η , is usually defined as the ratio of the actual heat

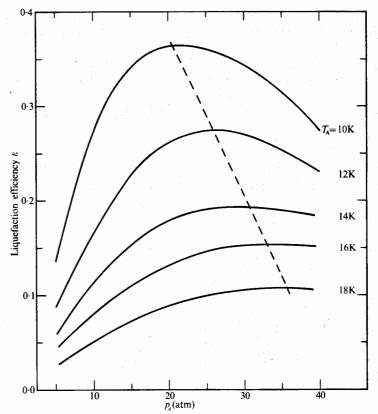


FIG. 1.6. Theoretical liquefaction efficiency of the Linde stage of a helium liquefier.

transferred from stream 1 to stream 2, to the total heat available for transfer.

As
$$\eta \to 1$$
, $T_B \to T_A$.

If $\eta = 0$, i.e. if there is no interchanger, then $T_B = T_G$ (where T_G is the temperature of the gas immediately after expansion), and so $H_B = H_G$.

For liquefaction to occur we require $T_G = T_L$, therefore $H_G = H_L + \lambda$, where λ is the latent heat, and so, for $\mathscr{E} \ge 0$, we should require $H_A \le H_L + \lambda$ if $H_B = H_G$ ($\eta = 0$). For helium this means $H_A \le 25$ J/g and therefore $T_A < 7.5$ K which is below the reach of other liquid refrigerants.

Figure 1.6 shows the liquefaction efficiency \mathscr{E} for helium as a function of the pressure p_A and temperature T_A , assuming $\eta \simeq 1$;

the curves have been calculated from enthalpy data for helium given by Keesom (1942) and Kropschot, Birmingham, and Mann (1968, Ch. 2).

Since \mathscr{E} is a maximum when H_A is a minimum, the conditions for maximum efficiency of this liquefaction stage include that

$$\left(\frac{\partial H_{\mathbf{A}}}{\partial p_{\mathbf{A}}}\right)_{T=T_{\mathbf{A}}}=0.$$

It follows from

$$C_{p}\mu = \left(\frac{\partial H}{\partial T}\right)_{p} \left(\frac{\partial T}{\partial p}\right)_{H}$$

that $\mu = 0$ satisfies this condition.

Thus the optimum entry pressure is a value of p_A lying on the inversion curve (see Figs. 1.4 and 1.6).

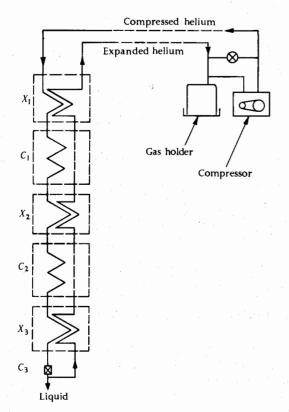


Fig. 1.7. A generalized flow circuit for a helium liquefier.

Principles of a Joule-Thomson liquefier

Consider the schematic diagram (Fig. 1.7) of a helium liquefier which relies on Joule-Thomson cooling for its final or liquefaction stage. The hydrogen liquefier is similar in principle but is more simple as one cooling stage can be omitted.

 C_1 , C_2 , C_3 are cooling stages, the final stage C_3 being the Joule-Thomson valve; X_1 , X_2 , X_3 are heat interchangers. The chief points that emerge are that:

- (i) The cooling stage C_2 , which may be liquid hydrogen or an expansion engine device, should be capable of producing an exit temperature for the gas stream of well below the inversion temperature and preferably $\leq 15 \text{ K}$ for high liquefaction efficiency.
- (ii) X_1 , C_1 , X_2 are all inessential in principle, but their form and efficiency determine the character of C_2 ; in practice C_1 may be either liquid air (or liquid nitrogen or oxygen) or an expansion engine.
- (iii) C_1 should generally act as both a purifying and precooling stage, although these may be in separate units with the purifying part—a charcoal trap at liquid-air temperature—external to the main liquefier.
- (iv) C_2 , if it be a liquid-hydrogen cooling stage, may also divided into two parts with a first part containing liquid hydrogen boiling under atmospheric pressure at 20.4 K and a second containing liquid hydrogen boiling under reduced pressure; such an arrangement considerably reduces the capacity required for the hydrogen pump.

TABLE 1.1
Physical data for gases

Gas	Inversion- temp. (K)	Boiling point (K)	Critical temp.	Critical pressure (atm)	Triple point (K)	Triple- point pressure (Torr)
Helium (³ He)	~40	3.2	3.34	1.15		
Helium (4He)	51	4.2	5.19	2.26	_	_
Hydrogen	205	20.4	33.2	13.0	14.0	54
Neon	270	27.1	44.4	25.9	24.6	324
Nitrogen	621	77.3	126	33.5	63.1	94
Argon	723	87.3	151	48	83.9	512
Oxygen	893	90.2	154	50	54.4	1.2

In Table 1.1 are the Joule-Thomson inversion temperatures for some common gases and other data governing their suitability as refrigerant liquids. (Note: $1 \text{ Torr} = 133 \cdot 3 \text{ Pa.}$)

3. Air liquefiers

Linde and Hampson

To the low-temperature physicist who either buys liquid nitrogen or oxygen commercially for 20 cents or 10 pence per litre, or who draws freely on the output of a large central laboratory liquefier, a description of the principles involved in air liquefiers may seem out of place in this text. However, these principles serve to illustrate and introduce the various types of helium and hydrogen liquefiers, and to explain historically the terms such as Linde, Hampson, Claude, which are frequently applied to particular designs of liquefiers. Because of the higher temperatures involved they introduce the methods of liquefaction without the complexity of a pre-cooling stage.

In the simple Linde air liquefier of Fig. 1.8, a compressor, heat exchanger X, and expansion throttle V are the important features. In 1895, the same year as Linde first used this simple pattern for air liquefaction, Hampson developed his air liquefier, which used a similar flow circuit but a different design of heat exchanger. Linde employed a countercurrent heat exchanger (see Fig. 1.8 and Ch. III) in which the two gas streams passed through concentric tubes. In the Hampson exchanger the high-pressure gas flows through a tube wound in a spiral pattern with the spiral

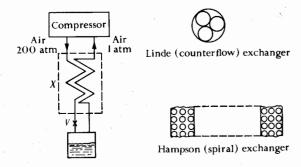


Fig. 1.8. Simple Linde air liquefier and section views of Linde and Hampson heat exchangers.

enclosed in the annular space between two cylinders, and the returning low-pressure gas passes up this annular space past the spiral of tubing. Linde later improved the efficiency of his air liquefier by letting the gas expand in two stages, first through a valve from 200 to 40 atm after which about 80 per cent of the gas returns through an exchanger to be recompressed; the remaining fraction is expanded to 1 atm. The resultant saving in work of compression improved the practical efficiency by about 100 per cent. A further improvement occurred when Linde introduced a liquid ammonia pre-cooling stage so that the compressed gas entered the exchanger at about -48° C.

Claude

As the name Linde is invariably associated with the Joule-Thomson process of cooling, so Claude is associated with expansion-engine liquefiers, although in the later form used by Claude and also developed by Heylandt early in this century both an expansion engine and a Joule-Thomson valve were incorporated (Fig. 1.9). Claude's first machines used simply isentropic expansion with liquid air being produced in the engine. However, the advantages of dividing the high-pressure stream and using Joule-Thomson expansion for the final liquefaction stage were considerable and this form has been used successfully over the

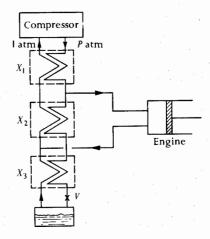


Fig. 1.9. Claude-Heylandt system of air liquefaction.

years. Claude used a pressure of about 40 atm and allowed 80 per cent of the gas to pass through the engine; Heylandt used 200 atm, passed about 60 per cent through the engine, and dispensed with exchanger X_1 . Thus in the Heylandt case gas enters the engine at room temperature which gives a somewhat higher operating efficiency.

The overall operating efficiencies of the Linde and Claude systems are not very different and both are still widely used together with the Philips-Stirling cycle and turbine-expanders.

Cascade liquefiers

Pictet's first partially successful attempt to liquefy oxygen in 1877 used the cascade process, although the 'mist' of liquid which he produced was probably a result of adiabatic expansion plus cascade cooling rather than purely the cascade process itself. In this method a suitable gas A is liquefied at room temperature under pressure and then expanded to evaporate under atmospheric or under reduced pressure at a lower temperature; provided that this lower temperature is below the critical temperature of a second gas B, then this gas B may be liquefied likewise by isothermal compression; thus in stages the critical temperature of air may be reached. In Pictet's case gas A was sulphur dioxide and B was carbon dioxide. Keesom (1933) has analysed the efficiency of a hypothetical four-stage cascade process using successively NH_3 , C_2H_4 , CH_4 , and N_2 as the final stage and found it to be higher than in conventional Claude and Linde processes.

Philips-Stirling cycle

Kohler and Jonkers (1954) at the Philips Company developed a small air liquefier, based on the principles of the Stirling hot-air engine, which is suitable for laboratory use. The closed cycle shown in Fig. 1.10 (Kohler 1960) consists of compression of gas in a compression space followed by a transfer of the gas through a regenerative heat exchanger to an expansion space where the gas is expanded and cooled before it is returned through the exchanger. This action is achieved by the out-of-phase motion of the two pistons B and C moving in the cylinder A. C may be called the displacer. The four distinct phases of the cycle are:

- (1) Compression in space D by piston B.
- (II) Transfer of gas through the regenerator G to space E by the movement of the displacer.

- (III) Expansion in the cold space E by the movements of C and B.
- (IV) Transfer of gas back through G to space D.

The heat of the compression is removed by the water-cooling coil H and the expansion is used to cool the cylinder head E or the coil J. With helium or hydrogen as the working substance in the closed circuit, air is condensed from the atmosphere onto the cooler cylinder head.

The smaller unit produced by Philips liquefies about 6 litres of air per hour with a starting-up time of about 10 min. The larger four-cylinder model liquefies about 30 l/h and includes a refrigeration-drier which allows over 100 h of continuous operation. If desired, fractioning columns may be attached to deliver liquid nitrogen.

A further development of this cycle has been to expand the gas in two stages (Prast 1963) and has resulted in the Philips Type A-20 'Cryogenerator' which uses helium as the working gas and can reach temperatures as low as 12 K or liquefy hydrogen at about 5 l/h.

Others

Various other forms of expansion cooling have been used. They include the turbo-expanders pioneered by Kapitza and others, the Gifford-McMahon cycle and the modified Taconis cycle. They are discussed briefly below for their use in helium

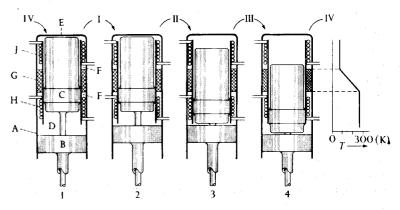


Fig. 1.10. The successive phases of the Philips-Stirling cycle, e.g. Phase I represents the compression of gas in space D by the piston B with heat of compression being removed in the cooler H (after Kohler 1960).

liquefaction and more fully by Collins (e.g. Collins and Cannaday 1958; also Ch. 3 of Kropschot, Birmingham, and Mann 1968), Croft (1970), and in *Liquid helium technology* (Proceedings of International Institute of Refrigeration, 1966, Pergamon Press, Oxford).

4. Hydrogen liquefiers

Hydrogen liquefiers have become a rarity in research laboratories but there are still many large-scale installations in industry. Both large and small liquefiers use Joule—Thomson expansion preceded by liquid nitrogen cooling and, in the case of large liquefiers, by expansion engines or turbines as well. These large liquefiers are discussed in *Liquid hydrogen* (International Institute of Refrigeration, 1966, Pergamon Press, Oxford), Collins and Cannaday (1958), and Scott, Denton, and Nicholls (1964). Particular features of hydrogen liquefiers are the possible need for *ortho-para* conversion (see also § 2.1) and safety considerations.

Small hydrogen liquefiers

The isenthalps and inversion curves for hydrogen (see Fig. 1.11 from Woolley, Scott, and Brickwedde 1948) show that much higher pressures are needed for optimum operation than for helium: for example, a suitable combination for the input temperature and pressure of hydrogen gas entering the final stage of a Joule-Thomson liquefier might be 60 K and 130 atm.

To avoid high-pressure compressors many of the small liquefiers were designed to be supplied by cylinders of compressed hydrogen. Air Products and Chemicals Inc. have marketed such a small liquefier-refrigerator of a few watts cooling capacity precooled by either liquid nitrogen or by nitrogen gas with its own Joule-Thomson cooling stage (Cryo-Tip).

The design principles and performance of cylinder-operated hydrogen liquefiers were discussed in detail by Starr (1941) who gave figures for the liquefaction efficiency as a function of input pressure and pre-cooling temperature. The construction details of some small liquefiers have been described by Ahlberg, Estermann, and Lundberg (1937), Fairbank (1946), and others. Some of the medium-sized Linde liquefiers with capacities of 7 to 50 l/h were those in Berlin (Meissner 1928), Zurich (Clusius 1953),

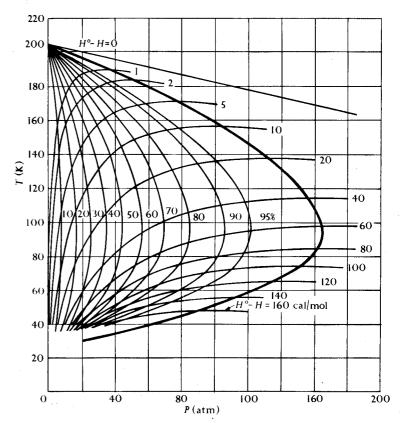


Fig. 1.11. Isenthalps (approximately horizontal curves) and inversion curve (heavy curve) for hydrogen (after Woolley, Scott, and Brickwedde 1948). The light curves drawn roughly parallel to the inversion curve are lines at which the refrigeration is the marked percentage of 100 per cent on the inversion curve.

Moscow (Zeldovitch and Philipenko 1960), and in Oxford (Jones, Larsen, and Simon 1948; Croft and Simon 1955). Most of these have operated with a hydrogen input pressure of approximately 150 atm, pre-cooling temperature (that \P s an entry temperature to the final Linde exchanger) of 63–66 K; they have liquefaction efficiencies in the range from 22 to 30 per cent and consume $1-1\frac{1}{2}$ litres of liquid air or liquid nitrogen per litre of liquid hydrogen.

The Oxford liquefier (Croft 1964), shown schematically in Fig. 1.12, produces over 25 l/h. It operates at a pressure of only

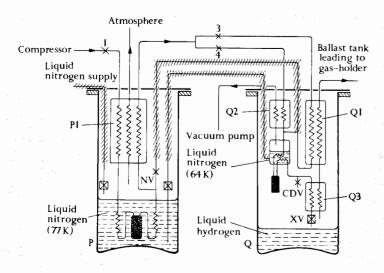


Fig. 1.12. Flow diagram of the Oxford hydrogen liquefier (after Croft 1964).

60 atm because of economic considerations in obtaining a compressor. The hydrogen gas is produced electrolytically, is compressed, and passes successively through an oil separating column, an activated alumina drier, 'Deoxo' purifier, a further alumina drier, and then into the charcoal purifier at 77 K which is shown in the diagram. The gas flow is then split by the valves marked NV, 3 and 4, so that the major fraction goes through valve 3 to the exchanger Q1. Heat exchangers are of the Collins-Hampson pattern made from thin copper tubing (Integron tubing from Imperial Chemical Industries) wound in a helix between two cylindrical sheets. Thermal insulation is provided by metal dewars for these stages. No effort is made to promote *ortho-para* conversion since the major part of the liquid hydrogen is used soon after production.

By contrast the large liquefier at the National Bureau of Standards in Boulder, Colorado (Johnson and Wilson 1955; Scott 1959, p. 43), can produce over 350 l/h of normal liquid hydrogen or 240 l/h of para-hydrogen. The hydrogen gas passes successively through a 'Deoxo' purifier (palladium catalyst supported on silica gel), compressor, oil and water separator, refrigeration drier (cooled to below $-100\,^{\circ}$ C), and silica gel purifier (to adsorb N_2 and any remaining O_2); it then pre-cools the refrigeration drier

and passes on into a Joule-Thomson liquefaction stage. The ortho-para conversion is catalysed by ferric hydroxide (see also Liquid hydrogen (International Institute of Refrigeration, 1966, Pergamon Press, Oxford) and Scott, Denton, and Nicholls 1964).

5. Helium liquefiers

Introduction

In many places liquid helium can now be bought if it is needed. Prices vary from \$3 to \$10 (or say, £2 to £6) per litre, depending on such factors as geographical location, return or non-return of gas, average consumption, local competition, etc. This may seem expensive and yet for an occasional user of small quantities it is cheaper than installing and maintaining a helium liquefier. The economic considerations are complicated as they depend on how a particular research laboratory receives its annual finances; whether it can find major sums for capital equipment or continuing finance for annual maintenance, also reliable technicians and available space and time in which to operate the liquefier. There is no universal answer to this problem and therefore it seems desirable that physicists using liquid helium should have at least a passing acquaintance with the various types of liquefiers, including the commercially available models and those which can be constructed most easily in a research laboratory.

Apart from the ability of a liquefier to supply a demand for a liquefied gas, two major features which determine its value are ease of construction and ease of maintenance. Except in the case of an expansion-engine liquefier where engines and crosshead impose their own constructional difficulties, the major constructional problem is usually the heat exchanger and the primary maintenance problem that of keeping the heat leakage at a sufficiently low value. If the heat exchanger allows of relatively easy construction and assembly, and the high vaccum surrounding the liquefier is maintained without much labour, the liquefier should be a successful design. In small-capacity liquefiers this first requirement can be met with Linde-pattern exchangers and the second can often be satisfied by exposing as few as possible of the working parts to the high vacuum space.

Simon expansion helium liquefiers

The principle of operation of single-expansion liquefiers was discussed in § 1 above, and Fig. 1.13 (Pickard and Simon 1948)

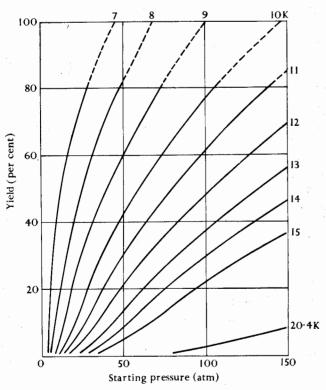


Fig. 1.13. Liquid-helium yield in the Simon expansion process (after Pickard and Simon 1948).

illustrates the dependence of percentage yield (i.e. percentage filling of the expansion vessel with liquid helium) on the pressure and temperature from which the expansion begins. While requiring a high-pressure helium supply together with liquid hydrogen, such a liquefier is itself of comparatively simple construction. Cooke, Rollin, and Simon (1939), Scott and Cook (1948), and Croft (1952) have described how a thick-walled vessel of copper or vibrac steel (corresponding to 1 in Fig. 1.2) is filled with helium gas to 100–150 atm and cooled to 10 or 11 K by pumping on liquid hydrogen in the dewar or an attached chamber. After this cooling, the helium is expanded adiabatically to 1 atm and the inner vessel is left with 60–80 per cent of its volume filled with liquid helium.

While the small-capacity Simon helium liquefier had an undoubted popularity at the Clarendon Laboratory, comparatively few have been constructed elsewhere and of these most have been operated from cylinders of compressed gas. A compressor suitable for delivering helium gas at over 100 atm pressure is a rather uneconomical proposition when only called upon to supply one small liquefier. As a result the small Linde-type liquefier has been more commonly used, as it operates efficiently with an input pressure of 20–30 atm and therefore can be supplied by a suitably modified commercial air compressor or from cylinders fitted with a pressure-reducing valve.

Linde helium liquefiers

A small helium liquefier is shown in Fig. 1.14 (Daunt and Mendelssohn 1948) in which the incoming helium gas, compressed to 20 atm, was pre-cooled in a separate dewar of liquid air

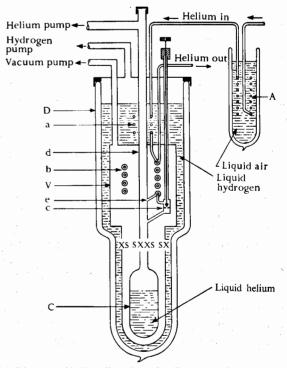


Fig. 1.14 Diagram of helium liquefier (after Daunt and Mendelssohn 1948).

and then by pumped liquid hydrogen in the main dewar. Similar liquefiers were later constructed and assembled in a period of three or four weeks by an experienced technician; they had a glass tail, attached by a copper-glass Housekeeper seal and Wood's metal joint to the brass vacuum jacket. Giving about 150 ml of liquid helium per hour with less than one hour starting time, this liquefier is very suitable for the visual observations on liquid helium for which it was intended. It has also served as a prototype for other small liquefiers, e.g. the 11/h liquefiers described by Hercus and White (1951), Parkinson (1954), and Brewer and Edwards (1956). The Joule-Thomson liquefier at Ohio State University (Daunt and Johnston 1949) with a production of 7.5 litres of liquid helium per hour and a liquid hydrogen consumption of 1.3 litres per litre of helium is a further example of the development. In this liquefier a Hampson-type heat exchanger is used to transfer heat from the incoming compressed gas to the low-pressure helium stream and to the evaporated hydrogen gas; this exchanger is designed to give a low pressure drop with the high flow rate used.

The helium liquefier at Oxford (Croft and Bligh 1961) survives as an example of a somewhat larger Linde liquefier which can be used successfully when adequate supplies of liquid hydrogen are available: there are three distinct stages in three separate dewars. In the first liquid-air dewar, the helium gas is purified by passing over charcoal and part of the helium stream is pre-cooled. The other part of the stream is pre-cooled by the returning cold helium gas; the incoming compressed helium is then further cooled by liquid hydrogen (reduced to a pressure of about 0.1 atm, say $14 \, \text{K}$) in the second dewar vessel before entering the final Linde stage in the third dewar. With a two-stage Reavell compressor $50 \, \text{m}^3$ of helium per hour are compressed to $27 \, \text{atm}$ and the liquefier yields about $12 \, \text{litres}$ of liquid helium per hour; the liquid hydrogen consumption is approximately $1.5 \, \text{litres}$ of hydrogen per litre of helium.

Linde hydrogen-helium liquefiers

The combined hydrogen-helium liquefier usually has a helium liquefaction as its main purpose with liquefaction of hydrogen as a necessary evil of the process. The small-capacity liquefiers made by Rollin (1936) and Schallamach (1943) used Joule-

Thomson expansion at the liquid-hydrogen stage and Simon expansion at the liquid-helium stage. Later Chester and Jones (1953) used isenthalpic cooling for both gases in a small liquefier. A larger combined Linde-liquefier was used for many years at the Mond Laboratory, Cambridge (Ashmead 1950) giving 4 l/h of helium and using 5 l/h of hydrogen (liquefied internally). The long life of this machine is a tribute to the method of construction: liquid air, liquid hydrogen, and pumped liquid hydrogen were contained in three brass cans which had domed faces brazed on and the cooling coils were soldered onto the outside of the cans.

A hydrogen-helium liquefier designed by Lacaze and Weil (1955) was produced commercially by TBT (Tres Basses Temperatures) of Sassenage, France. The outputs were 7 l/h of liquid helium and 13 l/h of liquid hydrogen, each produced by Joule-Thomson expansion and liquid nitrogen pre-cooling. Later when TBT became part of the L'Air Liquide organization, this design was replaced by one which used a Philips A-20 Cryogenerator to replace the liquid-hydrogen cooling stage (Chovet and Solente 1970); this is the ALP 300 included in the discussion below of helium liquefiers.

Kapitza's expansion-engine liquefier

The first successful helium liquefier which used an expansion engine rather than liquid hydrogen for pre-cooling was that of Kapitza (1934) which operated in the Mond Laboratory, Cambridge, for nearly two decades. Fig. 1.15 indicates the flow circuit in which helium gas, compressed to about 30 atm, is pre-cooled by liquid nitrogen, after which the majority of the gas is expanded in the engine E and returns through the heat exchangers C, B, and A. The minor fraction of compressed gas (about 8 per cent) passes on through exchangers to a Joule–Thomson expansion valve 4.

While this exemplifies the general principles of helium liquefaction discussed above (§ 2 and Fig. 1.7), it is also a direct development of the Claude process of air liquefaction with the addition of the liquid nitrogen pre-cooling. Kapitza used an unlubricated engine with a clearance of about 0.05 mm between the piston and cylinder, the small gas loss past the piston serving as a lubricant. The part of the liquefier below the nitrogen vessel

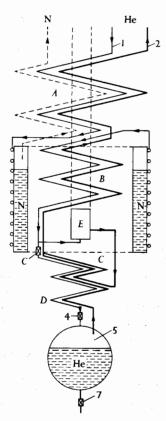


Fig. 1.15. Arrangement of heat exchangers and cooling stages in the Kapitza liquefier (after Kapitza 1934).

is surrounded by a radiation shield thermally anchored to the liquid-nitrogen container, and the whole assembly is suspended in a highly evacuated metal vessel. This liquefier produced about $1.7 \, l/h$ at an overall liquefaction efficiency of 4 per cent.

Collins liquefier (Authur D. Little, Inc.)

Closely related in principle of operation to Kapitza's liquefier is that developed by Professor Collins (1947; see also Latham and McMahon 1949) at the Massachusetts Institute of Technology. This liquefier and its commercial development by the Arthur D. Little Corporation has contributed to the present wide development of low-temperature research and to the familiar references

to the two eras of low-temperature physics as 'before and after Collins'. As illustrated in the flow diagram of Fig. 1.16 there is one obvious difference from the Kapitza model, in that there are two expansion engines, the first acting in place of the liquid-nitrogen cooling stage used by Kapitza. Other important features are:

- (i) A very hard nitrided nitro-alloy steel for the engines allows the use of a very small clearance (0.01 mm) between piston and cylinder wall and reduces the gas leakage to a negligible amount, without causing appreciable wear on either piston or cylinder.
- (ii) In the heat exchanger (Plates Ia and Ib, facing p. 24) the high-pressure helium at about 15 atm flows down through copper-finned cupro-nickel tubes of $\frac{1}{4}$ -in. diameter, and the low-pressure gas returns past these fins through the annular space between two cylindrical walls: the finned tubing is wound tightly on the inner slightly tapered cylinder and the outer jacket cylinder (similarly tapered) is forced up to cover the windings. A flexible cord is interwound with the exchanger tubing to force the return gas flow into more intimate contact with the copper fins, themselves solder-bonded to the cupro-nickel tubing.
- (iii) In this Collins machine the piston and valve rods are always under tension rather than compression which allows the use of relatively thin stainless steel rods and makes the heat inflow through these small.
- (iv) Finally and most important from the maintenance viewpoint is the fact that the working parts are surrounded by an

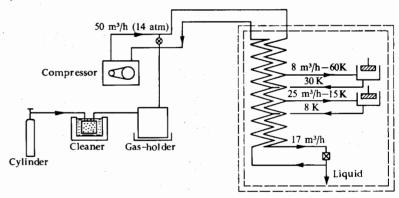


FIG. 1.16. Simplified diagram of a Collins helium liquefier. Flow rates are typical of the original Collins machine and the earlier commercial models.

atmosphere of helium, rather than a high vacuum. The whole assembly enclosed by the heat exchanger fits inside a stainless steel dewar vessel and the possibility of serious vacuum troubles is considerably lessened by having the engines, helium flow tubes, and couplings, etc., in a static helium atmosphere.

With the flow rates shown in Fig. 1.16 and with no liquid nitrogen cooling, the liquefaction rate is between 2 and 3 l/h. This could be increased to over 4 l/h and the starting time shortened from 4 to 2 hours by using liquid nitrogen to pre-cool the incoming helium and the radiation shield. The production could be further increased to 8 l/h by using two compressors and either increasing the engine speed from 360 to 600 rev/min or using a larger second engine.

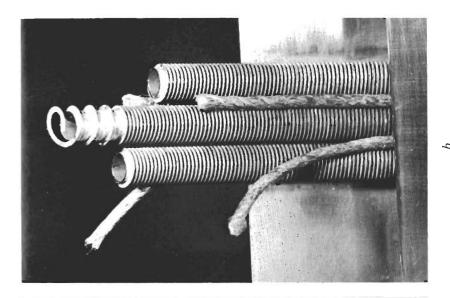
More than 300 of these Collins liquefiers were made by Arthur D. Little Inc. (later the division concerned became Cryotechnology Inc. or CTI) for laboratories around the world. This is a tribute to their success which was marred only occasionally by faulty solder joints or compressor seals.

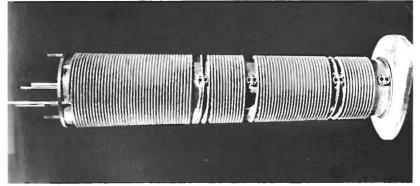
'New' Collins liquefier (Cryotechnology Inc.)

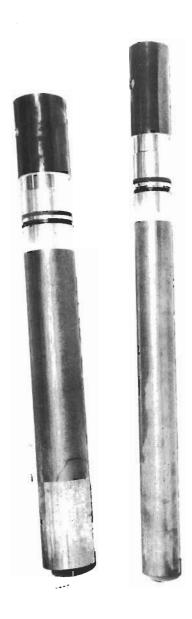
Collins (1966) successfully introduced plastic (micarta) pistons into the engines of his MIT liquefier and this heralded a new generation of CTI liquefiers. The long bonded-phenolic pistons (Plate II; facing p. 25) extend up to an O-ring seal at room temperature and discharge their power electrically in the crosshead. Engines and exchangers and cleaners are now side-by-side in an evacuated enclosure (Plate III; facing p. 42) rather than vertically arranged in a stagnant atmosphere of helium. Joints are all welded and must be high-vacuum tight but otherwise construction tolerances are generally greater than in the earlier machines. The liquid and expanded helium gas are taken through a triple-wall transfer tube to an external storage dewar and the gas is returned to the liquefier and exchangers. The latter are still of finned tubing in a 'Hampson' type of construction. The external collection and storage of liquid means that they can operate for days with little attention. There are different compressor and pre-cooling options available giving liquefaction rates ranging from 5 to 35 1/h.

Philips liquefier

In the commercial Philips helium liquefier, two 2-stage cryogenerators (A and B in Fig. 1.17) pre-cool the helium before







it expands, firstly from 20 to 2.5 atm in the expander-ejector device (Rietdijk 1966; also Croft 1970; and Kropschot *et al.* 1968, p. 118) and secondly through the Joule-Thomson valve. The cryogenerators use the Philips-Stirling cycle (Prast 1963) and have their own closed helium gas system. Gas for the liquefier section is compressed from 2.5 to 20 atm in a non-contaminating diaphragm compressor, passes through heat exchanger X_1 , then to first stage of A (cooling from 120 to 100 K), then to X_2 and first stage of B, to X_3 and second stage of A, to X_4 and second stage of B (cooling from 18 to 16 K). The other down-stream through the exchangers is for cooling the 'make-up' helium before it joins the main stream; this amounts to 10 per cent of the total circulation, equivalent to 10 l/h of liquid.

The expansion-ejector described by Rietdijk is important in raising the pressure of the returning gas stream to 2.5 atm which is needed for the inlet stage of the rolling-diaphragm compressor. Liquid and gas are taken from this to an external storage dewar through a triple-wall transfer tube as in the Collins-CTI liquefiers. Novel features of the liquefier include not only the ejector and compressor but also the heat exchangers. They consist of a stack of sheets, alternately of copper gauze and resinimpregnated paper with rectangular gas guidance holes punched in the latter. Sheets are pressure bonded into a cube (Vonk 1968; see also Croft 1970). All these novelties might be expected to lead to teething troubles but the problems which have been encountered by some operators have arisen rather from complexities of cool-down pipes, valving, etc., and can be largely solved by training programmes held at Eindhoven.

Linde-AG liquefiers

A helium liquefier was made commercially by the Linde-AG many years ago based on the design of Meissner (1942) and Meissner, Schmeissner, and Doll (1959). With liquid-air precooling, one expansion engine, and a Joule-Thomson expansion, 3-4 l/h were produced. Later modifications have included separating the helium circuits for cooling and liquefaction and introducing an expansion engine in which the piston controls the inlet and outlet (Doll and Eder 1964; Petzelt and Stephan 1973; Croft 1970, p. 40). Various models are available with outputs ranging from 6 to 100 l/h but all have separated gas circuits to avoid problems of impurities blocking the system. One circuit is a

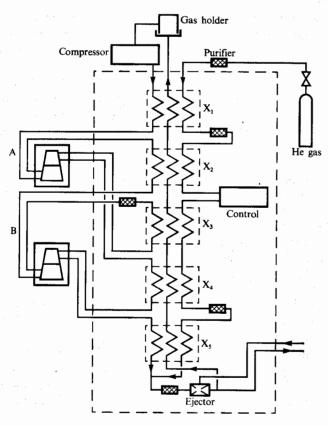


Fig. 1.17. Schematic diagram of a Philips helium-liquefier, incorporating two 2-stage cryogenerators and J-T expansion.

closed cycle with a 20-30 atm compressor, heat exchangers, engines, and Joule-Thomson expansion with all the gas returning through the exchangers to the compressor; in the other, the gas to be liquefied passes through drier, purifier, exchangers, and J-T valve before transfer to the external storage dewar. Linde also make a larger He II liquefier-refrigerator with a cooling capacity of 300 W at 1.8 K which uses two expansion turbines for precooling (Baldus 1971).

Gifford-McMahon cycle and Cryodyne liquefiers

Another external work cycle is shown in Fig. 1.18, this was developed by McMahon and Gifford (1960) at Arthur D. Little

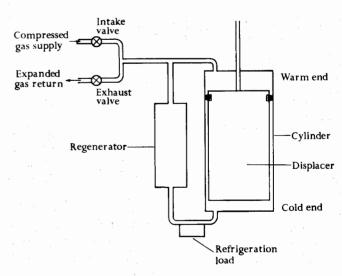


Fig. 1.18. A single-stage version of the Gifford-McMahon refrigerator (after McMahon 1960).

Inc. (later CTI). Called the 'Cryodyne', the cycle consists of four phases: in the first pressurization phase the displacer piston is at the cold end of the cylinder so that the warm volume is at a maximum. The intake valve is opened and compressed helium flows into the warm volume. Then during the intake phase the valve remains open and the displacer is moved upwards to enlarge the cold volume and reduce the warm volume. During this phase gas is therefore displaced through the regenerator to the cold end and more gas slowly enters in order to keep the pressure constant. The intake valve is then closed and the expansion phase begins when the exhaust valve is slowly opened. The cold volume is cooled by the expansion. The final exhaust phase occurs when the displacer is moved downwards to displace the remaining cold gas. After this the exhaust valve is closed and the cycle is repeated.

The three-stage or three-cylinder version of this can be used either as a refrigerator or for pre-cooling the helium supply to a Joule-Thomson liquefier as shown schematically in Fig. 1.19 (McMahon 1960; Stuart, Hogan, and Rogers 1967). The principal use of the 'Cryodyne' has been to provide small refrigerators which can operate without maintenance for long periods to cool

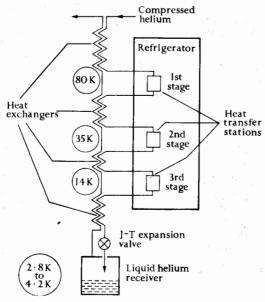


Fig. 1.19. A helium-liquefaction cycle containing three stages of Gifford–McMahon cooling and a final Joule-Thomson expansion (after McMahon 1960).

microwave equipment and optical devices to say 70, 20, or 4 K. Those produced by CTI operate at pressures of 17 atm, a repetition rate of 1 Hz, and have various refrigeration capacities from 1 to 100 W (see more details in Croft 1970 or Bailey 1971, Ch. VII).

Liquefiers with turbo-expanders (BOC, Sulzer, Linde-AG)

Due largely to the work of Sixsmith and his collaborators, small gas-lubricated turbines have been developed which are suitable for extracting work from a helium stream in a laboratory-scale liquefier (Mann et al. 1963; Sixsmith in Ch. VIII of Advanced cryogenics 1971; Clarke and Gardner 1976). British Oxygen Company and Sulzer Brothers produce helium liquefiers, respectively called 'Turbocool' and 'Turbofridge', in which two-stages of cooling are by turbines and the final cooling is by Joule-Thomson expansion. They yield 10-15 l/h of helium without liquid nitrogen pre-cooling but this may be increased to 30 to 40 l/h with pre-cooling and with added compressors. The turbines rotate at speeds up to 8000 Hz, gas enters at c. 10 atm, and liquid

collects in an external dewar. As mentioned above Linde-AG also use turbo-expanders on their larger liquefier-refrigerators of 300 W capacity (Baldus 1971).

Other liquefier-refrigerators

An interesting development in expansion engines was the first use of flexible bellows by Long and Simon (1953). They made a small helium liquefier with brass bellows, but due to metal fatigue it has a limited life of about half a million cycles. Later J. Cosier and A. J. Croft (private communication 1976) tested edgewelded stainless steel bellows and found them to have a much longer life.

Pye-Unicam Limited developed a promising refrigerator using two engines working on a modified Stirling cycle (Daly and Dean 1970; Croft 1970); each engine included a diaphragm compressor at room temperature, and a piston and cylinder working at low temperatures. The refrigeration capacity was 1 W at 4 K and prototypes operated successfully but there has been no commercial production.

As mentioned earlier, L'Air Liquide and Philips produce jointly a 3 l/h helium liquefier (ALP 300) using a Stirling cycle cryogenerator for initial cooling and then Joule-Thomson expansion (Chovet and Solente 1970).

The 'Cryo-Tip' series made by Air Products and Chemicals Inc. includes a refrigerator of $\frac{1}{2}$ W cooling capacity at 4 K which has liquid nitrogen pre-cooling followed successively by hydrogen and helium Joule-Thomson expansion stages.

The Cryomite (Malaker Laboratories of New Jersey) and Cryogem (North American Philips) are two other small Stirling-cycle refrigerators adapted largely to the needs of airborne and ground-based electronic and infra-red equipment. More details can be found in Bailey (1971), Croft (1970).

6. Gas purification and compression

The gas stream entering a liquefier should be free of significant amounts of any impurity which may condense in the working parts of the liquefier. This is particularly important in a 'circulation liquefier' employing expansion engines, as very small quantities of any impurity which may condense as a solid in the engine chamber can cause the engine to seize. Likewise, blockage of the

Joule-Thomson valve or of the heat exchanger is a considerable nuisance and may in fact be quite dangerous. In many small liquefiers this cleaning may occur in a liquid-nitrogen-cooled charcoal trap which also acts as a pre-coolant.

The major impurities likely to be present in a high-pressure helium stream may be divided into three groups: (i) oil vapour from the compressor, (ii) water vapour, (iii) gases such as oxygen, nitrogen, hydrogen. Those of group (iii) are most conveniently removed by a charcoal trap; water vapour may be removed by this if it is not present in such a quantity as to saturate the charcoal. If oil vapour is present in appreciable quantities this will rapidly saturate the charcoal and make it permanently ineffective as a gas adsorbent; compressors should be used which do not 'carry over' much oil vapour into the gas stream or an effective oil filter must be placed in the high-pressure exit line. Such a filter may be a vessel containing copper or steel wool and of sufficient dimensions that the velocity of the gas stream in it is not too great; this allows the oil particles to collect on the copper wool and then oil may be drained or blown out of the vessel at intervals through a drain-valve in the bottom.

Various types of compressors and methods of oil removal are discussed by Croft (1970) and by Strobridge (Ch. IV of Kropschot et al. 1968), including the oil-free compressors of the diaphragm type. We mentioned earlier that in some commercial liquefiers, for example those of Linde-AG, there are two separate helium gas circuits to reduce problems of impurity blockage; one closed circuit contains the working gas and in the other 'open' circuit is the gas to be liquefied which has to pass through the exchangers but not through the engines.

In most small liquefiers the total amount of water vapour present in the gas being circulated is relatively small and may be removed together with air and other gases by the charcoal trap. However, in large installations or in a hydrogen liquefier using electrolytic hydrogen, it is usual to place a silica gel drying column in the gas stream or to use refrigeration drying. When circulating hydrogen it is also usual to remove oxygen by a separate purifier—a 'Deoxo' unit which is a palladium catalyst supported on silica gel; these 'Deoxo' purifiers are commercially available from Baker and Company, Inc., of New Jersey.

A common form of charcoal cleaner is shown in Fig. 2.1 but a convenient small cleaning trap may be easily made from brass tubing. One end of the tube is sealed by a brass plate 'sweated' or silver-soldered to it and the entry and exit tubes for the gas stream are soldered through this plate; it is preferable to wrap fine metal gauze around the open ends of these two tubes to prevent charcoal dust being carried over by the gas. The main brass tube is then packed with coconut charcoal of adsorbent grade and the bottom end is sealed with a brass plate. The charcoal may then be activated by connecting the entry or exit tube to a mechanical pump and warming the unit with a gas flame or electrical heater to a temperature of $100^{\circ}-200^{\circ}$ C for a few minutes. It is placed in a convenient glass dewar which is kept filled with liquid nitrogen during the cleaning operation.

The amount of gas which can be adsorbed on activated charcoal before saturation depends somewhat on the gas and the type of charcoal. Brunauer (1943) quotes values of around 200 ml/g for the adsorption of N_2 , Ar, O_2 , CO_2 on coconut charcoal at 90 K and of 700–900 m²/g for the specific surface area of this charcoal. Other adsorbents such as activated alumina and molecular sieves (aluminosilicate pellets from the Union Carbide Corporation) are equally effective and commonly used for cleaning gas streams or as fore-pumps.

It should also be emphasized that high-pressure cleaning is more effective than low-pressure cleaning, i.e. passing an impure gas at 100 atm pressure through a cooled charcoal cleaner will yield a product with a lower percentage of impurity than by passing the same gas at 1 atm over the charcoal. In either case the adsorption pressure of the impurity at the surface of the charcoal is a function of the temperature and of the volume of impurity already adsorbed, and not of the total gas pressure; hence increasing the total pressure by a factor of 100 decreases the percentage of impurity that is retained by the gas stream by a like factor.

In liquefiers where there is a danger of the cleaning stages becoming ineffective due to passage of large amounts of impurities, a meter may be installed to monitor the impurity; such instruments for determining impurity contents in hydrogen and in helium are made by Gow-Mac Instrument Company, New Jersey.

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CHAPTER II

STORAGE AND TRANSFER OF LIQUEFIED GASES

1. Dewar vessels

Introduction

Although this section might be more appropriately termed 'containers for liquefied gases' than merely 'dewar vessels', Sir James Dewar's contribution to low-temperature research by the invention of the evacuated double-walled vessel can scarcely be over-emphasized.

The efficiency of storage of any liquefied gas is related to its latent heat of vaporization and normal boiling-point. The latter factor partially determines the extraneous heat inflow from the surroundings and the former governs the evaporation rate as a function of that inflow.

TABLE 2.1

Latent heat of vaporization, boiling point, and density at standard atmospheric pressure of cryogenic fluids

Gas	CO ₂ †	O ₂	N ₂	Ne	H ₂	⁴He	³ He
Latent heat (J/g)	173	213	199	86	441	20.6	8.2
Latent heat (J/ml)	933	243	161	103	31	2.6	0.48
Boiling point (K)	194.6	90.2	77.3	27.2	20.4	4.2	3.2
Density (g/ml)	1.63	1.14	0.81	1.20	0.070	0.125	0.059

† Solid.

In designing a container the problem is that of reducing the heat inflow to a minimum, determined by difficulties of construction and the allowable loss of liquid per unit time. The chief sources of heat are radiation to the walls of the containers, radiation down the neck of the storage vessel, heat conduction down the neck or walls, convection in the vapour above the liquid surface, and heat conduction through the residual gas in the surrounding vacuum space. Most of these factors are discussed in

detail in Chapter V and in various papers on the design of liquid-helium containers (for example, Wexler 1951; Sydoriak and Sommers 1951).

Liquid-air dewars

Glass dewar flasks, both silvered to reduce radiant heat inflow and unsilvered, are available commercially in a wide range of sizes. Usually of Pyrex, they can be made by any competent glass-blower with a suitable glass-blowing lathe. Frequently a special shape, length, or diameter of dewar is needed and this may have to be made. A description of the silvering and evacuation procedure has been given by Scott, Cook, and Brickwedde (1931). They found that after silvering by a modified Brashear process, the Pyrex dewar gave best results if slowly raised in temperature to 400 °C, then baked for a short period at 550 °C and later cooled to about 400 °C before sealing. The resulting evaporation rates for liquid air and liquid hydrogen showed that the emissivity of the silver coating is about 0.03. Quite satisfactory dewars also result if the baking temperature is only carried up to about 450 °C, and then the danger of distorting the glass walls, which will occur for Pyrex at temperatures slightly in excess of 550 °C, is eliminated.

For metal dewars, the difficulty of outgassing them completely makes it necessary to have an internal adsorbent trap. This usually consists of a hundred grams or so of coconut charcoal or 'molecular sieve' in a wire-gauze cage which is attached to the inner (cold) wall of the dewar and well exposed to the vacuum space. Spherical metal flasks are made of spun copper or aluminium with the inner neck of low-conductivity alloy such as stainless steel. Straight cylinders are usually welded from stainless steel but have been home-made successfully from fibreglass agricultural pipes cemented with epoxy resin. For efficient storage of liquid it is better to buy a commercial dewar (see Appendix for some suppliers) with superinsulation, i.e. multiple layers of aluminium foil and plastic or glass mat between the evacuated walls. The evaporation rate should be less than 1 per cent of capacity per day compared with 5 per cent or more for these without multi-layers.

Powder- and foam-insulation can be very useful for making liquid-air containers (Fig. 2.1). If the size and construction do not

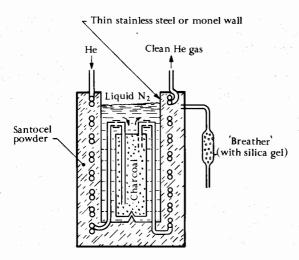


Fig. 2.1. A charcoal purifying trap cooled by liquid nitrogen.

allow evacuation, or if the vacuum that can be maintained is only of the order of a few Torr, a powdered insulator such as Santocel (Monsanto Chemical Company) provides good insulation by reducing conduction, convection, and radiation across the space between the walls.

Small conveniently shaped liquid-nitrogen containers can be cut from an 'exploded' polystyrene plastic, e.g. Styrofoam (Dow Chemical Company). Cutting may be done with a 'cork-borer' type of cutter, hacksaw blade, hot wire, etc. When cementing pieces of foamed plastic together, care should be taken with the type of glue used: polystyrene foams dissolve very readily in many organic solvents so that water-based glues or those recommended by the manufacturers are used. Polyurethane foams are not readily soluble. Great care should be exercised if liquid air or oxygen is to be put into such vessels. Many foamed plastics are highly inflammable in such a situation, although *some* polyurethane foams are relatively safe.

The thermal conductivity of powder insulators at atmospheric pressure and of foamed plastics are similar, being c. 20 mW/m K ($200 \mu\text{W/cm K}$) at an average temperature of 180 K (e.g. Fulk 1959 and Ch. II below). The conductivity of powders falls to less than 2 mW/m K when evacuated to pressures below 1 Pa

(\sim 0·01 Torr). Superinsulation has an effective conductivity in high vacuum of less than 0·1 mW/m K (1 μ W/cm K).

Liquid-hydrogen containers

Apart from its inflammable nature and small latent heat, liquid hydrogen poses an additional problem when storage for any appreciable period of time is desired. Hydrogen contains molecules of two different kinds, *ortho*-hydrogen and *para*-hydrogen, in which the spins of the two protons are respectively parallel and antiparallel. Due to the different energies of the two states, the equilibrium concentration varies from 100 per cent *para*-hydrogen at or below 20 K to about 25 per cent *para*-hydrogen at room temperature. At liquid-nitrogen temperature the states are almost equally probable.

In the absence of a catalyst the rate of conversion is relatively slow with a time constant of the order of 50 h, so that normal hydrogen gas cooled from room temperature, liquefied, and transferred to a storage container may contain nearly 75 per cent ortho-hydrogen when first stored. Over a period of days, orthopara conversion occurs with a heat of transformation of 670 J/g (see Larsen, Simon, and Swenson, 1948, for determination of rate of conversion and evaporation) to be compared with a heat of vaporization of 440 J/g. After 2 days nearly 30 per cent of the liquid has been lost purely due to this internal process. Obviously ortho-para conversion is important in large installations where economy demands efficient liquefaction and storage (e.g. Scott, Denton, and Nicholls 1964).

A good example is the large hydrogen liquefier at the National Bureau of Standards in Boulder, Colorado, where it was shown that ferric hydroxide is an efficient catalyst to promote conversion in the liquid immediately after liquefaction (Weitzel, Van Valin, and Draper 1960). The large liquefiers listed in *Liquid hydrogen* (p. 246, International Institute of Refrigeration, Pergamon Press, Oxford, 1966) all use this catalyst or iron oxide. Other magnetic materials such as chromic oxide, iron–nickel alloys, oxygen, etc., can also catalyse the conversion and this can be a nuisance in storage vessels and transfer tubes when conversion is not wanted (Croft and Robertson 1969).

The use and storage of liquid hydrogen are now rather uncommon on the laboratory scale but the occasional user should be

aware of the storage problems; these include the fact that metal dewars often seem to have a larger heat leak with liquid hydrogen in them than with helium, probably because of slow release of dissolved hydrogen gas from the walls into the vacuum space and the absence of cryopumping (cf. Scott 1957). These and safety problems are dealt with more fully by Scott, Denton, and Nicholls (1964) and Croft (Ch. 2 of Bailey 1971).

Liquid-helium dewars for research cryostats

Various research investigations require dewars of various shapes and sizes as will be seen in Chapter VI which discusses cryostat design. The evaporation rate of the refrigerant is not usually a prime consideration provided it is not so high as to require frequent refilling. Metal dewars may be chosen if the geometry is complicated by a need for X-ray or optical windows, narrow tails, etc. Conventional shapes can also be made in metal but may be more easily and cheaply provided in glass.

Glass dewars do pose one problem. Helium gas diffuses through glass, the diffusion rate in the hard boro-silicate glasses being quite high (see Keesom 1942, for references and data; also Rogers, Buritz, and Alpert 1954). Whereas the diffusion rate at room temperature for soft glass and for Jena 16 III measured in cubic centimetres diffusing per second through $1~\rm cm^2$ of wall 1 mm thick with 1 atm pressure difference is about 0.4×10^{-12} , it amounts to 0.5×10^{-10} for Pyrex.

Fortunately the diffusion rate decreases very rapidly with temperature and most of the inner wall of a helium dewar is well below room temperature, much of it at $4\,\mathrm{K}$. It is found in practice that a figure of $\sim\!100\,\mathrm{h}$ or $6\!-\!10$ days of research operation are quite feasible with a Pyrex dewar before it becomes sufficiently 'soft' that the evaporation rate is markedly higher and therefore needs re-evacuation. The English Monax glass and its near equivalent in the United States, Kimball N51A glass, are both much less permeable (Lane and Fairbank 1947), but are not always readily available in the sizes required for making experimental dewar vessels.

To illustrate the helium evaporation rates which may be encountered in experimental research, Fig. 2.2 shows a rather typical glass helium dewar pumped to a high vacuum and surrounded by a dewar vessel filled with liquid nitrogen. The helium

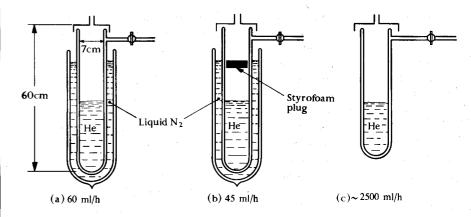


Fig. 2.2. Rate of evaporation of liquid helium from a glass dewar.

dewar is 60 cm in length and 7 cm internal diameter; it is approximately half-filled with liquid helium and is (a) silvered except for a 1-cm-wide viewing slit along its length, (b) as before but having a loose-fitting plug of styrofoam, 5-cm thick, suspended about 12 cm from the top of the dewar, (c) silvered except for the slit but not surrounded by liquid nitrogen. Some approximate figures for evaporation rate in millilitres of liquid helium per hour are shown on the figure.

To simplify the repeated re-evacuations necessary in Pyrex dewars, the writer has found the following arrangement satisfactory. A short glass side-tube is provided near the top of the dewar, to which a small stop-cock is attached by plastic tubing. The flexible connexion reduces the chance of breakage; the vacuum space is flushed with air and re-evacuated for a few minutes on a mechanical pump or a diffusion pump after every 6 to 7 days of experimental use. In other cases an extended glass 'pip' may be put on the tail of the dewar for repumping but should be sufficiently extended that it can be broken and resealed without introducing strains into the bottom of the dewar. Unless the dewar is also to be used with liquid air, the degree of vacuum is not important as the liquid helium rapidly freezes out any air left in the vacuum space. Indeed, it is often convenient to leave about 1 mm air pressure to assist pre-cooling by the liquid air in the outer dewar.

Metal dewars do not suffer from this 'diffusion' problem.

However, they are more difficult to make in a completely vacuum-tight condition. After sealing, slow evolution of gas from the metal walls makes it necessary to have either a charcoal adsorber cooled by liquid air or cryopumping by the contained liquid helium. Materials normally used in construction are 18/8 stainless steels (AISI 321 or 347) for the inner walls which need to be of low conductivity, high-conductivity copper or aluminium for the radiation shields, and brass, aluminium, or stainless steel for the outer vacuum jacket. A liquid-air chamber is usually provided to cool the radiation shield but effective use of the evaporating helium gas can make this unnecessary; for example Fradkov (1962) has described a metal dewar which has no liquid air but has two radiation shields attached at suitable levels in the neck and an evaporation rate of only 60 ml/h.

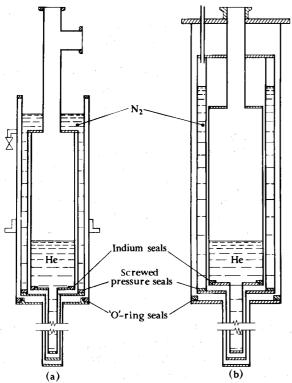


FIG. 2.3. Schematic diagrams of two common types of metal cryostat. Both have demountable tail sections.

Metal dewars of straight cylindrical shape or with narrow tails, windows, rotating bottoms, demountable bottoms, etc., can now be bought in standard sizes or made to specific dimensions by a number of firms (see Appendix). Figure 2.3 illustrates schematically two dewars which are demountable in that their tail sections can be removed and replaced by others. In some commercial dewars the surfaces exposed to the vacuum are gold-plated to preserve a low emissivity and low radiative heat inflow. Addition of aluminium foil or superinsulation can assist this.

Liquid-helium storage dewars

Obviously the relatively high evaporation rates make dewars of the type shown in Fig. 2.2 unsuitable for long-term storage. Even when fully silvered and surrounded by liquid nitrogen, the large heat inflows down the neck of a cylindrical dewar produce evaporation rates which over a 24-hour period leave little liquid helium.

In 1951 at the Westinghouse Research Laboratories, Wexler and his collaborators analysed the problem of heat inflow; their analysis led to the design and construction of a spherical metal dewar of 12.5-litre capacity which when surrounded by liquid nitrogen gave an evaporation rate of only 100 ml of liquid helium per 24 h (Wexler 1951; Wexler and Jacket 1951). This very low evaporation was obtained using a 20-cm length of 16 mm diameter inconel tube (0.25 mm wall) as the dewar neck, blackening the inner surface of the tube to prevent any 'funnelled' radiation reaching the helium, and also inserting a metal test-tube down the neck as a further radiation trap. They showed that this residual evaporation was due principally to radiation from the liquid-nitrogen-cooled outer sphere to the inner highly polished copper sphere. Thermal conduction down the narrow inconel tube is quite small as fairly efficient heat exchange occurs between the evaporating cold helium gas and the tube wall.

In dewars with relatively wide or short necks the evaporation rate can be lowered considerably by placing vapour-cooled radiation baffles near to the 80 K temperature-level in the neck (Lynam *et al.* 1969). The large dewars (~10001) use the cold helium vapour to cool radiation shields in the vacuum space.

As a result of this work by Wexler, many manufacturers now produce liquid-helium storage vessels of $10-10\ 000$ litre capacity

with evaporation rates of c. 1 per cent of their capacity per day. Evaporation of liquid nitrogen or air from the shield vessel makes it necessary to refill this about once a week. Storage dewars are also available with superinsulation in place of the liquid nitrogen; these have helium evaporation rates of 2–3 per cent of capacity per day; such vessels are much lighter and more suitable for transport by air.

Plate IV (facing p. 43) shows a 251 liquid-helium container with a transfer tube and rubber bladder for producing an overpressure to force liquid helium through the tube. When the transfer tube is removed, the central vent is connected by rubber tube to the helium gas storage system or sealed with a non-return valve to stop air or water condensing in the neck. Likewise condensation in the liquid-nitrogen vents is prevented by the length of rubber tubing which has a 5 cm slit in it to allow evaporated nitrogen-gas to escape.

To avoid the necessity of recooling the inner helium container from 77 to 4 K (requiring several litres of liquid helium) it is desirable to leave a small quantity of liquid helium in the dewar. Of course this is no longer true when there is an interval of weeks between successive transfers of liquid helium.

Gonzalez, White, and Johnston (1951), have described low-evaporation-loss containers which can be constructed by modifying standard liquid-air dewars (Fig. 2.5).

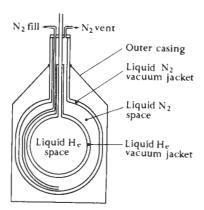
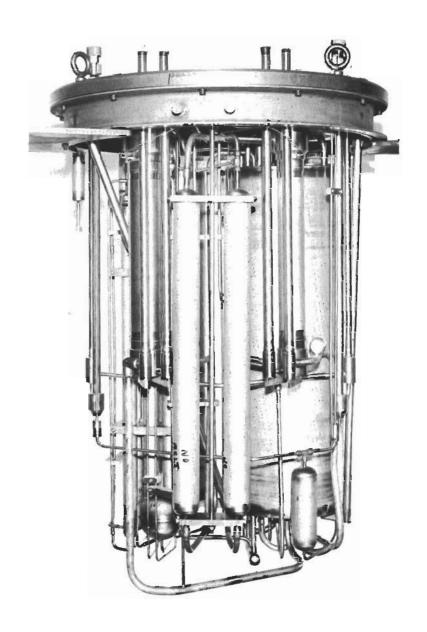
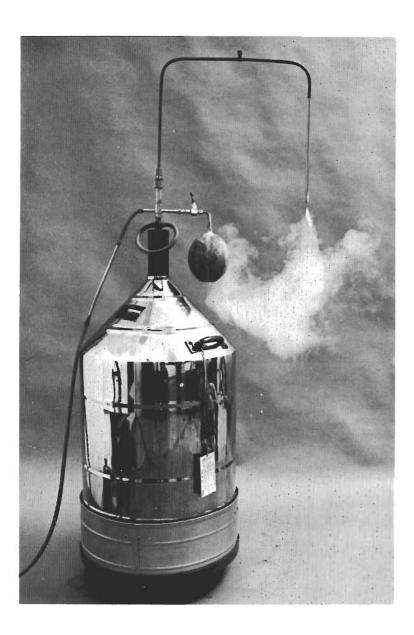
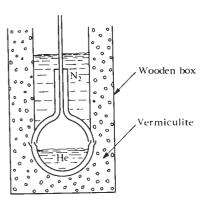


Fig. 2.4. A commercial metal dewar for the storage of liquid helium or liquid hydrogen.







F_{1G}, 2.5. A commercial copper (liquid-air) dewar modified for storing liquid helium (Gonzalez, White, and Johnston 1951).

2. Transfer siphons

Introduction

In low-temperature physics, the term 'transfer siphon' has come to mean a tube suitable for transferring low-boiling-point liquids without serious loss by evaporation, although the actual transfer is usually initiated and sustained by a gas overpressure rather than by a siphoning action.

Apart from ease of construction and mechanical reliability, the design of a transfer tube is largely governed by loss considerations; the total heat of the inner wall of the transfer device and the total heat inflow to the stream of liquid during transfer should be small in comparison with the latent heat of vaporization of the liquid being transferred.

Liquid air

If liquid air, nitrogen, or oxygen is being transferred a distance of a metre in a quantity of a litre in 10 or 15 s, then the tube can be simply a length of thick-walled rubber tube (6 mm i.d., 15 mm o.d.). The inner wall of such a rubber tube rapidly freezes hard so that the tube is rigid, but due to its poor heat conductivity the outer surface remains relatively warm and pliable during a brief period of transfer—say about 1 min required to fill a 4-litre flask with an overpressure of $\frac{1}{4}$ to $\frac{1}{2}$ atm on the storage container; thin-walled rubber tubing will freeze hard, become brittle, and may fracture. Alternatively, any metal tube which can be bent to

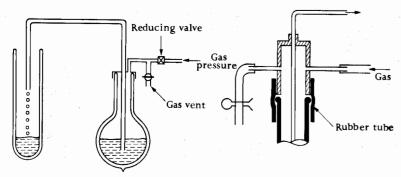


FIG. 2.6. The transfer of a liquefied gas; inset shows a simple brass coupling for use with a narrow-necked metal dewar.

the required shape is suitable for liquid-air transfer, but if the transfer tube is to be left in the storage container over long periods of time, it is desirable that the tube in the neck of the container should be a low-heat-conductivity alloy—monel, stainless steel, cupro-nickel. If the liquid-air transfer is to be rather slower and occupy many minutes, then a wrapping of glass wool, asbestos tape, etc., may be sufficient to make the losses negligible.

When the transfer is of long duration and/or over an appreciable distance, more efficient insulation is desirable. A very convenient covering for the metal tube is a flexible foamed plastic such as Armaflex (Armstrong Cork Company, Pennsylvania). In the form of tube this slips onto the metal pipe easily and seals against condensation of moisture. Other foam or powder insulators are thermally efficient but are often more difficult to attach to the transfer tubing.

Double-wall metal vacuum siphons are laborious to construct and are therefore more commonly reserved for liquid hydrogen and helium (see below), but can be used for liquid air provided that there is some adsorbent charcoal exposed in one or other end of the vacuum enclosure to act as a cryopump (Jones and Larsen 1948). The tubes and charcoal should be well warmed with a flame to outgas them during evacuation and prior to sealing off. With the aid of petrol (or refrigeration) unions a number of such tubes, either straight or bent, can be joined together to carry liquid air from storage flasks to various points where it is required.

In the case of liquid air it is most common to use compressed gas from cylinders or supply lines, to force the liquid through the transfer siphons. If such transfers are fairly frequent, the process of pressurizing and depressurizing the container at each transfer both wastes and frequently contaminates the liquid. In cases where cost and purity are important it is convenient to leave the container sealed by a spring-loaded blow-off valve—designed to blow-off at $\frac{1}{4}$ atm; by means of a valve in the transfer tube, liquid can be drawn off under this pressure head when desired. A more expensive alternative is an electrically operated pump with a plastic impeller: these are available commercially.

Helium and hydrogen

In designing a transfer tube for liquid helium (or hydrogen), the much smaller latent heat of vaporization imposes extra restrictions. For example, if the inner wall of a transfer tube is stainless steel (atomic weight $\sim\!60$, density $\sim\!8$ g/ml, Debye temperature $\theta_{\rm D}\!\sim\!400\,\rm K$) of 3 mm o.d., 0·25 mm wall thickness, and length 2 m, then the enthalpy at room temperature of the tube is about 2700 J. If the latent heat of liquid helium only were to be used in pre-cooling this tube, about one litre of liquid would be needed. Fortunately, the heat capacity of the evaporated gas also does some cooling: each millilitre of liquid produces gas with a heat capacity at constant pressure of 0·65 J/K equivalent to an enthalpy at room temperature of 190 J. If we make use of half the cooling content of this gas then only c. 30 ml of liquid are needed for pre-cooling.

A simple way of making a transfer siphon is shown in Fig. 2.7 (Dowley and Knight 1963). Spacers of Teflon separate the two tubes of well-annealed stainless steel. They are bent using ice as a filler to stop crimping; alternatively Cerrobend or acetamide can be used as fillers during the bending. Dowley and Knight did not evacuate their siphon but relied on cryopumping. A rather similar siphon, produced by the Oxford Instrument Company, has a small brass side-arm for evacuation; in this side-arm is a 7-mm diameter steel ball-bearing resting on a rubber O-ring to act as a one-way valve.

For some years most of our transfer tubes have been made rather like that shown in Fig. 2.8 (Whitehouse *et al.* 1965). The inner tube of 3 mm diameter 0.3 mm wall, is annealed stainless

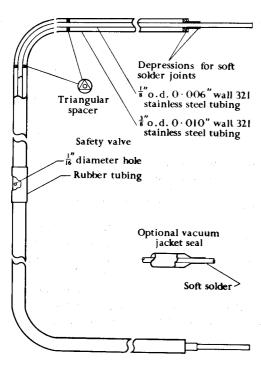


Fig. 2.7. Details of a transfer tube for liquid helium (after Dowley and Knight 1963).

steel and is wrapped with fishing line; the two coaxial tubes are bent around a radius as small as 6–8 cm without a filer. The inner tube is then pushed tightly up into the jacket while soldering the joints 'S'. This allows for differential thermal contraction on cooling which amounts to roughly 3 mm per metre. Care should be taken to remove all traces of flux after soldering. As can be seen from Plate IV, these transfer tubes can be made with quite long side arms to accommodate height differences between the storage dewar and the cryostat. Rubber O-rings provide a seal between the outer stainless-steel tube and the tops of the dewars.

Transfer tubes can be made with brass or copper elbows to avoid bending, as described by Stout (1954), Croft and Jones (1950), and Jacobs and Richards (1957). Flexible siphons are sometimes needed and can be made with corrugated (bellows)

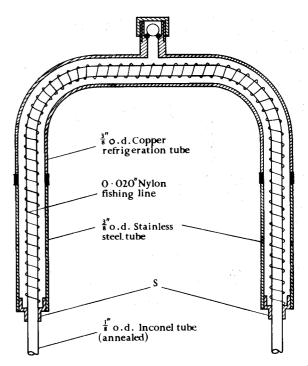


Fig. 2.8. A transfer tube for liquid helium, based on that described by Whitehouse et al. (1965).

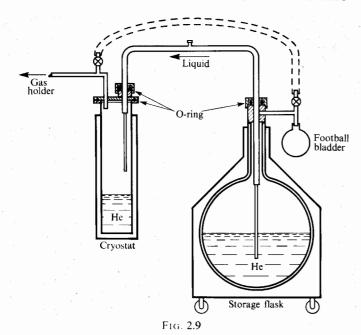
metal tubing or plastic from designs of Mathewson (1955), Kimber (1963), and Fradkov and Ginodman (1970) etc. and are also available commercially.

If the transfer of liquid helium takes only a few minutes then the amount of radiant heat reaching the liquid stream is not serious. If as in the example above, we assume an inner tube of 3 mm diameter, 2 m long and further assume that its emissivity $\varepsilon \approx 0.05$ and that it is exposed to room temperature radiation from a surrounding black body, then the heat inflow

$$Q = \sigma A \varepsilon (T_1^4 - T_2^4)$$

= 5.7 \times 10^{-8} \times 0.02 \times 0.05 \times 300^4
= 0.46 W,

which is enough to evaporate about 10 ml of liquid helium per minute.



The most common way of transferring liquid helium (and hydrogen) is shown schematically in Fig. 2.9. and in the photograph of Plate IV. The diagram includes provision for conserving the evaporated gas, that is a return line to a gas holder, O-ring seal in the cryostat, and a rubber bypass tube. Use of a rubber bladder to produce an overpressure in the storage dewar is a common practice and works well with helium and hydrogen; a fluctuating pressure applied with the fingers to the 'bladder' causes an oscillation of warm gas into the flask and maintains easily the pressure needed for transfer. In cases where a substantially higher overpressure is required, e.g. where the pressure in the gas holder (and therefore in the gas-return pipe and cryostat dewar) is relatively high, a gas cylinder with reducing valve can supply the overpressure required to force the liquid through the transfer tube.

Considerable care should be taken when first transferring liquid helium into either a warm dewar or into a partially filled dewar, otherwise litres of liquid can be evaporated needlessly. If the dewar is warm (say 80 K) and particularly if it contains

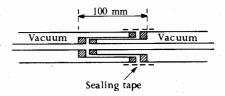


Fig. 2.10. A coupling for liquid helium (or hydrogen) transfer tubes.

equipment of large heat capacity, a slow initial transfer allows the cooling capacities of the liquid and vapour to be used more fully. If liquid is already in the dewar, a slow build-up of pressure in the storage flask (helped by closing the relief valve in Fig. 2.9 a few minutes beforehand) is essential to avoid having a warm stream of helium gas hitting the liquid surface. The novice is well advised to use a flow-rate meter or monitor on the gas recovery system to check the progress of the transfer. A little care can result in liquid collecting after, say, $\frac{1}{2}$ m³ of gas are evaporated (equivalent to $\frac{1}{2}$ litre of liquid helium).

A junction in a transfer tube is useful sometimes; for example when two parts of the siphon are permanently attached to the respective dewars from which and to which the liquid is being transferred. Fig. 2.10 shows a sleeve coupling which can be sealed against leakage by a strip of plastic type. A more elegant version incorporating springs and an O-ring seal is described by Cardoni and Baldacchini (1975).

A valve is sometimes required in a transfer siphon, for example when drawing off liquid helium from a liquefier. The example in Fig. 2.11 shows a stainless-steel needle (total taper 10°-20°) seating in cylindrical bush of brass or some other metal softer than the stainless-steel needle; this bush also seals the end of the double-walled vacuum siphon. The valve is actuated by a knurled brass piece which screws on to two brass sleeves, one soldered to the upper outside transfer tube and the other to the low-conductivity metal tube which moves the valve needle; one of the threads is right hand and the other is left hand, and a metal pin prevents the lower sleeve from turning as the knurled head is turned. Descriptions of such needle valves and also ball valves used for the same purpose have been given by Croft and Jones (1950), Scott and Cook (1948), and in the manuals of CTI-Cryogenics which describe their Collins liquefier.

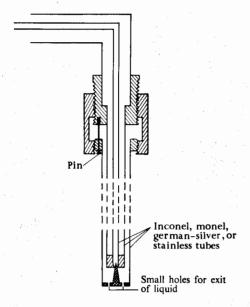


Fig. 2.11. A valve on a transfer tube.

3. Liquid-level indicators and depth gauges

Introduction

A number of devices for determining the level of a liquefied gas in a dewar have been described in the past few years; some of these have been suitable for only one or two liquids and others for most liquefied gases; some have been essentially discontinuous in nature, i.e. only registering when the liquid reaches a certain level, and other have been continuous recorders of level; some also have been used to actuate a transfer of liquid into the dewar. Many indicators are thermometric in principle, e.g. the change in vapour or gas pressure with temperature, or the change in electrical resistance or expansion of a bimetallic strip are used in level detectors which depend on the change in temperature at or near the liquid surface.

Examples

The devices most commonly used to give a continuous indication of liquid level or liquid depth depend on measurement of (a) hydrostatic pressure difference between bottom of liquid and vapour above it, (b) electrical resistance of a wire partially immersed in liquid, (c) electrical capacitance between coaxial cylinders immersed in the liquid and vapour, or (d) flotation.

In the hydrostatic pressure-head type of depth gauge, an oil-filled U-tube or some other form of differential manometer records the difference in pressure between the base of the column of liquid in the container and the pressure above the surface. These are universally applicable to liquids, but they are rather insensitive for those of very small density such as helium. Magnehelic pressure gauges (F. Dwyer Manufacturing Co., Indiana) have been used successfully for this purpose by Trujillo and Marino (1964), Lyon and Gillich (1965), etc. Cryenco (Division of CTI) use them on their commercial helium storage dewars.

Electrical resistance wires which give a continuous recording most conveniently are of materials which are superconducting in the liquid (helium) but have a relatively high and temperatureindependent resistance when they are in the normal state, that is above the liquid level. Although tantalum and vanadium wires of ~0.1 mm diameter have been used (e.g. Feldmeier and Serin 1948; Rovinskii 1961), it is easier to use an alloy such as manganin or constantan coated with Sn/Pb or In/Pb solder (Ries and Satterthwaite 1964; Chopra 1973; Rose-Innes 1973) or the niobium alloys (e.g. NbTi) used for superconducting magnets. One such in current use at the Clarendon Laboratory (Croft 1977, private communication) is Niomax CN A/61/05 from Imperial Metal Industries which is operated with an initial 1 s pulse of 150 mA to drive the wire in the vapour phase normal and then at half this current. A number of commercial firms listed in the Appendix, market depth gauges which use fine superconducting wires of similar type.

The other popular method of determining liquid depth is with the capacitance gauge which depends on the difference in dielectric constant of liquid and vapour, e.g. 1.05 for liquid helium and 1.00 for helium vapour. Most of these gauges have been two-terminal capacitors with one tube inside another (Fig. 2.12) with electrical detection by means of an LC meter (Meiboom and Obrien 1963; Preshkov, Vetchinkin, and Elkonin 1969; Blair and Matheson 1970) or an a.c. bridge (Capocci and Gugan 1967; Vrba 1971). Others have preferred the three-terminal capacitance in which a third guard (earth) tube surrounds the other two

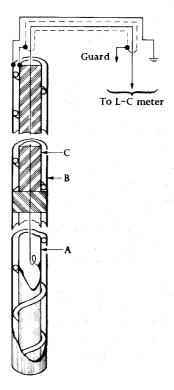


Fig. 2.12. Cylindrical capacitor depth gauge made from stainless-steel tubes and a nylon fishing line as a spacer (after Meiboom and O'Brien 1963).

coaxial (active) tubes and the signal is measured on a three-terminal bridge; this eliminates the influence of the lead capacitance (Williams and Maxwell 1954; see also Thompson 1958). Developments in the past decade in transistors and integrated circuits make many of the older detector systems obsolete. One which is currently used by colleagues of the writer and is relatively simple is shown in Fig. 2.13 (kindly supplied by I. Harvey, private communication). C is the coaxial capacitance in the cryostat (plus lead capacitance) and C_0 is selected to balance this approximately. A Wien-type oscillator (10^4 rad/s) supplies the bridge through an electrostatically-shielded ratio transformer with a 25-turn primary and 13+13 turn (centre-tapped) secondary. The amplifier following and amplifier-rectifier contain type 741 operational amplifiers. Note that the lead capacitance can be

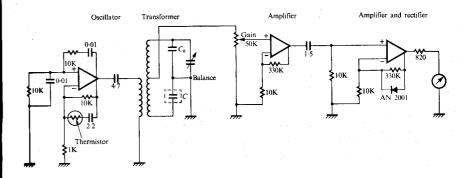


Fig. 2.13. Circuit for a capacitance depth gauge (I. Harvey, private communication); C is the coaxial capacitance in the cryostat.

balanced out and that drifts in it are less significant than the effects of temperature change on the dielectric constant of liquid helium.

Float gauges are another simple way of showing continuous changes in liquid level, using thin-walled metal bulbs or blocks of foamed plastics. Beads of foam plastic can also be useful for making a liquid surface more readily visible (Allen 1960).

For locating or detecting the liquid surface, rather than measuring depth, the simplest methods in increasing order of popularity are optical dipstick (e.g. Kitts and Harler 1954; Geake 1954), a semiconductor electrical detector (e.g. Maimoni 1956; Sauzade *et al.* 1965), and the diaphragm dipstick first described by Gaffney and Clement (1955).

For electrical detection a small carbon resistor (e.g. $56\,\Omega$ Allen-Bradley) on the end of a stainless-steel tube with a small bridge-circuit at the top was often used until the advent of transistors. Now it is more common to use a silicon transistor as a diode—showing the change in forward voltage with immersion in liquid helium by means of a LED (light-emitting diode) (Croft 1977, private communication).

The diaphragm device is shown in Fig. 2.14 and is easily made with a small piece of thin rubber sheet cut from a rubber glove which seals the top of a small brass cup at the end of an open tube of ~ 3 mm diameter. Spontaneous oscillations in the gas column (of helium) in the narrow tube cause the diaphragm to vibrate with a frequency which drops markedly when the tube

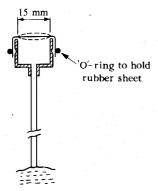


Fig. 2.14. A rubber diaphragm level finder for liquid helium (Gaffney and Clement 1955).

reaches the liquid level. Instead of rubber which perishes, thin brass shim (0.05 mm thick) can be used as the diaphragm and this produces an easily audible note. These should not be left sitting in the dewar of liquid because of the increased heat inflow which the thermal oscillations produce.

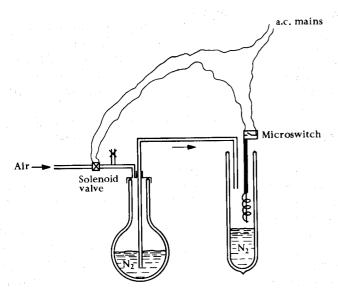
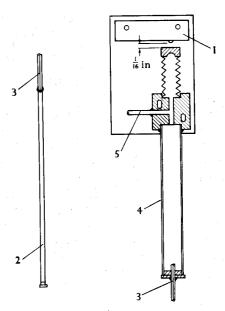


FIG. 2.15. Automatic transfer of liquid nitrogen (air, O₂) controlled by bimetallic strip.



F1G. 2.16. A liquid-nitrogen-level controller (after Davies and Kronberger 1952).

4. Liquid-level controllers

A type of level indicator which can also activate a transfer of liquid is very useful in many low-temperature laboratories. The problem of keeping liquid-air traps filled by some automatic process is often important, e.g. in charcoal purifiers, pre-cooling dewars, etc. Two simple devices for doing this are shown in Figs. 2.15, 2.16. In the first (based on that of Lounsbury 1951) a commercial bimetallic strip thermostat activates a microswitch relay; this in turn operates a solenoid valve allowing compressed air into a storage container, forcing the liquid across into the dewar. When the liquid reaches the bimetallic strip, the relay opens, the solenoid valve closes and the overpressure in the container is slowly released through a 'bleed' valve (e.g. needle valve which is slightly open) or by means of a second solenoid valve, and then the transfer stops.

An alternative to the bimetallic strip is the vapour-pressure controller (Fig. 2.16 after Davies and Kronberger 1952). Davies and Kronberger fill a small bulb (2) with a pressure of about 2 atm of the gas, the level of whose liquid phase is being

controlled; by having a relatively large dead volume (4) at room temperature they ensure that the operation of the microswitch does not depend too critically on the temperature of the vapour above the liquid surface. Other vapour-pressure controllers have been described by Jones (1948), Croft (1970, p. 116), Sherwood (1952), Roizen and Gannus (1962), etc.

Most of the level sensors discussed in the previous section can be made to operate a refilling system; descriptions of many occur in the pages of the periodicals Journal of Scientific Instruments (or J. Phys. E), Review of Scientific Instruments, and Cryogenics. Examples include the use of carbon resistors (Davies and Gosling 1963), thermistors (Flinn and Moore 1959), germanium diodes (Bose et al. 1974), floats (Leefe and Liebsen 1960), capacitance (Nechaev 1962), etc. Usually an electrical signal from the sensing system activates a valve (or heater) on the storage dewar or a valve on the gas-pressure supply line.

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CHAPTER III

HEAT EXCHANGERS

1. Introduction

While the topic of 'heat exchangers' is a very general one, the use of the word in low-temperature physics is usually confined to systems in which heat is transferred from an entering warm gas stream to a returning cold gas stream; the mathematical formulae developed for dealing with these systems can also treat cases where heat is transferred from a gas stream to a cold liquid bath. The problem of calculating desirable dimensions for countercurrent heat exchangers and for cooling coils is common to both the design of gas liquefiers and such associated equipment as purifying traps.

As was discussed (§ 1.2) above, the heat exchanger is essential in the Joule-Thomson process for liquefying helium; in the many cases where it is not essential, economy of operation makes the role of the heat exchanger very important. Generally we are faced with a task of reducing the wastage of 'cold' by utilizing the cooling capacity of returning gas streams to cool the incoming gas. In a liquefier these returning gas streams may be the cooled (but unliquefied) portion of the gas being circulated, or may be cold gas evaporated from a liquid refrigerant used in the cooling or purifying stages. For maximum efficiency in the interchange process a maximum amount of heat should be transferred from the incoming gas stream to the outgoing streams, so that the temperature of the outgoing gas at its exit approaches closely the temperature of the incoming gas at its entry point into the system. In Fig. 3.1 a warm gas enters at temperature T_1 and leaves at T_x , exchanging heat with a cold gas entering at T_0 and leaving at T_2 .

In the limit of maximum efficiency $T_2 \rightarrow T_1$ and temperature $T_0 < T_x < T_1$, but the value of T_x can only be found if the relative heat capacities of the two gas streams are known, i.e. the mass flow per second in each stream and the specific heat of the gas in each stream. Of course, in the case where the returning stream

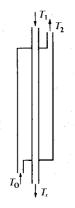


Fig. 3.1

has a greater heat capacity than the downflowing stream, then $T_x \to T_0$, and T_2 may be appreciably less than T_1 , but this is an artificial condition which is scarcely likely to arise in the cases with which we are concerned.

Associated with the calculation of efficiency of heat transfer is the calculation of the pressure drop for the gas flowing through the exchanger. It is generally necessary that the pressure drop be small in comparison with the total entry or exit pressure of the gas.

2. Calculation of pressure gradient and heat transfer

Pressure drop

Consider a gas of density ρ , viscosity η , flowing at a mass rate m in a circular pipe of diameter D and length L. Classical hydrodynamics and dimensional analysis show (e.g. Jakob 1949; McAdams 1954) that the pressure drop Δp is

$$\Delta p = \frac{1}{2} \psi \frac{LG^2}{D\rho} \quad \text{where} \quad G = \frac{4m}{\pi D^2}, \tag{3.1}$$

and ψ is a dimensionless factor which is given by

$$\psi = 64 \left(\frac{\eta}{GD} \right) \tag{3.2}$$

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for laminar flow (Poiseuille flow) or

$$\psi = 0.316 \left(\frac{GD}{\eta}\right)^{-0.25} \tag{3.3}$$

for turbulent flow (see Fig. 3.2).

The dimensionless factor (GD/η) is usually called the Reynolds number, denoted by Re. In the case of a straight pipe of circular section, the condition for turbulence is that Re>2300, but this critical Reynolds number varies considerably for different shapes of the carrying tube. In most applications to low-temperature equipment, Re>2300 and the flow will be turbulent, a fact that is assumed in the calculation of heat transfer coefficients given below.

For generality the equation for Δp may be extended to the case of non-circular section tubes, by defining a hydrodynamic diameter D_h given by

$$D_{\rm h} = 4 \times \frac{{
m cross-sectional~area~of~tube~considered~(A)}}{{
m total~perimeter~of~surfaces~in~contact}};$$
 with gas stream (P) (3.4)

then G is the mass flow rate per unit area, i.e. G = m/A, and

$$\Delta p = \psi L G^2 / 2\rho D_{\rm h}. \tag{3.5}$$

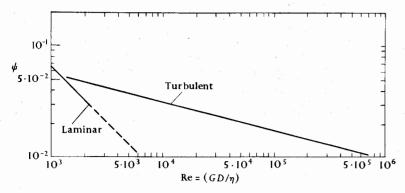


Fig. 3.2. The dimensionless factor ψ as a function of the Reynolds number.

Heat transfer coefficient

If the gas flowing through the tube is at a temperature different by an amount ΔT from the temperature of the tube wall, heat will be transferred at a rate

$$\dot{Q} = h\Delta T$$

where the coefficient h is the 'heat transfer coefficient'. For turbulent flow, the temperature is sensibly constant across the section of the tube and the major temperature difference occurs across the thin layer of gas at the tube surface. By dimensional arguments Nusselt (1909) related the heat transfer coefficient h to the thermal conductivity λ of the gas, the effective diameter $D_{\rm e}$, the dimensions of the tube, viscosity of the gas η , and its heat capacity $C_{\rm p}$. The effective diameter $D_{\rm e}$ is defined by

$$D_e = 4 \times \frac{\text{cross-sectional area of tube considered}}{\text{perimeter of surface to which the gas stream}}$$
transfers heat

(3.6)

so that in some cases $D_{\rm e}$ may be quite different from $D_{\rm h}$. For example, in the simple counter-current exchanger of two concentric tubes (in Fig. 3.3), the gas stream flowing in the annular space 1 will suffer a viscous drag due to surfaces of

perimeter =
$$\pi D_1 + \pi D_2$$
;

for our purposes the gas transfers heat only to the inner tube of perimeter πD_2 .

Therefore to calculate Δp , we use

$$D_{\rm h} = 4 \frac{(\pi D_1^2/4 - \pi D_2^2/4)}{\pi D_1 + \pi D_2} = (D_1 - D_2),$$

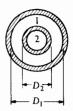


Fig. 3.3

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and to calculate h_1 , we use

$$D_{\rm e} = 4 \frac{(\pi D_1^2/4 - \pi D_2^2/4)}{\pi D_2} = \frac{(D_1^2 - D_2^2)}{D_2} \,.$$

Nusselt's equation for h in the dimensionless form is

Nu = const.
$$(Re)^x (Pr)^y (D_c/L)^z$$
,

where

Nusselt's number $Nu = hD_e/\lambda$,

Reynolds number Re = GD_h/η ,

and

Prandtl's number
$$Pr = \eta C_p / \lambda$$
. (3.7)

Experimental values for the constant and for the indices x, y, z have been obtained under various conditions. z is found to be extremely small so that $(D_c/L)^z \simeq 1$; it is also found that x = 0.8, $y \simeq 0.4$, and the constant has a value of about 0.02.

In the form given by McAdams (1954) for turbulent flow $hD_e/\lambda = 0.023(D_eG/\eta)^{0.8}(C_p\eta/\lambda)^{0.4}$. This can be reduced to the more useful dimensional form

$$h = \frac{0.023}{(\text{Pr})^{0.6}} C_p \frac{G^{0.8} \eta^{0.2}}{D_c^{0.2}}, \tag{3.8}$$

where h is in W/m² K if λ is in W/m K, C_p in J/kg K, etc.

General equations for heat interchange

By applying considerations of conservation of energy to a section of the exchanger shown in Fig. 3.4, an equation relating the heat transfer coefficients h_1 and h_2 of the two gas streams and their heat capacities m_1c_1 , m_2c_2 to the dimensions and temperature distribution may be obtained.

Here c_1 and c_2 are the specific heats of the gases, T_{L_1} is the entry temperature of gas stream no. 1 and T_{0_1} its exit temperature; similarly T_{0_2} and T_{L_2} are the entry and exit temperatures respectively of the second gas stream (upflowing stream). If this countercurrent exchanger consists of two concentric tubes, and the inner tube has an internal diameter D_1 and external diameter D_2 then (Mandl 1948)

$$L = \frac{\alpha}{\gamma} \ln \frac{T_{L_1} + \beta/\gamma}{T_{O_1} + \beta/\gamma}, \qquad (3.9)$$

where

$$\alpha = m_1 c_1 \left(\frac{1}{h_1 S_1} + \frac{\Lambda}{\lambda' S'} + \frac{1}{h_2 S_2} \right), \tag{3.10}$$

$$\beta = \left(\frac{m_1 c_1}{m_2 c_2} T_{0_1} - T_{0_2}\right),\tag{3.11}$$

$$\gamma = 1 - m_1 c_1 / m_2 c_2, \tag{3.12}$$

the heat-transfer perimeters

$$S_1 = \pi D_1,$$

$$S_2 = \pi D_2,$$

$$S' = \pi (D_2 - D_1) / \ln(D_2/D_1),$$

and the thickness of the wall of the inner tube is

$$\Lambda = (D_1 - D_2)/2;$$

 λ' = thermal conductivity of material of the inner tube.

An important and common case is when $m_1c_1 = m_2c_2$, i.e. when the same quantity of the same gas flows in each stream, then (3.9) reduces in the limit as $m_1c_1 \rightarrow m_2c_2$, to

$$L = \frac{\alpha}{\beta} (T_{L_1} - T_{0_1}). \tag{3.13}$$

In a more general case where the downflow is through n identical parallel tubes (each of inner and outer diameter D_1 and

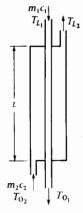


Fig. 3.4

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 D_2 respectively) and each carries a mass m_1/n of gas (3.9) and (3.13) are modified to become

$$L = \frac{\alpha}{\gamma n} \ln \frac{T_{L_1} + \beta/\gamma}{T_{0_1} + \beta/\gamma}$$
 (3.14)

and

$$L = \frac{\alpha}{\beta n} (T_L - T_0). \tag{3.15}$$

Physical data for gases

Values of the specific heat, thermal conductivity, and viscosity which are needed in calculating heat exchange can be found in Thermophysical properties of matter (Vols 3, 6, and 11, Plenum Press (1970–5)), Tables of thermal properties of gases (NBS Circular 564, US Govt. Printing Office (1955)), the Landolt-Bornstein tables, etc. The values are not very sensitive to pressure below 200 atm and C_p is also insensitive to temperature change. Table 3.1 gives some representative values of C_p , λ , η , and density ρ as well as Prandtl's number Pr at 180 K and 50 K. Note that $(Pr)^{0.6}$ seldom lies outside the range 0.8 to 0.9 which makes approximation possible in calculating h (eqn 3.8) particularly as η and D appear as $(\eta)^{0.2}$ and $(D)^{0.2}$ which will be fairly insensitive to change. The assumption that $\eta \sim 10^{-5}$ Pa s and $D \sim 0.01$ m leads to $(\eta/D)^{0.2} \sim 0.25$, and if $(Pr)^{0.6} \approx 0.85$, eqn (3.8) reduces to

$$h \approx 0.006 G^{0.8} C_{\rm p}.$$
 (3.16)

Summary of formulae:

$$\Delta p = \psi L G^2 / 2\rho D_{\mathbf{h}} \tag{3.5}$$

where

$$\psi = 64/\text{Re (laminar flow)}$$
 {(3.2)}

$$\psi = 0.316 (\text{Re})^{-0.25} \text{ (turbulent flow)}.$$
 (3.3)

or

$$h = \frac{0.023}{(\text{Pr})^{0.6}} C_{\text{p}} \frac{G^{0.8} \eta^{0.2}}{D_{\text{c}}^{0.2}} \quad (\text{Pr} = C_{\text{p}} \eta / \lambda)$$
 (3.8)

$$L = \frac{\alpha}{\gamma n} \ln \frac{T_{L_1} + \beta/\gamma}{T_{0_1} + \beta/\gamma} \quad (m_1 c_1 \neq m_2 c_2)$$
 (3.14)

$$L = \frac{\alpha}{n\beta} (T_{L_1} - T_{0_1}) \quad (m_1 c_1 = m_2 c_2), \tag{3.15}$$

Table 3.1

Values of heat capacity, density, viscosity, heat conductivity, and Prandtl's number for gases

	N ₂	O_2	H ₂	He
C _p (J/kg K) at 0° C	1038	916	14 200	5230
$\rho(kg/m^3)$ at s.t.p.	1.250	1.428	0.090	0.179
$\eta(10^{-6} \text{ Pa s}) \text{ at } 180 \text{ K}$	11.8	13.3	6.3	13.9
at 50 K		_	2.5	6.3
$\lambda (10^{-3} \text{ W/m K}) \text{ at } 180 \text{ K}$	16.5	16.5	116	107
at 50 K	4.9	4.5	36	46
$Pr = \eta C_p/\lambda$ at 180 K	0.74	0.74	0.77	0.68
at 50 K	- .,	_	0.84	0.72
			001	0 72

$$\beta = \frac{m_1 c_1}{m_2 c_2} T_{0_1} - T_{0_2}, \tag{3.11}$$

where

$$\gamma = 1 - m_1 c_1 / m_2 c_2, \tag{3.12}$$

$$\alpha = m_1 c_1 \left(\frac{1}{h_1 S_1} + \frac{\Lambda}{\lambda' S'} + \frac{1}{h_2 S_2} \right), \tag{3.10}$$

and

$$\simeq m_1 c_1 \left(\frac{1}{h_1 S_1} + \frac{1}{h_2 S_2} \right),$$
 (3.17)

where $S_1 = \pi D_1$, $S_2 = \pi D_2$.

Cooling of a gas stream by a liquid bath

The cooling of a gas by passing it through a coil immersed in a cold liquid is common; eqns (3.14) and (3.11) are easily simplified to give the cooling efficiency as a function of length. It is assumed that heat transfer both from the wall to the liquid and across the tube wall are very good in comparison with that from the gas stream to the wall of the carrying tube; then the second and third terms in the bracket on the right-hand side of (3.10) can be neglected. If the bath temperature be T' and a stream m of gas of specific heat c enters a tube at temperature T_L and leaves the tube (of length L) at temperature T_0 , then

$$L = \frac{mc}{hS} \ln \left(\frac{T_L - T'}{T_O - T'} \right), \tag{3.18}$$

where h is defined by eqn (3.8) and S is the inner perimeter of the tube. For a given efficiency, that is for given values of $(T_L - T')/(T_0 - T')$, the required length L is proportional to m/hS: so that, for a circular tube of diameter D,

$$L \propto m/hD \propto m/G^{0.8}D \propto D^{0.6}m^{0.2}$$

As the diameter is increased, the pressure drop in the gas stream decreases very rapidly (as $D^{-4\cdot25}$) and the required length increases slowly with diameter (as $D^{0\cdot6}$).

3. Methods of construction

Introduction

Many types of heat exchanger have been made but most appear to be derivatives of the two basic patterns mentioned in Chapter I—those of Linde and Hampson. In considering their relative merits, a number of factors must be borne in mind: (i) the relative difficulties of construction, (ii) the difficulty of mathematical analysis, (iii) the efficiency of heat transfer that can be obtained while keeping the pressure drop within reasonable bounds, (iv) the total mass and hence total heat capacity of the assembly. As far as factor (ii) is concerned, the Linde pattern lends itself to mathematical treatment, while in the Hampson pattern it is usually extremely difficult to make any theoretical estimate of the pressure drop or heat transfer in the low-pressure gas stream; thus in the latter case a combination of experience and experimental trial are needed to produce an efficient exchanger. The factor (iv) concerning heat capacity is particularly important in most laboratory liquefiers where a fairly short cooling-down time is desired; the time required to reach the equilibrium temperature distribution increases with the mass of the heat exchanger.

The Linde type of exchanger

Some examples of Linde-pattern exchangers are shown in Fig. 3.5. In (a), (b), and (c) the tubes are concentric and the outer wall contributes seriously to the pressure drop in the gas stream occupying the outer annular space, but assists very little in raising the heat transfer coefficient, since there is merely a touch contact between the inner tube and the outer tube. Frequently the central tube(s) is used for the high-pressure stream, and the low-pressure

stream occupies the annular space between the tubes; however, there are often advantages in a construction such as (c) where a large inner tube may be used for the low-pressure stream to minimize $\Delta p/h$ and the high-pressure flow is through a narrow gap between the tubes.

Those shown in (d) and (e) are solder-bonded parallel-tube exchangers which are also amenable to mathematical analysis and are efficient, provided that the solder-bonding between the tubes is adequate. These are most simply made by tying the tubes together at intervals of a few inches with a twist of wire and then drawing the long bundle of tubes slowly through a molten bath of soft solder. The solder bath may be contained in a length of channel iron supported above bunsen burners; care should be taken to clean the tube surfaces of dirt or grease and to wet them thoroughly with soldering flux before they enter the solder bath.

The Fig. 3.5f shows a section of a twisted-tube exchanger in which the inner tube is flattened and twisted into a 'corkscrew' shape before insertion into the outer jacket tube. This twisted tube exchanger was devised by Nelson over 60 years ago and first described by Bichowsky (1922).

In concentric tube exchangers, heat transfer in the outer space can be improved by winding a copper wire helically around the inner tube, and bonding it with soft solder. This increases the heat transfer surface and the turbulence, but also increases the pressure gradient.

Hampson exchangers

The Linde exchanger is at its greatest disadvantage when one gas stream is at low pressure—allowing only a small pressure gradient—and the flow rate is large. The Hampson-type exchanger largely avoids this by shortening the low-pressure return path of the gas stream. As mentioned before it is much more difficult to treat mathematically with any degree of accuracy and also must be constructed accurately with uniform spacing between the tubes that build up the spiral pancake pattern. The main heat exchanger used by Collins (1947) in his helium liquefier (see Ch. I and Plates Ia and Ib) is a particularly efficient type of Hampson exchanger in which the high-pressure tubing (6 mm diameter cupro-nickel) is 'finned' with copper ribbon and wound in a helix in the annular space between two co-axial

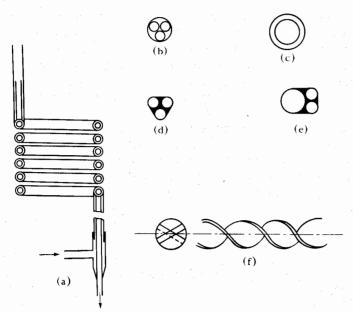


Fig. 3.5. Some heat exchangers of the Linde pattern.

cylinders of low thermal conductivity metal. The copper ribbon $(3\times1~\text{mm})$ is edgewound and solder-bonded to the high-pressure tubing, and with the aid of the cotton cord interwinding produces a good heat transfer between the low-pressure returning helium stream and the high-pressure tube. Finned copper tubing for heat exchangers is now produced commercially by Imperial Metal Industries Ltd. in the United Kingdom. Called Integron, the helical fin is rolled out of the wall of the parent tube; Cosier and Croft (1970) have described its use in a tight-wound countercurrent heat exchanger.

Another useful form of Hampson exchanger is the coiled-coil construction used in making very small and compact liquefiers (Parkinson 1955).

Others

A novel design in the Philips helium liquefiers (Vonk 1968) uses a stack of copper-gauze sheets interleaved with sheets of resin-impregnated paper. The stack is bonded with pressure and adhesive to form a 80 mm cube with a header at top and bottom

to guide gas into or out of the appropriate channels. This is not unlike the geometry used in some of the ³He/⁴He dilution refrigerators (Ch. VIII) where sintered metal powder or metal foil is stacked into the two counter-flow channels to increase the effective surface areas for heat transfer while preserving low viscous-drag.

Regenerative exchangers

In continuous-flow liquefiers, heat storage is not needed in the exchangers but in the Stirling-type or Gifford-McMahon refrigerators it is essential because the hot and cold streams do not flow continuously or simultaneously. Therefore their enthalpy must be stored briefly in part of the solid material of the heat exchanger. In the Philips air liquefiers, the regenerative exchangers contain tightly-packed copper gauze (Kohler 1960) but at lower temperatures materials with a higher heat capacity are needed, e.g. lead.

Numerous investigations into regenerative exchangers and suitable materials are described in the proceedings of the cryogenic engineering conferences, e.g. by Bretherton, Granville, and Harness (1971), and Lins and Elkam (1975).

Some general remarks

The material used for heat-exchanger tubing is largely dictated by the availability of tube of the required dimensions and by the fact that it must be bent, for most low-temperature equipment, into a helix or a spiral without splitting or crimping. Both copper and copper-nickel (annealed) bend easily and if a trial bend shows there is a danger of their crimping they may be filled with Cerrobend, Wood's metal, acetamide, or ice.

Copper may be an undesirable material in some instances because of its high heat conductivity. The heat flow along the exchanger due to thermal conduction should be negligible in comparison with the heat content of the gas stream. The formulae and the analyses which we indicated in § 2 are only valid if the exchange of thermal energy between the heat exchanger and the surroundings is very much smaller than the energy exchanged between the gas streams; this also implies that the exchanger should be in an evacuated chamber or in a stagnant gas atmosphere within a dewar vessel.

In the Linde type of heat exchanger, a rough calculation will often show that copper is quite acceptable as a tube material due to the long length of path which the heat must travel; in a Hampson exchanger the major heat conduction will occur along the walls of the two cylinders which enclose the annular space, and this usually necessitates the use of stainless steel, monel, or inconel for these walls.

4. Example of heat-exchanger analysis

(a) Helium heat exchanger operating between liquid oxygen and liquid hydrogen temperatures

In this example from a Linde liquefier illustrated by Fig. 3.6 helium at 20 atm pressure enters the heat exchanger at temperature $T_L = 90 \text{ K}$, flowing at 8 m³/h. The returning gas stream at a pressure of 1 atm enters the exchanger at temperature $T_{0s} = 15 \text{ K}$, the flow rate being 7 m³ (at s.t.p.)/h (assuming a liquefaction efficiency ε of 0.14). At the average temperature

$$\bar{T} = 52.5 \text{ K}$$

viscosity

$$\eta = 7 \times 10^{-6} \text{ Pa s}$$

$$\lambda = 46 \times 10^{-3} \text{ W/m K}$$

$$C_p = 5.23 \text{ J/g K}$$

$$\rho(\text{s.t.p.}) = 0.179 \times 10^{-3} \text{ g/ml.}$$

Hence

$$m_1 = 0.4 \text{ g/s}$$
 $\rho_1 = 1.8 \times 10^{-2} \text{ g/ml}$
 $m_2 = 0.35 \text{ g/s}$ $\rho_2 = 0.9 \times 10^{-3} \text{ g/ml}$.

High-pressure circuit

Assume the compressed gas flows through two inner tubes (n = 2) of copper, 1.5 mm i.d. in parallel.

Since

$$D_h = 1.5 \text{ mm}, \qquad G_1 = 11 \times 10^4 \text{ g/m}^2 \text{ s.}$$

Therefore

Re =
$$2.4 \times 10^4$$
 (turbulent flow)
 $\psi = 2.5 \times 10^{-2}$

 $m_1c_1(high pressure)$

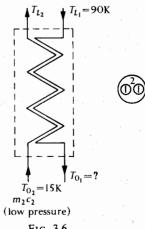


Fig. 3.6

and so, from (3.5)

 $\Delta p = 0.056$ atm/m length.

Also Prandtl's number

$$Pr = 0.80$$

and

$$D_c = 1.5 \text{ mm}$$

Therefore, from (3.8), the heat transfer coefficient

$$h_1 = 2.01 \times 10^3 \text{ W/m}^2 \text{ K}.$$

Low pressure circuit

The jacket tube of 5 mm i.d. cupro-nickel encloses the two copper tubes (2.4 mm o.d., 1.5 mm i.d.) so that the low-pressure stream flows through an annular gap of area = $\frac{1}{4}\pi\{(5^2) - 2 \times (2 \cdot 4)^2\}$ and total perimeter is given by $P = \pi(2 \times 2 \cdot 4 + 5)$.

Then

$$D_{\rm h} = \frac{4A}{P} = 1.38 \text{ mm}$$

and proceeding as before

$$\Delta p = 0.15$$
 atm/m.

HEAT EXCHANGERS

In the case of heat transfer, the effective perimeter is simply the circumference of the two inner tubes, i.e. the outer jacket is neglected.

Then

$$D_e = 2.8 \text{ mm}$$

and we obtain

$$h_2 = 0.69 \times 10^3 \text{ W/m}^2 \text{ K}.$$

Length L as a function of T

Assuming

$$\varepsilon = 0.14$$

so that

$$m_1c_1/m_2c_2=1.14.$$

Then from 3.11, 3.12, and 3.10

$$\beta = 1.14T_{0_1} - 15$$

$$\gamma = -0.14$$

and

$$\alpha = 0.4 \times 5.23 \left(\frac{1}{2.0 \times 10^3 \times 0.0047} \right) + \left(\frac{1}{0.69 \times 10^3 \times 0.0075} \right)$$

(using $S_1 = 4.7 \text{ mm}$, $S_2 = 7.5 \text{ mm}$).

Note that the second term in eqn (3.10), $t/\lambda\pi\bar{D}$, has a value which is negligible in comparison with the two terms involving h_1 and h_2 . Thence

$$L = \frac{\alpha}{\gamma n} \ln \left(\frac{T_{L_1} + \beta/\gamma}{T_{0_1} + \beta/\gamma} \right)$$
$$= 5.14 \log_{10} \frac{1.14 T_{0_1} - 27.6}{T_{0_1} - 15}$$

which for

$$T_{0_1} = 25 \text{ K gives } L = 5.37 \text{ m}$$

30 K gives $L = 1.83 \text{ m}$
35 K gives $L = 1.09 \text{ m}$.

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CHAPTER IV

TEMPERATURE MEASUREMENT

1. Introduction

ACCORDING to the zeroth law of thermodynamics any two bodies which are in thermal equilibrium with a third body are in thermal equilibrium between themselves; that is, when placed in thermal contact there is no transfer of heat from one to the other. Such bodies are said to be at the same temperature. A temperature scale may then be defined in terms of any of a number of thermometric properties of the system, and the scale and the size of particular temperature intervals may be fixed by reference to such common physical phenomena as boiling-points, meltingpoints, phase changes, etc. Thus the thermal expansion of a solid, liquid, or gas, the electrical resistance or thermoelectric power of a metal, and the magnetic susceptibility are all physical parameters which in the case of a particular chosen substance could be used to define a temperature scale, with the scale being a linear (or other chosen function) of the particular parameter for that substance. But, even if the same numbers on each of these scales were used to represent the temperatures of two or more chosen fixed points, there is no obvious reason why the different scales should agree at other temperatures or why any one of them should have a particular fundamental significance. Such a multitude of scales would be obviously rather unsatisfactory and very unsatisfying.

However, useful temperature scales can be based on the physical properties of particular systems and one particularly important scale depends on the properties of gases as determined experimentally: it has been found that at sufficiently low pressures the isotherms of gases are described by Boyle's law, i.e. the product of pressure and volume, pV, is constant. The 'perfect' or 'absolute' gas scale of temperature assigns numerical values to the temperature θ on the basis of the relation $\theta = a(pV)$ in the limit as $p \to 0$.

If it is then agreed that there shall be 100° between the ice

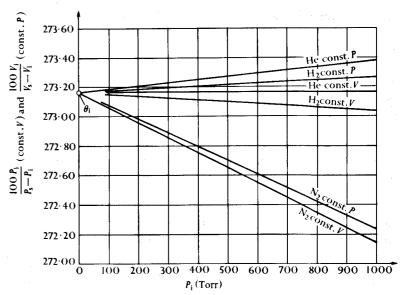


FIG. 4.1. The absolute ice point determined by graphical extrapolation (from Heat and thermodynamics, 2nd edn., by M. W. Zemansky. Copyright, 1943, McGraw-Hill Book Co.).

point and steam point, the constant a is fixed so that

$$a = \frac{100}{\lim(pV)_{s} - \lim(pV)_{i}}$$

and the ice-point temperature,

$$\theta_{\rm i} = 100 \frac{\lim(pV)_{\rm i}}{\lim(pV)_{\rm s} - \lim(pV)_{\rm i}}$$
.

For such a centigrade absolute gas scale, it has been found experimentally for a number of gases (see Fig. 4.1) that in the low-pressure limit, θ , has a value of $273 \cdot 15^{\circ}$.

The real significance of this scale goes beyond this apparent wide applicability to various gases. The second law of thermodynamics may be stated in the form 'that no heat engine operating in a closed cycle, can transfer heat from a reservoir at a lower temperature to a reservoir at a higher temperature'. From this follows an alternative statement that no engine can be more efficient than an ideal Carnot engine, which operating between

two reservoirs has an efficiency depending only on the temperatures of these reservoirs.

Such a Carnot engine, taking in heat Q_1 at a temperature θ_1 in a reversible isothermal process and rejecting heat Q_2 at temperature θ_2 , has an efficiency

$$\eta = 1 - \frac{Q_2}{Q_1} = f(\theta_1, \theta_2).$$

In such a Carnot cycle the two portions of the isotherms (Fig. 4.2) are bounded by a pair of adiabatic lines. It may be shown generally that

$$Q_1: Q_2: Q_3: Q_4: \dots = f(\theta_1): f(\theta_2): f(\theta_3); f(\theta_4): \dots$$

By identifying this ratio $f(\theta_1): f(\theta_2): f(\theta_3):...$ etc., directly with the ratio $T_1: T_2: T_3:...$ etc., a temperature scale independent of the system or of the working substance can be defined. This scale is called the Kelvin scale or absolute thermodynamic scale.

For a perfect gas, or for a real gas in the limit of low pressures, pV is a function of temperature only and hence the internal energy is only a function of temperature so that such a gas could be used as the working substance in a Carnot cycle. It can be shown that

$$\frac{T_1}{T_2} = \frac{\theta_1}{\theta_2}.$$

In 1887 the International Committee of Weights and Measures adopted as the standard thermometric scale, the Centigrade Scale of the hydrogen gas thermometer, having for fixed points the melting point of ice (0°) and the steam point (100°) (review by

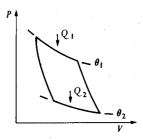


Fig. 4.2. A Carnot cycle.

Quinn and Compton 1975). In 1948 they changed the name of the unit from degree Centigrade to degree Celsius.

On the thermodynamic scale there is a temperature at which the heat Q_1 taken in (Fig. 4.2) is zero and this corresponds to a temperature $T_1 = 0$, called the absolute zero of temperature. That such a temperature exists follows from the second law; that such a temperature is unattainable in a finite number of steps follows from the third law, as was discussed at the beginning of Chapter I.

Kelvin proposed in 1854 that since the absolute zero constituted one fixed point, only one other was necessary to establish a thermodynamic scale. Giauque proposed this again in 1938 and finally in 1954 the Tenth General Conference of Weights and Measures adopted the proposal, using the ice-point or triplepoint of water (0.01 °C above the ice-point) and relegating the steam-point to secondary reference status. So that now to quote from Preston-Thomas (1976), 'The unit of the fundamental physical quantity known as thermodynamic temperature, symbol T, is the kelvin, symbol K, defined as the fraction 1/273·16 of the thermodynamic temperature of the triple point of water. For historical reasons, ... it is common practice to express a temperature in terms of its difference from that of a thermal state 0.01 kelvins lower than the triple point of water. A thermodynamic temperature expressed in this way is known as a Celsius temperature, symbol t, defined by

$$t = T - 273 \cdot 15$$
.

The unit of Celsius temperature is the degree Celsius, symbol °C, which is, by definition, equal in magnitude to the kelvin ...'.

The realization of thermodynamic temperatures above 1 K was achieved by means of the constant volume gas thermometer until the 1960s when other methods such as measurement of acoustic velocities in gas, thermal noise in solids, and magnetic susceptibilities were begun. These are all difficult to carry out with high precision and generally cannot match the reproducibility, ease of measurement, and sensitivity of the electrical resistance as a temperature sensor. However properties like electrical resistance are not simple functions of thermodynamic temperature so that many 'fixed points' are needed for their calibration and these

points now form the present International Practical Temperature Scale.

2. International practical temperature scale

The first practical scale adopted by the 1927 Conference on Weights and Measures was based on the ice point $(0 \,^{\circ}\text{C})$ and the steam point $(100 \,^{\circ}\text{C})$ with the electrical resistance, R, of platinum as a means of interpolation. R was to be expressed in the Callendar equation or its equivalent, namely $R_t = R_0(1 + At + Bt^2)$ for $T > 0 \,^{\circ}\text{C}$. To quote from Hall (1956):

the original aim of the international scale was to provide a practical scale of temperature reproducible to very high accuracy and as nearly as possible identical with the thermodynamic Celsius scale. That is to say, it should be identical with the thermodynamic Celsius scale to within the limits of measurement with the gas thermometer, but it should offer the higher reproducibility obtainable with such instruments as the platinum resistance thermometer, not in themselves capable of defining an absolute scale.

Later the boiling point of oxygen $(-182.97 \,^{\circ}\text{C})$ was added to extend the scale below $0\,^{\circ}\text{C}$ and the Callendar-Van Dusen equation (or its equivalent) used to express R(t) in the region from $0\,^{\circ}\text{C}$ to $-183\,^{\circ}\text{C}$:

$$R_t = R_0 \{ 1 + At + Bt^2 + C(t - 100)t^3 \}.$$

Then the triple point of water $(0.01 \, ^{\circ}\text{C})$ was substituted for the ice point and in 1968 the IPTS was extended down to $13.81 \, \text{K}$ with the platinum thermometer (PTR) still as the standard instrument. A simple polynomial could no longer express R(T) adequately for this whole range down to $13.81 \, \text{K}$. Instead the basis of T_{68} was a table of values of reduced resistance

$$W(T_{68}) = R(T_{68})/R_{273 \cdot 15}$$

calculated from the weighted mean of the W values for a group of eight particular PTRs. The table was later expressed as a reference function

$$T_{68} = \sum_{i=0}^{20} a_i \left(\frac{\ln W_{\text{CCT-}68}(T_{68}) + 3.28}{3.28} \right)^i,$$

coefficients of which are given in the amended edition of the text of IPTS-68 (see Preston-Thomas 1976). Any other PTR can then

TABLE 4.1

Defining fixed points of IPTS-68 and 1976 Provisional Scale (where different)

	$T_{68}(K)$	$T_{76}(K)$
Triple point of water	273.16	
Condensation point of oxygen	90.188	
Triple point of argon	83.798	
Triple point of oxygen	54.361	
Boiling point of neon	27.102	
Triple point of neon		24.559
Boiling point of equilibrium hydrogen	20.28	20.2733
e-H ₂ with vapour pressure of 25/76		
standard atm.	17.042	17.0372
Triple point of e-H ₂	13.81	13.8045
Superconducting transition (T_c) of lead	_	7.1999
Boiling point of ⁴ He		4.2221
T _c of indium	_	3.4146
T _c of aluminium	_	1.1795
$T_{\rm c}$ of zinc	_	0.851
T _c of cadmium	·	0.519

be calibrated in terms of T_{68} by measuring R at the various defining fixed points 13.8, 17.0, 20.28 K, etc. (see Table 4.1), determining the deviations W of the measured values from the IPTS-68 tabulation (or reference function) and using interpolation formulae in between these points. The rather involved procedures are discussed in various articles in Metrologia (e.g. Orlova $et\ al.$ 1966; Preston-Thomas and Bedford 1968; Kirby and Bedford 1972; Preston-Thomas 1976). The extension of the scale had a beneficial effect in stimulating better measurements of the thermodynamic temperatures of the fixed points by means of gas, acoustic, and magnetic thermometry. Table 4.1 shows not only the defining points of IPTS-68 but also 'improvements' (called T_{76}) recommended by the Consultative Committee on Thermometry in 1976 (Durieux $et\ al.$ 1976).

3. Thermodynamic temperatures and national scales

Before 1968, there were four distinct temperature scales used below 90 K, each based on gas thermometry. These were: NBS-55, established at the National Bureau of Standards, Washington,

by Hoge and Brickwedde (1939), and later lowered by 10 mK in 1955, PSU-54 at Pennsylvania State University (Moessen, Aston, and Ascah 1954), PRMI-54 at the Physico-Radio-Technical Measurement Institute, Moscow (Borovick-Romanov, Orlova, and Strelkov in *Temperature* 3, 13, 1962), and NPL-61 at the National Physical Laboratory, Teddington (Barber and Horsford 1965). These scales were intercompared in 1964 at both the NPL and PRMI with platinum thermometers calibrated on the various scales and this revealed differences of up to 40 mK (see Fig. 4.3 from Bedford *et al.* 1969). When adjusted to common oxygen and hydrogen boiling-points, the differences were reduced and a

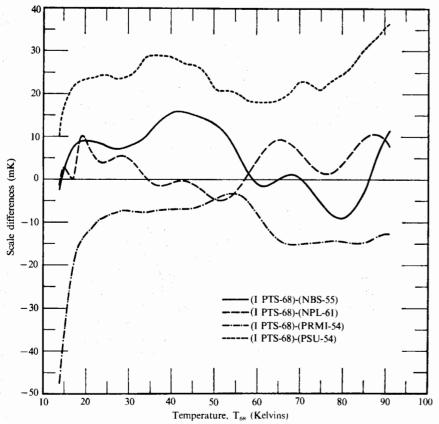


Fig. 4.3. Differences of the temperature scales NBS-55, NPL-61, PRMI-54, and PSU-54 from the IPTS-68 (after Bedford *et al.* 1969).

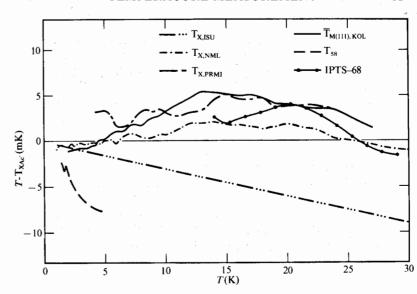


Fig. 4.4. Comparison of magnetic and practical temperature scales with the ISU Magnetic scale, T_{XAc}, (after Besley and Kemp 1977).

mean scale was calculated down to 13.8 K and called IPTS-68.

Internationally accepted helium-vapour pressure scales were also in existence prior to 1968 (see also § 4.5): T_{58} was based on the vapour-pressure of 4 He between 0.5 and 5.2 K and T_{62} on the vapour-pressure of 3 He from 0.3 to 3.3 K. Because of the gap between 5.2 and 13.8 K, the disparities between these four national scales and evidence of lack of smoothness (in thermodynamic terms), there have been important efforts to establish better thermodynamic temperatures using constant volume gas thermometry and magnetic susceptibility: these have included:

- (i) The NML gas thermometer at the National Measurement Laboratory, Sydney, (Rogers *et al.* 1968) from 2 to 24 K and linked to NBS-55.
- (ii) The PRMI gas thermometer in Moscow (Astrov, Orlova, and Kytin 1969) from 4.2 to 20 K, tied to the normal-hydrogen boiling point.
- (iii) The NBS Acoustic Scale in Washington (Plumb and Cataland 1966) which was based on isotherms of the speed of sound in helium gas from 2 to 20 K as a function of pressure.

- (iv) The NPL-75 gas scale was based on isotherms as a function of pressure taken at 20·271 K and other temperatures from 2·6 to 27 K (Berry 1978).
- (v) ISU Magnetic Scale (Cetas and Swenson 1972) which used the susceptibilities of the paramagnetic salts CMN (cerium magnesium nitrate), CMA (chromium methylammonium alum), and MAS (manganous ammonium sulphate) from 0.9 to 34 K. The constants were determined by tieing them to NBS-55 from 18 to 34 K. The scale was called $T_{\rm X,ISU}$. Later it was adjusted to correspond more closely to both IPTS-68 above 27 K and to the data of Berry with a scale denoted by $T_{\rm XAc'} = 1.0003~T_{\rm X,ISU}$.
- (vi) NML Magnetic Scale (T_{X,NML} by Cetas 1976) was established in Sydney from 1 to 83 K using MAS and gadolinium sulphate, being best-fitted to IPTS-68 over the range 27 to 63 K.
- (vii) KOL Magnetic Scale at the Kamerlingh Onnes Laboratory, Leiden, which used gadolinium and manganous salts from 1·7 to 20 K (van Rijn and Durieux in *Temperature* 4, 73, 1972) tieing to IPTS-68 at 13·81 and 20·28 K.
- (viii) PRMI Magnetic Scale in Moscow (Shkraba et al. 1974) which used MAS from 2 to 30 K and was best fitted to IPTS-68 from 13.8 to 30 K.

All of these scales were intercompared from $1\cdot 1$ to $30\,\mathrm{K}$ by Besley and Kemp (1977) at NML using 30 germanium thermometers which originated in the various national laboratories and the deviations of the magnetic scales and IPTS-68 from the ISU magnetic scale ($T_{\mathrm{XAc'}}$) as a base are shown in Fig. 4.4 to be less than 5 mK. They appear to be internally smoother than the gas scales because of finer resolution and if all had been fitted to common reference temperatures, agreement might be of the order of $\pm 1\,\mathrm{mK}$ (Besley and Kemp 1977). For this reason they were selected to form the basis of the 1976 Provisional Scale from 0.5 to $30\,\mathrm{K}$ (EPT-76 in Durieux et al. 1977) which is represented by the fixed points in Table 4.1.

Unfortunately accurate realization of many of these fixed points is difficult and beyond the scope of the average research laboratory; these difficulties include problems of supercooling and impurities in oxygen and argon, isotope effects in neon and ortho-para equilibrium in hydrogen (e.g. Ancsin 1977). The superconducting fixed points are more accessible, because the National Bureau of Standards (through its Office of Standard Reference Materials in Washington) sells a device SRM 767 composed '... of small cylinders of pure lead, indium, aluminium, zinc and cadmium mounted in a threaded copper stud and enclosed by a mutual inductance coil ...'. These transitions and the boiling point of ⁴He can be used to calibrate other secondary sensors below 7·3 K or for checking an existing calibration.

Some of the national laboratories mentioned above in § 4.3 calibrate thermometers commercially below 90 K. At present the national laboratories are trying to improve the thermodynamic realization of the fixed points in the range 1 to 90 K by gas and noise thermometry; magnetic thermometers can be used for interpolating the thermodynamic scale in this region. For practical purposes there is also the search for simpler calibration procedures for the secondary thermometers.

4. Gas thermometry

Introduction

Gas thermometry with a level of precision of 2 mK or even 10 mK is very difficult to achieve because of uncertainties in surface absorption of gas in the containing bulb, effective dead volume of the connecting tube, expansion corrections for the bulb, non-ideality of the gas, and thermomolecular pressure corrections. Pressure measurements themselves have become more accurate with the use of diaphragms to separate the gas in the thermometer bulb from that in the pressure gauge, capacitance transducers to detect the diaphragm and mercury levels, piston gauges, etc.

The classic studies of earlier years at MIT have been described by Beattie (*Temperature* 2, 1955) and later developments by Borovick-Romanov et al. (*Temperature* 3, 113, 1962), Preston-Thomas and Kirby (1968), Guildner et al. (1972), Berry (1978), and in the review by Quinn and Compton (1975).

Details of precision gas thermometry are not appropriate to the present monograph but a brief account of less accurate and more common types of gas thermometers which are used in low-temperature research may be useful. Gas thermometry in its

simpler form not only gives results directly in terms of absolute temperature and has a sensitivity which can be increased by using higher filling pressures at lower temperatures but is unaffected by magnetic fields and is easily adapted to differential thermometry, i.e. measurement of small temperature differences.

Simon's gas thermometer

Figure 4.5 shows the particularly simple form due to Simon (see Ruhemann 1937) in which the thermometer, usually helium gas-filled, is essentially constant volume due to the very small change in volume of the Bourdon spiral in the pressure gauge B. The bulb A which is at the low temperature to be measured, has volume V and is connected by a fine capillary to the gauge of volume v.

If we assume the thermometric gas is 'perfect' within the required limits of accuracy, then for a constant mass of gas,

$$\frac{pV}{T}$$
 = constant.

The system may be filled to a pressure p_0 at room temperature T_0 ; then, neglecting the capillary volume, the pressure p at a temperature T is given by

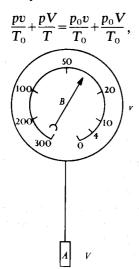


Fig. 4.5. A simple gas thermometer.

whence

$$p = p_0 \frac{(v+V)T}{VT_0 + vT} \tag{4.1}$$

or

$$\frac{1}{T}(VT_0) + v = \frac{1}{p}(p_0v + p_0V).$$

If one or if neither of the volumes v and V are known, they can be found by calibrating the system using two or three known temperatures. Then 4.1 can be used to determine the unknown temperature T from the pressure reading p.

As discussed by Woodcock (1938), the sensitivity of this type of thermometer can be increased considerably at low temperatures by making v large in comparison with V. Then only at low temperatures will the majority of the gas be in the bulb A, so that at high temperatures it is very insensitive to change in T (but unfortunately sensitive to changes in room temperature T_0). Therefore the scale on the gauge in Fig. 4.5 can be expanded at the low-temperature end as mush as desired by making v/V sufficiently large. In such cases the thermometer is of little use at higher temperatures, although it may be capable of an accuracy of $\pm \frac{1}{20}$ K at temperatures below 30 K.

Note that if a linear dependence of p on T is required, so that the sensitivity is more or less independent of the temperature, then V must be large in comparison with v; this means physically that the major part of the helium gas is in the variable temperature bulb A at all temperatures and therefore to a first approximation p is proportional to T.

Other manometers

A simple home-made pressure gauge is shown in Fig. 4.6; a thermometer bulb (volume $V \gg v$, temperature T) is connected by fine capillary tubing (say 0.5~mm o.d., 0.3~mm i.d. stainless steel) to a glass manometer. This constant volume manometer is filled with mercury or butyl phthalate and the liquid is adjusted to the fiducial mark 'O' in the right-hand arm by means of the liquid reservoir below. Butyl phthalate, which has a density of about 1.04~g/ml, is very suitable and allows the use of a brass sylphon bellows for the reservoir and capillary tubing (say, 1.5~mm bore)

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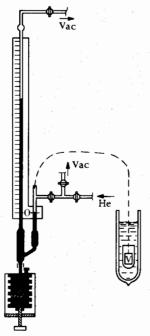


Fig. 4.6. A constant-volume gas thermometer.

in the manometer. Due to the effects of surface tension in these capillary tubes, it is advisable to use precision bore tubing (e.g. 'Veridia' from Chance Bros. (England) or precision bore Pyrex from H. S. Martin, Illinois, or Wilmad Glass Company, New Jersey) particularly for differential thermometry when a second short manometer arm is added to the system. Mercury has certain advantages as a manometer fluid as it is easily outgassed of air and does not absorb helium, but it requires a wider bore manometer tubing (at least 10 mm i.d.) and a slightly different form of adjustable reservoir, e.g. a stainless-steel piston sealed with an O-ring, moving in a stainless-steel cylinder or stainless-steel bellows.

We may generalize the formulae given above to include the case where the dead volume v is at room temperature t, and the system is filled to a pressure p_0 at a fixed point T_0 other than room temperature; then T(p) is given by

$$\frac{T}{p} = \frac{T_0}{p_0} \left(\frac{1 + vT/Vt}{1 + vT_0/Vt} \right) = \frac{T_0}{P_0} \frac{(1 + \Delta)}{(1 + \Delta_0)}.$$
 (4.2)

In a cryostat used by the writer, the copper bulb of volume V was limited by the experimental conditions to about 5-ml capacity and v made small (0.5-1.0 ml). The value of V is found by volume measurement or from the construction, and v is found from 4.2 by filling at $T_0 = 273 \text{ K}$ or $T_0 = 295 \text{ K}$ and then cooling to 90 or 77 K. Having found v, and assuming that t always remains at 295 K (an air-conditioned room), a convenient table of $(1+\Delta)/(1+\Delta_0)$ is drawn up for various temperatures, e.g. for $T_0 = 295 \text{ K}$, $T_0 = 77.3 \text{ K}$, $T_0 = 4.2 \text{ K}$. Finally the pressure p is read by means of a reflecting glass scale marked from 0 to 100 cm with lines 1 mm apart; such scales are commercially available.

Used in this way, the thermometer gives readings which appear to be correct to $\pm \frac{1}{20}$ K in the range 90–55 K over which it can be checked against the vapour pressure of liquid oxygen. Again, from 4.2 to 1.8 K it is correct to $\frac{1}{100}$ K.

However, if the thermometer bulb is near, say, 40 K and part of the connecting capillary is in liquid helium, then with small bulbs a substantial fraction of the gas is in the capillary (even if it is only 0·3 mm i.d.); corrections should be applied if the temperature is to be known to an accuracy of 2 per cent or better. This, of course, depends on the relative dimensions of the bulb and capillary; the use of larger thermometer bulbs reduces such corrections. Between room temperature and about 100 K it is advisable to correct for the contraction of the thermometer bulb as the total change in bulb volume amounts to about 1 per cent in cooling from room temperature to 100 K.

More expensive alternatives to the home-made liquid-in-glass manometer, are the quartz-spiral gauge (Texas Instrument Co. and Ruska Corp.) and capacitance sensing systems (Datametrics and MKS Instruments Inc.—see Appendix).

A differential manometer

For measurement of thermoelectric power or thermal conductivity, small temperature differences are measured and a gas thermometer of the type just discussed is easily adapted (see Fig. 4.7). For this, the absolute temperature T_A and T_B of two thermometer bulbs A and B are read as before by measuring the height h in centimetres of oil with respect to the fiducial mark 'O'. Then

$$\frac{T}{p_{(\text{cm oil})}} = \frac{T_0}{p_{0(\text{cm oil})}} \frac{1 + \Delta}{1 + \Delta_0}$$

If the cross-sectional area of the bore of the capillary tube is $A \text{ cm}^2$, it is easily shown that

$$\frac{\delta T}{\delta p} = \frac{T}{p} \left(1 + \frac{vT}{Vt} \right) + \frac{AT^2}{Vt} \text{ where } \delta T = T_A - T_B \text{ and } \delta p = \delta h_{\text{cm oil}},$$

whence

$$\frac{\delta T}{\delta p} = \frac{T_0 (1 + \Delta)^2}{P_0 (1 + \Delta_0)} + \frac{A T^2}{Vt}.$$

By tabulating $(1+\Delta)^2/(1+\Delta_0)$ for the different values of T_0 normally used and also tabulating AT^2/Vt , $\delta T/\delta p$ can be quickly read off the table and the conversion from δh to δT made. The small difference δp is usually read with a cathetometer although we have found that where $\delta h \leq 15$ mm a geodetic survey level, e.g. Wild N3 level, can be used more speedily and gives δh to $\pm \frac{1}{100}$ mm with less trouble in levelling.

Butyl phthalate manometers similar to the type shown in Fig. 4.71 were described by Hulm (1950).

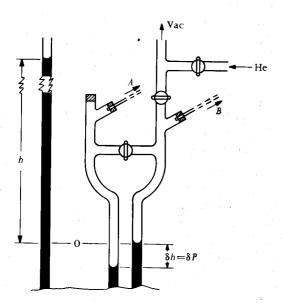


Fig. 4.7. A differential manometer.

Corrections for a non-perfect gas and for thermo-molecular pressure difference

Before leaving the subject of gas thermometry it is pertinent to illustrate the magnitude of the corrections that may arise from non-ideality of the gas and from thermo-molecular pressure differences.

If the equation of state of a gas is expressed as

$$pv = A(1 + Bp + \text{terms in } p^2, \text{ etc.}),$$

the virial coefficients B, etc., can be found experimentally and can be used to correct the real gas scale to the true thermodynamic scale. Whereas the third and fourth virial coefficients are very small, the second virial coefficient B has values (see Table 4.2 from Keesom 1942; see also Kilpatrick, Keller, and Hammel 1955) which even for helium can produce a significant correction to the gas scale, particularly at high pressures and low temperatures.

TABLE 4.2

T K	2.6	4.0	14.0	22.0	50	100	300
$10^{3}B$	-5.30	-3.61	-0.549	-0.101	+0.338	+0.492	+0.508

The effects of uncertainty in values of B in determining T are shown by Rogers *et al.* (1968); the most recent determinations of B are by Berry (1978).

The other correction due to thermomolecular pressure difference arises when the mean free path of the gas molecules is sufficiently large to be comparable with the width of the capillary connecting the thermometer bulb to the manometer; that is, at very low pressures there is a difference in pressure between the ends of the capillary tube when a temperature difference exists between the bulb and the manometer. Our knowledge of the magnitude of this effect is largely a result of experimental work done at Leiden (see Keesom 1942, for summary and references). This work indicates that for helium in the hydro-dynamic region, i.e. when the diameter of the capillary 2R is greater than the mean free path, the thermomolecular pressure difference Δp is given by

$$\frac{\Delta p}{p} = 724 \cdot 2 \frac{1}{(Rp)^2} \left\{ 1 - \left(\frac{T_2}{273 \cdot 1} \right)^{2 \cdot 294} \right\}.$$

This assumes that the temperature at the hot (manometer) end is $273 \cdot 1 \text{ K}$, T_2 is the temperature at the cold end, R is in centimetres and p in microbars. Thus if $T_2 = 4.2 \text{ K}$, R = 1 mm, $p \approx 13\,000 \,\mu$ bar (1300 Pa), then $\Delta p/p \sim 4 \times 10^{-4}$. In most thermometry applications this correction is negligible but in some vapour-pressure measurements where the total pressure p is of the order of 10 Pa (or 0.1 Torr) or less, the mean free path for helium atoms may be comparable with the tube width. At 10 Pa pressure the mean free path in helium is about $\frac{1}{100}$ mm at 4 K and ~1 mm at 300 K. For further information the reader is referred to Keesom (1942), Roberts and Sydoriak (1956), and Berry (1978).

TEMPERATURE MEASUREMENT

5. Vapour-pressure thermometry

Introduction

The vapour pressure of a liquefied gas is a rapidly varying function of the temperature and therefore forms a convenient secondary thermometer. The vapour pressures of the commonly used liquids have been measured and tabulated as a function of the absolute thermodynamic temperature so that they form a reliable series of 'primary' scales of temperature for many lowtemperature physicists. Thus over the respective temperature ranges from 1 to 4.2 K, 14 to 20 K, 55 to 90 K, 63 to 77 K, the vapour pressures of liquid helium, hydrogen, oxygen, and nitrogen can be used to calibrate resistance or thermoelectric thermometers and to check the accuracy of gas thermometers.

Theoretically the vapour pressure of a liquid may be obtained by integration of the Clausius-Clapeyron relation

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta S}{\Delta V} = \frac{L}{T\Delta V},$$

where ΔV is the change in volume at vaporization and L is the latent heat.

If L is constant,

$$\log P = \frac{A}{T} + B,$$

and more generally, if L is a linear function of temperature,

$$L = L_0 + aT;$$

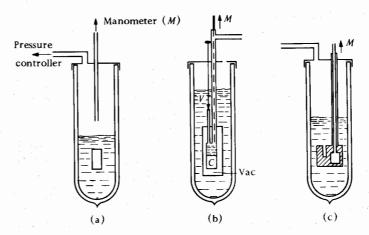


Fig. 4.8. Vapour pressure measurement.

therefore

$$\log P = \frac{A}{T} + B \log T + c. \tag{4.3}$$

Although equations of this type can be fitted quite closely to the experimental values of vapour pressure, it is usually convenient to tabulate P as a function of T and use such a table to find T(P)from experimental values of the vapour pressure.

Some typical experimental situations in which vapour pressure is measured are sketched schematically above (Fig. 4.8). In (a) a liquid is boiling under atmospheric or some controlled pressure and the vapour pressure above the surface is measured by a tube which leads to a pressure gauge. In such an instance temperature inhomogeneities in the liquid may make the recorded vapour pressure a rather poor indication of the true temperature at points within the liquid. Efforts have been made to avoid or allow for these inhomogeneities in oxygen and helium baths. Berry (1962) has used absorbent cotton in oxygen as a means of preventing superheating and achieving a stability of better than a millidegree. In liquid helium Swim (1960) has shown that gradient of a few millidegrees exist near the liquid surface. These cannot be correlated with hydrostatic pressure effects (see also Hoare and Zimmerman 1959).

The second case (b) shows a fairly common type of cryostat in

which the inner space C has a small chamber attached which can be filled with liquid from the dewar through the valve V. A tube connected to the pressure gauge at one end is taken down to a point close to the surface of the liquid in the small chamber. This liquid may be boiling under atmospheric or under reduced pressure. If this chamber is of a good heat-conducting metal (e.g. copper), and there are no points along the sampling tube which are colder than the liquid in the chamber, then the vapour pressure will form a good indication of the liquid temperature. However, in either of these cases (a) or (b) a trace of impurity in the liquid will affect the result markedly, e.g. a trace of oxygen in nitrogen or vice versa alters considerably the vapour pressure of the liquid at a given temperature. For accurate calibration of other thermometric instruments, the type of cryostat shown in Fig. 4.8c is commonly used. Here a copper block is immersed in the liquefied gas and a small hole or capsule in the copper block forms a vapour-pressure bulb into which pure gas is condensed.

The form of the pressure sensing tube is important because of dangers of 'cold' spots, heat leakage down the tube, and thermal oscillations (in the case of helium). A vacuum jacket, assisted perhaps by an electrical heater around the tube, can prevent cold spots but may lead to excessive heat inflow. A good compromise is to provide an outer jacket tube, that is to make the sensing tube to the vapour-pressure bulb of a double wall, but to allow vapour into this space. An interesting account of measuring helium pressure has been given by Cataland, Edlow, and Plumb (Temperature 3(1), 413, 1962).

There are special problems in measuring the vapour pressure of liquid helium-4 below the λ -point because of He II film flow up the tube wall. This film evaporates higher up at a warmer level and refluxes back to the bulb causing a steady heat inflow and a temperature difference between the liquid and the wall of the bulb; this difference is accentuated by the Kapitza thermal resistance at the boundary. Montgomery and Pells (1963) have shown that these discrepancies can reach 10 or 15 millidegrees at 1.5 K: to avoid or reduce such errors it seems best either (i) to have a 3 He vapour pressure bulb, (ii) to have a pumped 4 He chamber, as shown in Fig. 4.8b for measurements below the λ -point and a bulb above the λ -point, (iii) to solder copper fins or gauze inside the bulb to increase the effective heat-transfer surface, or (iv) to

have a constriction $(\frac{1}{2} \text{ or } 1 \text{ mm diam.})$ in the tube above the He II bath to reduce film flow (see also Cataland *et al.* in *Temperature* 3(1), 413).

Liquid hydrogen also presents a special problem because of the existence of the *ortho*- and *para*- forms discussed in Chapter II. Normal hydrogen (75 per cent *ortho*, 25 per cent *para*) boils under standard pressure at $20 \cdot 39 \, \text{K}$, while equilibrium-hydrogen (practically pure *para*-hydrogen in thermodynamic equilibrium at its boiling point) boils at $20 \cdot 28 \, \text{K}$. If a very precise determination is required, then a small quantity of a suitable catalyst such as of neodymium oxide, ferric hydroxide gel, or chromic anhydride (see Ch. II and Ancsin 1977) may be placed in the bulb; then by allowing an hour or so to elapse before measurement, it may be assumed that the liquid present is equilibrium-hydrogen. Ferric hydroxide which is the most commonly used catalyst becomes ineffective after prolonged use or exposure to the atmosphere and water vapour but can be reactivated by outgassing it for a few hours at a temperature of $100-120 \, ^{\circ}\text{C}$.

For purposes of pressure measurement, a mercury column or accurate dial gauge (e.g. Budenberg standard vacuum gauge or a Wallace and Teirnan gauge) may be used at normal pressures, and an oil manometer, McLeod gauge, or hot-wire gauge for lower pressures. Another useful but more elaborate manometer is the quartz-spiral gauge which is direct reading from 1000 Torr down to a few microns.

As was mentioned in the previous section, the effect of the thermo-molecular pressure difference must be taken into account when the pressure to be measured is sufficiently low that the mean free path of the gas molecules becomes comparable with the diameter of the connecting tubes. At room temperature the mean free path $l \sim 1$ mm at a pressure of $10 \, \text{Pa} \ (\sim 0.1 \, \text{Torr})$; l decreases approximately linearly with T.

Data

Table A in the Appendix gives values for the vapour pressure of liquid helium-3, helium-4, normal- and equilibrium-hydrogen, nitrogen, and oxygen. The units of pressure, p, are millimetres of mercury at 0 °C and standard gravity (9.806 65 m/s²) so that readings taken with a mercury column at room temperature or in places where gravity is appreciably different must be corrected.

Note that 1 mm Hg=1 Torr=133·322 Pa. The units have not been changed to SI in the table as they are taken directly from original publications listed; nor have they been corrected for changes in temperature scale which should be borne in mind if discrepancies of a few mK exist between the tabulated values and more recent algebraic expression involving T_{68} .

(a) Helium. Values for ³He and ⁴He are abbreviated respectively from the compilations called 'The 1962 ³He Scale of Temperatures' (Sherman, Sydoriak, and Roberts 1964) and 'The 1958 ⁴He Scale of Temperatures' (Brickwedde et al. 1960). The origin of these scales which cover the range from 0·3 to 5·2 K are discussed in reviews of Quinn and Compton (1975), Roberts et al. (1964), and Van Dijk (1960). They have been demonstrated by more recent work (e.g. Gonano in Temperature 4, 121, 1972) to agree in their ranges of overlap. But the post 1960 work on magnetic and gas scales (see § IV.3) has shown that they give temperatures which are too low by about 0·2 per cent up to 4 K. Differences between EPT-76 and these vapour pressure scales are (Durieux et al. 1977):

$$T_{58,62} - T_{76} = -3.1 \text{ mK } (1 \text{ K})$$

$$= -4.3 \text{ mK } (2 \text{ K})$$

$$= -6.2 \text{ mK } (3 \text{ K})$$

$$= -7.1 \text{ mK } (4 \text{ K})$$

$$= -7.1 \text{ mK } (5 \text{ K}).$$

(b) Hydrogen. Values in Table A for equilibrium- and normal-hydrogen are taken directly from Woolley, Scott, and Brickwedde (1948). The data for e-hydrogen obtained later by Hoge and Arnold (1951) and Barber and Horsford (1963) differ from these tabulated values by 5 mK or less over the range 14 to 20 K. If closer relations between thermodynamic temperature and vapour pressure are needed, then the algebraic expressions should be used from the text of the IPTS-68 (see Preston-Thomas 1976):

$$\log \frac{p}{p_0} = A + \frac{B}{T_{68}} + CT_{68} + DT_{68}^2 \qquad (T > 13.8 \text{ K})$$

where for e-H₂

$$A = 1.711 \ 466$$
, for n-H₂, $A = 1.734 \ 791$
 $B = -44.010 \ 46$ $B = -44.623 \ 68$
 $C = 0.023 \ 590 \ 9$ $C = 0.023 \ 186 \ 9$
 $D = -0.000 \ 048 \ 017$ $D = -0.000 \ 048 \ 017$.

Ancsin (1977) has made further measurements from 13.8 to 20.3 K including the effects of impurities and *ortho-para* conversion behaviour.

(c) *Neon*. Values are not given in Table A but can be calculated from the secondary reference equation in IPTS-68 (Preston-Thomas 1976):

$$\log \frac{p}{p_0} = A + \frac{B}{T_{68}} + CT_{68} + DT_{68}^2$$

where
$$A = 4.61152$$
, for range 24.56 to 40 K
 $B = -106.3851$
 $C = -0.036833$
 $D = 4.24892 \times 10^{-4}$.

There are later measurements from 19 to 30 K by Tiggelman, van Rijn, and Durieux (in *Temperature* 4 (1972)).

(d) Nitrogen. Values in Table A are from Armstrong (1954) above the triple point and from work of Keesom and Bijl (1937) below it. Later measurements by Moussa, Muijlwijk, and Van Dijk (1966) from 63 to 78 K gave values of T about 20 mK smaller due chiefly to difference in temperature scale. A later recalculation of the Moussa data (see Tiggelman and Durieux in Temperature 4, 1972) gives much closer agreement and is the basis for the reference expression in IPTS-68 for the range 63 to 84 K:

$$\log \frac{p}{p_0} = A + \frac{B}{T_{68}} + C \log \frac{T_{68}}{T_0} + DT_{68} + ET_{68}^2$$

where
$$A = 5.893271$$
, $B = -403.96046$
 $C = -2.3668$, $D = -0.0142815$
 $E = 72.5872 \times 10^{-6}$ $T_0 = 77.344$.

From 63 down to 45 K, values of p have been measured by Frels, Smith, and Ashworth (1974).

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(e) Oxygen. Values in Table A are taken directly from Muijlwijk, Moussa, and Van Dijk (1966). Recalculation of their results on the T₆₈ scale gives the reference expression (Preston-Thomas 1976) for the vapour pressure from 54.361 to 94 K:

$$\log \frac{p}{p_0} = A + \frac{B}{T_{68}} + C \log \frac{T_{68}}{T_0} + DT_{68} + ET_{68}^2$$

where A = 5.961546.

 $B = -467 \cdot 45576$

C = -1.664512

D = -0.01321301

 $E = 50.8041 \times 10^{-6}$ $T_0 = 90.188 \text{ K}.$

Tiggelman and Durieux have made measurements on different oxygen samples which agree well with this equation near 90 K but depart by 4 mK near to 70 K.

Gravity and temperature corrections

Readings of vapour pressure recorded from a 'liquid column' pressure gauge are subject to gravity and temperature corrections. Therefore for precise measurements in cases where the value of the acceleration due to gravity g is substantially different from that at sea-level at latitude 45°, or where the temperature of the mercury column is substantially different from that used in the table, correction is necessary.

Gravity corrections, which are usually extremely small, are given in various physical tables (e.g. Smithsonian physical tables, 9th revised edition (1954), p. 608) and are simply proportional to the difference between the acceleration due to gravity g, at the place considered and standard gravity, 980.665 cm s⁻².† Hence the correction to barometric height h is

$$\Delta h = + \frac{(g - 980 \cdot 665)}{980 \cdot 665} \times h.$$

Similarly, the correction Δh due to a difference in temperature ΔT between the barometric column in question and the standard column referred to in the tabulation, is proportional to ΔT , i.e.

$$\Delta h = -\alpha \Delta T \cdot h.$$

For a mercury column and glass scale, this correction constant $\alpha = 0.000172$ per deg C and for a mercury column and brass scale $\alpha = 0.000163$ per deg C (see, for example, Smithsonian physical tables, 9th revised edition (1954), p. 607).

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The correction to be applied to a reading of height of a mercury column at sea-level and an ambient temperature of c. 20 °C is about minus 1 part in 300 before comparing it with the vapour-pressure table.

6. Electrical resistance of metallic elements

Introduction

In a metal, the free electrons responsible for electrical conduction are scattered by imperfections in the crystal lattice and by the thermal vibrations of the lattice. These processes limit the conductivity and so determine the electrical resistivity ρ . This resistivity is a function of the number of free electrons per atom n, the velocity of the electrons v, the electronic charge e, and the effective mean free path. The mean free path l, being partly limited by thermal vibrations whose amplitude is temperaturedependent, is itself therefore a temperature-dependent quantity. The charge e is a constant and n and v are practically independent of temperature so that this effective mean free path is the principal factor in determining the temperature variation of electrical resistance.

We may define a resistivity ρ , due to the static imperfections either chemical impurities or physical impurities—and a resistivity ρ_i caused by thermal vibrations. Due to the static character of the impurities, ρ_i is the quantity which we expect to change with temperature and the total resistivity may be written, assuming the validity of Matthiessen's rule,

$$\rho = \rho_{\rm r} + \rho_{\rm i}. \tag{4.4}$$

The thermometric property with which we are concerned is therefore ρ_i and $d\rho_i/dT$ determines the sensitivity of the electrical resistance thermometer. ρ_i for most metallic elements is approximately proportional to temperature down to temperatures in the vicinity of $\theta_D/3$; θ_D is the Debye characteristic temperature. Below this ρ_i decreases more rapidly with temperature and between about $\theta_D/10$ and $\theta_D/50$ (the lower limit of reliable

[†]The figure of 980.665 is the standard value adopted in 1901 for use in barometer reductions and is quite close to the value for normal gravity at sea-level at latitude 45°.

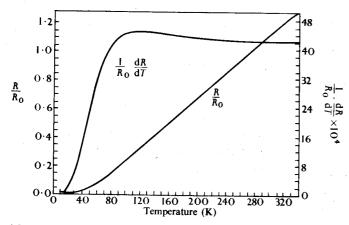


Fig. 4.9. Variation of resistance ratio and the temperature coefficient of resistance with temperature for a copper resistance thermometer (after Dauphinee and Preston-Thomas 1954).

investigation) $\rho_i \propto T^n$, where 3 < n < 5. Therefore at very low temperature, the sensitivity of electrical resistance as a thermometric element decreases rapidly (Fig. 4.9 after Dauphinee and Preston-Thomas 1954), and in the case of metallic elements of the highest available purity $\rho_i \ll \rho_r$ at temperatures in the vicinity of $\theta_D/100$. This enables us to determine ρ_r , which experimentally appears to be constant at the very low-temperature end of the scale.†

It is fairly obvious that the ideal metallic element for use as a resistance thermometer should have the following properties:

- (i) A resistivity ρ_i which has a variation with T at higher temperatures which is as close to linear as possible; this simplifies the task of interpolation considerably.
- (ii) For low-temperature use, the θ_D should be as low as possible so as to preserve a high sensitivity to a low temperature.
- (iii) The element should be obtainable in a state of high purity so that ρ_r will be insignificant over a wide temperature range.
- (iv) It should be a metal which is chemically inert and should have a high stability of resistance, so that its calibration is

† Some metallic elements become superconducting, i.e. their total electrical resistance falls sharply to zero at a critical temperature, and this may prevent an accurate estimate of ρ_r .

- retained over long periods of time and not affected by thermal cycling.
- (v) It must be capable of being mechanically worked, i.e. drawn into wire and wound into required forms.

Platinum thermometers

The noble metal platinum fulfils these requirements best and is the chosen instrument for the International Practical Temperature Scale from 13.81 K to $630.74 \,^{\circ}\text{C}$. The text of the IPTS states also that '... the thermometer resistor must be strain-free, annealed, pure platinum. Its resistance ratio $W(T_{68})$, defined by

$$W(T_{68}) = R(T_{68})/R(273.15 \text{ K})$$

where R is the resistance, must be not less than 1.392 50 at $T_{68} = 373.15$ K. Below 0°C the resistance-temperature relation of the thermometer is found from a reference function and specified deviation equations. From 0°C to 630.74°C two polynomial equations provide the resistance temperature relation....' (Preston-Thomas 1976).

The necessity that $W(100\,^{\circ}\text{C}) \ge 1.392\,50$ implies a purity roughly equivalent to a resistance ratio $R(273\,\text{K})/R(4\,\text{K}) \ge 1500$ or $W(4\,\text{K}) \le 7 \times 10^{-4}$. Such platinum wire is readily available (see Appendix) but it must be wound into a form where it is not too constrained and can be annealed. The more common and successful forms are well described in the NBS Monograph 126, called *Platinum resistance thermometry* (Riddle, Furukawa, and Plumb, 1973): a wire of $\sim 0.1\,\text{mm}$ diameter is wound into a 25 Ω resistor in various ways, including

- (i) the early Meyers' design of a coiled filament wound helically on a notched mica cross;
- (ii) the later Meyers' single filament on a notched mica cross;
- (iii) Barber's fine helix freely suspended in a glass U-tube;
- (iv) the Russian design with a fine helix supported in bifilar fashion on opposite sides of a twisted silica ribbon;
- (v) Rosemount Engineering Company have filament threaded through a number of four-hole ceramic tubes.

Both Tinsley and Co. and the Leeds and Northrup also make strain-free platinum thermometers, the latter using the later Meyers' design. These commercial thermometers are expensive (over \$600) four-lead devices which are encapsulated in silica, pyrex, gold, or platinum with a small pressure of oxygen and helium gas, and annealed. The capsules are generally about 6 mm diameter and 50-60 mm long excepting those of Minco which are smaller, about 4 mm by 10 mm.

Smaller and cheaper unencapsulated platinum resistors are made by Rosemount, Minco, Hartmann and Braun. They do not usually have such a high resistance ratio and are not so reproducible, being more subject to strain, but can be very useful as sensing and control elements.

About 40 of the encapsulated thermometers were tested by thermal cycling at NPL (Ward and Compton 1977) and found to reproduce their resistances to the equivalent of $0.2 \, \text{mK}$ or better. Most are robust but the rigors of transport can sometimes produce a significant change due to mechanical strain. Self-heating at normal temperature from a 1 mA measuring current is typically about 1 mK and at low temperatures ($\sim 20 \, \text{K}$), 5 mA may be used without significant heating.

The magnetoresistance increases considerably at low temperatures so that platinum resistors are not very useful in high magnetic fields. Neuringer and Rubin (in *Temperature* 4, 1085, 1972) measured the effects of fields up to 15 T at temperature from 77 K down: for example, the increase in resistance $\Delta R/R$ due to a 2·5 T field is about 1 per cent at 45 K and 40 per cent at 20 K.

Although IPTS-68 only extends down to 13.8 K, platinum resistors can be used as thermometers successfully below this, albeit with decreasing resolution. Tiggelman and Durieux (*Temperature* 4, 489, 1972) have reviewed much of the experimental work and have shown that a simple polynomial could represent R(T) or W(T) within experimental accuracy of 2 mK at 4 K, 0.5 mK at 8 K, etc. The advent of germanium and rhodium-iron thermometers (§ 4.7) with their higher sensitivity at low temperatures has rather lessened interest in using platinum below 12 or 13 K.

Procedure at low temperatures

More errors in physical data measured at low temperatures arise from bad thermometry than any other single cause. This is

chiefly due to inadequate thermal anchoring of the thermometer to the system being measured, although errors in electrical measurement and calibration contribute. The thermometer capsule itself should be attached as closely as possible by fitting into a sleeve with vacuum grease and the leads should be well anchored to a post or tie-down strips which are as close as possible to the same temperature as the system, otherwise heat leaks along these leads to the sensor will produce a temperature difference.

The resistance of the thermometer can be measured with potentiometer or a digital voltmeter of $0.1~\mu V$ resolution down to 14 or 15 K unless a temperature resolution of better than 2 mK is needed. A typical platinum thermometer (25 Ω at room temperature) has a sensitivity of $0.008~\Omega/K$ at 15 K so that with a 6 mA measuring current, voltage sensitivity is $50~\mu V/K$. For more precise measurement, there is the Kusters current comparator (Guildline Instruments Ltd.: $0.1~\mu\Omega$ resolution) or a.c. bridges such as the NPL Hill-Miller (Automatic Systems Ltd.).

Calibrations are done by some of the national laboratories and some commercial suppliers but in the latter case care should be taken that they are reliable and traceable to a national laboratory; Cryogenic Calibrations Ltd. is one such. Calibrations can be expensive and if many thermometers are involved it may be prudent to set up an intercomparison cryostat with one or two calibrated thermometers as reference 'standards'. The intercomparators usually contain a copper block, provision for cooling, adequate temperature control (Ch. VI), and thermal anchoring (see for example Rusby, Chattle, and Gilhen 1972; Compton and Ward 1975; Besley and Kemp 1977).

Those who do not have calibration facilities or do not need to know temperatures in thermodynamic terms to better than say 20 mK (above 30 K) or 100 mK at 14 K, should simply use a tabulated function for a 'standard' thermometer. That is, they measure the ice-point and helium-point resistance R_{273} and R_4 and also any intermediate values (e.g. R_{90} , R_{54} , R_{20}) that are possible and compare $(R_T - R_4)/(R_{273} - R_4)$ with a tabulated function for a 'standard' thermometer whose characteristics are similar. If Matthiessen's rule for the additivity of a temperature-independent impurity resistance, $R_{\rm r}$, and an impurity-independent 'thermal' resistance, $R_{\rm i}$, were valid then a function

of the type

$$Z = (R_{T_1} - R_{T_2})/(R_{T_0} - R_{T_2})$$

would be identical for all resistors made of a particular metallic element. Unfortunately this additivity hypothesis is not exactly valid, and the departures are greatest between 10 and 30 K where the impurity and 'thermal' resistances are comparable in magnitude. Therefore the Z-function should only be used with care and awareness of its weaknesses. Cragoe at the National Bureau of Standards first proposed and tested its usefulness over the restricted range from 54 to 90 K where it seemed fairly successful. Later examination of Z-values for wider ranges 20 to 90 K, etc., showed deviations of many hundredths of a degree. Therefore various efforts have been made to produce corrections, for example by Hoge (1950b), Los and Morrison (1951), Van Dijk (1952), and Corruccini (1960). An illuminating review of resistance thermometry by Barber (1960) discusses this question as also do articles by a number of these authors in Temperature **3**(1).

Since most research laboratories have liquid helium on hand rather than liquid hydrogen, it is most practical to consider a Z-function based on this, viz:

$$Z = \frac{R_T - R_4}{R_{273} - R_4}$$
 or $Z = \frac{R_T - R_4}{R_{90} - R_4}$. (4.5)

Z-values in Table B (Appendix) are the mean for 50 high-quality platinum thermometers from five different manufacturers. They were calculated by Besley and Kemp (1978) from intercomparison data gathered at NRC in Ottawa (Kirby, Bedford, and Kathnelson 1975) and at NPL (Ward and Compton 1977). Figure 4.10 shows the deviations of individual points from the mean. Besley and Kemp discuss the rough correlation between the departures of Z from the mean and electrical purity W_4 and show how an approximate correction can be made based only on W_4 , which reduces the magnitude of the 'envelope' (in Fig. 4.10) several times.

The bracketed values of Z in Table B, from 11 to 13.5 K, are averages from four thermometers listed in the second edition of this book: the NRC-NPL data did not extend below 13.8 K except for the measurements at 4.2 K.

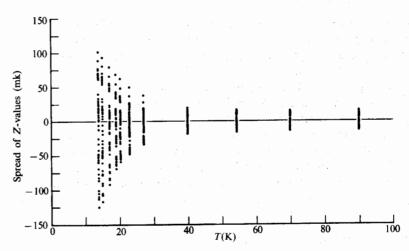


Fig. 4.10. Deviations of Z-values from the mean for 50 platinum thermometers, expressed as a temperature difference (after Besley and Kemp 1978).

Other metallic elements as thermometers

Another very useful form of resistance thermometer is that in which an insulated strain-free wire of a suitable metallic element (necessarily isotropic in its thermal expansion) is wound onto a former of the same element, so that differential contraction on cooling is small. Dauphinee and Preston-Thomas (1954) described the use as thermometer of commercial enamelled copper wire (46 B. & S. gauge), wound and held by baked Formel varnish on a copper calorimeter. They reported a high degree of reproducibility and found that for a number of different thermometers made from the same commercial wire, the deviation from one another in terms of $(R_T - R_{4\cdot 2})/(R_{273} - R_{4\cdot 2})$ represented considerably less than $0.1 \, \text{K}$. Rose-Innes (1973, p. 126) has also described a simply constructed platinum thermometer in which the wire is wound onto a thin piece of varnished platinum sheet which is rolled up to form a small cylinder.

Other elements suitable for thermometers include gold, palladium, and silver as they have relatively low Debye temperatures (200–300 K), high ductility, and high reproducibility due to their cubic structure. They are chemically inactive and can be obtained in a high state of purity.

If, on the other hand, metallic elements with a $\theta_D \sim 100 \text{ K}$ are

suitable on other grounds, their resistance will be an approximately linear function of temperature down to about 30 K and their sensitivity as thermometers should be tolerably good down to 4 or 5 K. Unfortunately most elements in this category are unsuitable for some reason or other. Two of the best possibilities are bismuth and indium. Indium is readily available in the state of highest 'electrical purity', with a resistance ratio, $W_4 < 10^{-4}$. It is easily extruded into wire but this is very soft and difficult to handle. Due to its tetragonal structure it is anisotropic and may therefore not be sufficiently reproducible for a standard. It has been used as a thermometer by White and Woods (1957; see also James and Yates 1963; Orlova, Astrov, and Medvedeva 1964).

7. Metallic alloys as resistance thermometers

Introduction

In an alloy the major part of the electrical resistance at all temperatures is due to scattering by fixed impurities, so that the electron mean free paths are fairly constant and the total resistivity $\rho \simeq \rho_r$. In most alloys the total resistivity is considerably greater than the intrinsic resistivity of the individual constituents and is rather insensitive to temperature. Exceptions are some alloys containing a magnetic element and, at low temperatures, alloys with superconducting inclusions (see review by Daunt in Temperature 2, 327, 1955).

Magnetic alloys including rhodium-iron

Manganin and constantan are two common high-resistance alloys whose resistivity decreases quite markedly below about $200\,\mathrm{K}$ and continues to fall at liquid-helium temperatures. They have been used as thermometers and temperature-control sensors but are a little lacking in sensitivity. A useful temperature sensor whose resistance varies nearly linearly (within ± 1 per cent) with T from $4\,\mathrm{K}$ to room temperature has been made by combining manganin and nickel films (Snelson in Temperature 4, 871, 1972). They have application in direct read-out and control systems.

Research on the 'mysterious' minimum in the electrical resistance of some alloys now known as the Kondo effect and attributed to inelastic scattering of conduction electrons by magnetic spins localized on the impurity atoms, revealed that some alloys

behave like manganin and constantan but with larger relative changes in resistance. Coles (1964) first pointed out that RhFe might be suitable as a thermometer material. The alloy finally chosen for production was Rh+0·5 at.% Fe which as 0·05 mm diameter wire is coiled, supported in a glass tube, annealed, and encapsulated in a platinum sheath with some helium gas (Tinsley and Co.). It is rather similar in size to a platinum-thermometer capsule and has a resistance of 50 Ω at 273 K and 3·5 Ω at 4·2 K, the temperature dependence being illustrated in Fig. 4.11 (after Rusby 1975). The voltage sensitivity is similar to that of platinum near 30 K but increases below this, e.g. to about 150 μ V/K at 10 K with 0·5 mA current. The reproducibility and stability were thoroughly checked over a two-year period at NPL (Rusby 1975) and found to be better than 1 mK. R(T) can be represented by polynomials of the form

$$\log R = \sum_{n=0}^{m} A_n (\log T)^n$$
 with $m = 8-10$,

below 30 K and also above 30 K but it is difficult to fit data accurately with the same polynomial from 1 to 300 K. RhFe can

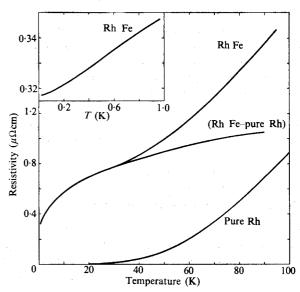


Fig. 4.11. Resistivity of Rh-0.5.% alloy, pure Rh, and $\rho(\text{alloy})-\rho(\text{Rh})$ (after Rusby 1975).

be used as a thermometer down to $10\,\text{mK}$ or less (R. Soulen of NBS, private communication) but thermal contact problems arise with the encapsulated type below $0.5\,\text{K}$.

Numerous other alloys containing small amounts of Fe, Ni, and Co are now known to have a positive temperature coefficient over a wide range of T (e.g. Rusby 1974). One of them, Pt+0.5 at.% Co, has been investigated recently as a thermometer in Japan at their national laboratory (NRLM) and found satisfactory.

Superconducting inclusions in alloys

Some alloys which contain a small proportion of a superconducting element show a marked decrease in resistance at liquid helium temperature which may extend over several degrees. In particular leaded phosphor-bronze wires (~0.1 per cent Pb) were used as resistance thermometers by Keesom and Van den Ende (1930), Daunt (1955), etc., and also leaded brass by Parkinson and Quarrington (1954). The unfortunate features of this class of thermometers, apart from their narrow range of usefulness, are the slight dependence of resistance on measuring current, their sensitivity to a magnetic field, and the critical nature of the metallurgical preparation. Germanium and carbon have now filled the requirements for a sensitive thermometer at helium temperature, although thin films of the superconductors Al and Sn are sometimes operated as very sensitive thermometers (and bolometers) in the vicinity of their superconduction transition (e.g. Liebenberg and Allen in Temperature 4, 875, 1972). Also thermistors, p-n junction diodes and carbon-in-glass have proved successful as low temperature thermometers for different requirements.

8. Semiconducting resistance thermometers

Introduction

Suitable semiconductors make excellent resistance thermometers in the low range of temperatures where metallic elements have become too insensitive. The first semiconductors to be used as thermometers were the films of carbon-black or 'Aquadag'

(Giauque, Stout, and Clark 1938). Later the commercial radioresistors (Clement and Quinnell 1950) became and still are widely used. However a high degree of reproducibility was not achieved until the crystals of doped germanium and silicon were tried in the pioneering efforts of Friedberg and Estermann at the

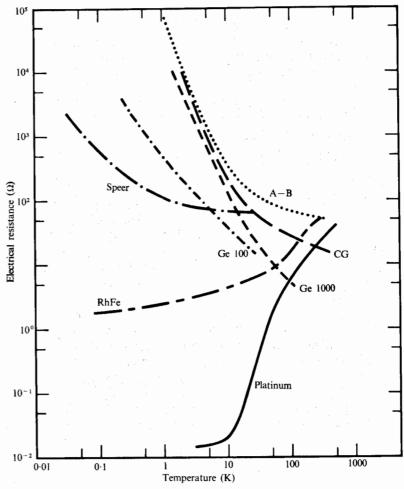


Fig. 4.12. The electrical resistance of some typical thermometers. A-B denotes Allen-Bradley carbon resistor, Speer is a carbon resistor, and CG is carbon-inglass; Ge 100 and Ge 1000 are Cryocal germanium thermometers.

Carnegie Institute of Technology (review by Friedberg in *Temperature* **2**, 355, 1955), and Geballe and his collaborators at the Bell Telephone Laboratories.

Germanium, silicon, etc.

At high temperatures the conductivity is intrinsic, i.e. due to excitation of electrons from the valency band (otherwise full) to the conduction band (otherwise empty). The conductivity is a function of the number of charge carriers and their mobility, and in the intrinsic region it may be shown that

$$\rho \simeq A \exp(\Delta E/2kT)$$
,

where A is almost temperature independent. E is the energy gap between the valence and conduction bands, having values of 0.72 eV for Ge, 1.12 eV for Si.

At low temperatures, where $kT \ll \Delta E$, the conductivity is due to the presence of impurities which contribute electrons which may be excited across a gap of energy ΔE_D to the conduction band, or accept electrons from the valence band across a gap ΔE_A leaving conduction holes in the valence band. Thus, depending on the dominant type of impurity, the conduction at low temperatures is n-type (due to electron carriers) or p-type (due to hole carriers).

Kunzler, Geballe, and Hull (1957) used arsenic-doped germanium and mounted the elements in the way shown in Fig. 4.13. The 'bridge' shape is cut from a single crystal and four gold wires are welded to it as current and potential contacts. These wires are in turn welded to four platinum leads. It is carefully mounted to avoid strains and piezoelectric effects. These were found to be reproducible within the limits of measurement—better than 1 mK at 4·2 K (see e.g. Lindenfeld in *Temperature 3*, 399, 1962) and led to the commercial production by Minneapolis Honeywell which was later transferred to Cryocal Inc. (see Appendix). Then other four-lead germanium sensors, encapsulated ir. small copper cylinders, with or without helium exchange gas, were also made by Scientific Instruments Inc. and Lake Shore Cryotronics, etc., and two-lead devices by Texas Instruments. In

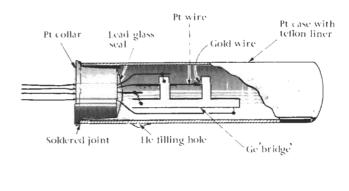


Fig. 4.13. Encapsulated thermometer (after Kunzler, Geballe, and Hull 1957).

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some of the commercial thermometers the 'potential' arms shown in Fig. 4.13 became shortened so that the gold weld is in the active area of the thermometer which may be a reason for occasional instabilities (e.g. Martin 1975). A careful programme of 100 thermal cycles by Besley and Plumb (1978) has shown that in a group of 30 thermometers various patterns emerge: some drift, some jump after a number of cycles, some jump to and fro. Most were stable to better than 5 m Ω (equivalent to <1 mK at 20 K) but a few showed instabilities in excess of 10 m Ω (or >2 mK at 20 K). Note that these instabilities would be insignificant (<1 mK) at liquid helium temperatures.

In the capsules most heat is dissipated via the leads and self-heating effects should be checked by changing the measuring current. Generally, $100 \,\mu\text{A}$ can be safely used above $20 \,\text{K}$, $10 \,\mu\text{A}$ above $4 \cdot 2 \,\text{K}$, and $1 - 2 \,\mu\text{A}$ below 4 K. The power dissipation should be limited to $0 \cdot 1 \,\mu\text{W}$ at most.

Sensitivity to magnetic field varies with doping and temperature. Data published for one of the Honeywell series (Blakemore, Schultz, and Myers 1962) indicate that at 4.2 K

$$\Delta R/R_0 \approx 2 \times 10^{-2} H^2$$

corresponding to a 2 per cent increase in 1 T field or 30 mK error in temperature measurement (see Fig. 4.14 from Dicker and Laquer 1969).

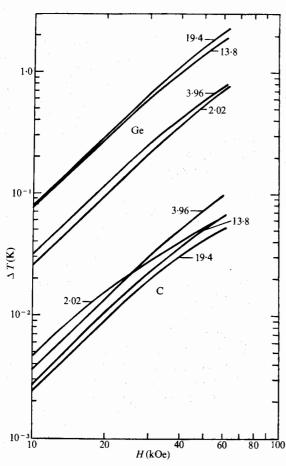


FIG. 4.14. Error in indicated temperature due to magnetoresistance of germanium and carbon thermometers. $\Delta T = T$ (actual) – T (apparent) (after Dicker and Laquer 1969).

In this respect and in others silicon thermometers offer some advantages but have not yet been produced commercially. Silicon has a larger Debye temperature and therefore a much lower heat capacity at low temperatures. Slices cut from a boron-doped silicon crystal have been used without encapsulation as thermometers at the Bell Telephone Laboratories for some years for calorimetry. These slices have been cemented onto button-shaped alloy samples (<13 mm diam.) with $\frac{1}{4}$ -mil Mylar and

cement as insulation between them. In this form they have an extremely small heat capacity and show no measurable hysteresis (Morin and Maita 1963).

Frossati *et al.* (1975) at Grenoble have made ion-implanted silicon thermometers and found them stable over some years and useful from 4 K down to 10 mK or less.

Accurate representation of R(T) for germanium has proved more difficult than for carbon (see section following) as there is a bump in the sensitivity between 4 and 10 K (e.g. review of Swenson 1970). Even over a restricted range of 1 to 4 K the simple relations such as $A \log T = B - \log R$ leave a substantial error curve (Lindenfeld 1961). It is now usual to computer-fit a polynomial of the form

$$\log R = \sum_{n=0}^{m} A_n (\log T)^n$$

or

$$\log T = \sum_{n=0}^{m} A_n (\log R)^n$$

(Cataland and Plumb 1966; Osborne, Flotow, and Schreiner 1967), where m=8 to 14 for the range 1 to 30 K. The calibration points should number about 4m and be equally spaced on a logarithmic scale (Ward 1972) with one or two additional points at each end of the range. There have been numerous discussions of the errors and 'wiggles' that arise in fitting. It now seems clear that if the input data are sufficiently precise and smooth, for example by calibration against a magnetic salt, then spurious 'wiggles' are not a serious factor (Van Rijn *et al.* on p. 815 and Collins and Kemp on p. 835 of Temperature **4,** 1972; Martin 1975).

Measurement methods and problems of thermal contact were discussed above in § 4.6 (see also review of Swenson 1970). Note that a.c. and d.c. determinations of resistance may differ due to Peltier heating (Swenson and Wolfendale 1973). This will vary with frequency and the thermal diffusivity of the sensor but may give significant differences in temperature above 20 K.

Carbon thermometers

These are composed partly of graphite either in the form of a film or composition. The resistance increases markedly at sufficiently low temperatures and in many cases the relation $\ln \rho \propto T^{-1}$ is roughly followed. They are not semiconductors in the strict sense for the following reasons.

Crystalline graphite is highly anisotropic, the resistivity in a natural crystal flake along the basal plane (usually denoted by ρ_{\perp} as this is perpendicular to the hexagonal axis) being about $1\times 10^{-4}\,\Omega$ cm at room temperature and perpendicular to the basal plane ρ_{\parallel} being approximately $1\,\Omega$ cm. Whereas ρ_{\perp} decreases with decrease in temperature, ρ_{\parallel} increases as the temperature is decreased. This behaviour suggests that in the direction parallel to the basal plane, there is a very small band overlap (cf. bismuth) but in the direction normal to the plane there is a narrow band gap; hence a single crystal should behave as a poor metallic conductor in one direction and a semiconductor in the other.

The early use in California (Giauque, Stout, and Clark 1938) of colloidal carbon films was followed in the ensuing twenty years by many applications of dry carbon blacks or colloidal suspensions of graphite ('Aquadag', indian ink, etc.) for very low-temperature thermometry.

These film thermometers have high sensitivity at sufficiently low temperatures, small heat capacity, and intimate thermal contact with the substrate. They do, however, show hysteresis effects when warmed up to room temperature and cooled again and therefore must be recalibrated.

Clement and Quinnell (1952) found that the radio-type resistors manufactured by the Allen-Bradley Company have a resistance which varies rapidly with temperature, particularly below about 20 K (Fig. 4.12) and may be expressed to within ± 0.5 per cent by the semi-empirical expression (Fig. 4.15)

$$\log R + K/\log R = A + B/T.$$

Later some other brands of resistor were found to be useful also, including LAB or ERIE in Europe and Ohmite in the United States. For temperatures from 1 K to 0.01 K those made by Speer Carbon Co. of Pennsylvania have proved very useful as they have a lower sensitivity than the Allen-Bradley (see Fig. 4.12 and review by Anderson in *Temperature* 4, 773, 1972).

An attractive feature of carbon thermometers is that they are less sensitive to magnetic fields than germanium. Clement and Quinnell (1952) first showed that $\Delta R/R_0$ varies approximately as

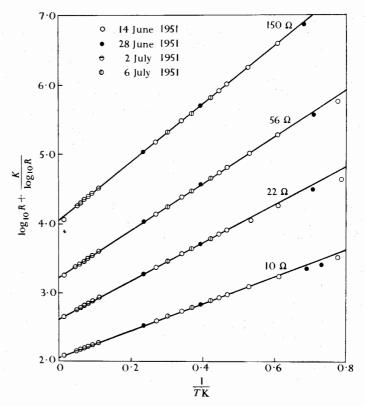


Fig. 4.15. Graphical test of $\log R + K/\log R = A + B/T$ for four carbon resistors (after Clement and Quinnell 1952).

 H^2 for the Allen-Bradley and at 4.2 K was $1-2\times10^{-3}$ H^2 , which is ten times smaller than for germanium (see Fig. 4.14).

Neuringer and Rubin (in *Temperature* **4,** 1085, 1972) have reviewed the behaviour of carbon, germanium, and platinum thermometers, thermistors, and GaAs diodes in magnetic fields up to 15 T with temperatures of 1·8 to 77 K and concluded that carbons are the best below 20 K and that the sensor of highest resistance should be chosen consistent with the measurement instrument. They do not give data for the Speer carbons but Anderson's review in the same volume shows that $\Delta R/R$ is small for a 220 Ω Speer at 4·2 K but large and negative at 0·2 and 0·1 K.

The reproducibility of a carbon composite clearly depends on the stresses induced in thermal cycling due to expansion effects, water vapour, or cryogenic liquids in the carbon, and can be improved by encapsulation or drying and potting in a resin (see Lindenfeld in *Temperature* 3, 399, 1962; Anderson in *Temperature* 4, 773, 1972; Ricketson 1975).

With encapsulated or potted resistors, it might be expected that small instabilities would still exist due to anisotropic expansion of the individual carbon grains and resulting stresses. Reports of reproducibility differ somewhat but a rough consensus has emerged: if encapsulated or potted resistors are thermally cycled to 'age' them, then many will thereafter show insignificant drift or 'jump' effects (<mK) while some others certainly will show instability; those of lower resistance are liable to be worst affected (e.g. Kopp and Ashworth 1972; Ricketson 1975).

Some of the algebraic expressions which have been used for representing R(T) are as follows:

(i) $(\log R/T)_2^1 = a \log R + b$ (Clement and Quinnell 1952) and equivalent

$$\log R/T = a(\log R)^2 + b'\log R + c'$$

- (ii) $(\log R/T)^{\frac{1}{2}} = a(\log R)^2 + b \log R + c$ (Zimmerman and Hoare 1960)
- (iii) $\log R = a(\log R)^2 + b \log T + c/T + d$ (Kes, Van der Klein, and de Klerk 1974)
- (iv) $\log T = a(\log R)^2 + b \log R + c$ (Veal and Rayne 1964)
- (v) $\log R = a + b/(T + \theta)$ (Van Dijk, van Rijn, and Durieux at 15th Annual Calorimetry Conference 1960)
- (vi) $\log R = A + B/T^p$ (Kopp and Ashworth 1972).

Perhaps now with desk computers close at hand it is easier to fit a shortened version of the polynomial used for germanium, i.e.

$$\log T = \sum_{n=0}^{m} A_n (\log R)^n$$

with m=3 to 6 (Star, Van Dam, and Van Baarle 1969). However this does require 10–20 calibration points to fit. Ricketson (1975) has described an alternative in which changes in calibration (on cycling) can be adjusted by measuring the resistance at just two temperatures, preferably in the higher part of the range. His procedure is based on the observation that $\log (dR/R dT)$ versus

 $\log T$ plots are parallel and nearly straight for carbon resistors between 10 and 1000 Ω nominal.

Therefore

$$\log R - B = A''(T)^{-m}$$

which equation can be normalized and scaled to define a function

$$F(T) = A' \left(\frac{\log R_{4\cdot 2} - B}{\log R - B} \right) = \frac{A}{\log R - B}.$$

This function F(T) is first obtained by calibration over the range and then constants A and B found. With changes in calibration, F(T) remains the same and only A and B are altered and can be found from two points; he reports accuracy of $\pm 10 \, \text{mK}$ over $2\text{-}60 \, \text{K}$.

Carbon-in-glass thermometers

These consist of carbon filaments deposited in the voids of a leached borosilicate glass. They were developed by Lawless (1972) at Corning Glass Works and are now sold commercially by Lake Shore Cryotronics Inc. R(T) is shown in Fig. 4.12 to be qualitatively similar to the Allen-Bradley carbon resistors. Sensitivity is a little higher and reproducibility of the encapsulated models is better. Tests by Lawless show that cycling does not give changes significantly greater at $4.2~\rm K$ than $\pm 1~\rm mK$. The dimensions of the encapsulated units are similar to germanium thermometers, about 3 mm diam \times 10 mm long.

In a magnetic field $\Delta R/R_0 \sim 3 \times 10^{-3} \ H^2$ at $4.2 \ K$, which is about double the magnetoresistance for an Allen-Bradley but much smaller than for Ge, Pt, and <u>Rh</u>Fe thermometers, the error at $4.2 \ K$ due to 2T field is about $20 \ mK$ (Lawless 1972).

Diode thermometry

The forward voltage drop across a p-n junction diode carrying a constant current increases smoothly as the temperature drops. The possibilities of GaAs diodes as low temperature thermometers were pointed out by Cohen, Snow, and Trefola (1963) and since then both GaAs and silicon diodes have been widely used for measurements in which an inaccuracy of $0.1 \, \text{K}$ is tolerable. With a current of $\sim 10 \, \mu \, \text{A}$, voltage sensitivity is about $3 \, \text{mV/K}$ at $77 \, \text{K}$; at lower temperatures it decreases somewhat for GaAs and

increases considerably for silicon. Their virtue is in simplicity of operation using a constant current source and a digital voltmeter, in a wide temperature range of 1 to 400 K and in being inexpensive. A disadvantage is that electrical noise limits the current to $10 \,\mu\text{A}$ or above and therefore heat dissipation becomes serious at helium temperature. A review of diode thermometry by Swartz and Swartz (1974) and the commercial bulletin of Lake Shore Cryotronics Inc. both give reproducibility and stability figures of 0.1 K. For selected diodes inaccuracy may be reduced to the order of 10-30 mK as tests of Pavese and Limbarino (in Temperature 4, 1103, 1972) have shown.

TEMPERATURE MEASUREMENT

The magnetoresistance is larger than for carbon thermometers, the error due to a 2T field being of the order of 0.1 K from 4-40 K (Swartz and Gaines in Temperature 4, 1117, 1972).

9. Electrical capacitance thermometers

All the secondary thermometers mentioned hitherto, excepting vapour pressure, are affected by magnetic fields as they depend on electron mean-free-paths and/or on magnetic spins. The dielectric constant of a crystal is not so affected. Brand et al. (1971) (also Hartmann and McNelly 1977) showed that alkali halide crystals containing impurity dipoles, e.g. KCl:Li and KCl:OH, could serve as sensitive thermometers from c. 0.1 to 30 K. The electrical capacitance C was $\sim 10 \, \mathrm{pF}$ and could be represented by

$$C = a + b/T$$

over much of this range and be measured on a three-terminal bridge with a temperature sensitivity of ~1 mK. Power dissipation was negligible and there was no measurable change in C for fields up to 10 T. They were stable at low temperatures but had significant hysteresis after cycling to room temperature.

A more robust sensor of higher capacitance was developed by Lawless (1971) at Corning from a ceramic-glass containing perovskite SrTiO₃ crystals. For these the capacitance has a maximum near 70 K and a minimum near 0.1 K; below this. from 7 to 25 mK, they had a fairly constant sensitivity of d ln $C/dT \sim -10^{-4}$ /mK (Bakalyar et al. 1972). Rubin and Lawless could find no dependence on magnetic field up to 14 T within their measurement uncertainty of ± 1 mK. The chief drawback to

the glass-ceramic elements being currently produced (Lake Shore Cryotonics Inc.) is in the ageing or drift effects which occur after cooling (Lawless 1975; Swenson 1977). There is also a serious hysteresis after warming up to room temperature and recooling which may be 0.1 K. Apart from these effects, if the capacitor is kept at low temperatures (T < 10 K) for some hours it can then be a relatively stable and sensitive sensor at the millikelvin level with electrical noise being the ultimate limitation as far as sensitivity is concerned.

10. Thermocouple thermometers

Introduction

In the metallic bar (Fig. 4.16a) electrons travel up the bar under a thermal gradient carrying excess thermal energy. To preserve the requirement of no net current flow (since this is an open circuit electrically), a return flow of electrons carrying their normal charge '-e' but no excess thermal energy, takes place. This return flow is produced by an electrical driving force, a potential difference ΔE , called the absolute thermoelectric force of the metal. The absolute thermoelectric power is then defined as

$$S = \frac{\Delta E}{\Delta T}$$
.

In practice it is usually convenient and necessary to measure the difference in absolute thermoelectric power between two metals. Thus in the situation of Fig. 4.16b two dissimilar metals A and B have their junctions at temperatures T_1 and T_2 . By measuring the

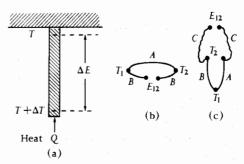


Fig. 4.16. Thermoelectric force.

thermoelectric voltage E_{12} , we have a thermometric indicator available for establishing the difference between T_1 and T_2 . If A or B are not particularly suitable metals for constructing long strain-free connecting leads to the measuring instruments, then two junctions at a common temperature T_2 between A and a suitable third metal C, and between B and C (Fig. 4.16c) are made; the potential difference E_{12} at the ends of the leads C is still a direct measure of the thermoelectric potential difference between junctions AB at T_1 and AB at T_2 . In practice T_1 is usually an unknown temperature, T_2 is an ice pot (or in some low-temperature applications a bath of liquid helium or liquid nitrogen), and the leads C are of copper.

In a complete circuit of one homogeneous metal, irrespective of the presence of temperature gradients, no net thermoelectric current flows nor will a thermoelectric e.m.f. be observed on breaking the circuit at a point provided the two adjacent ends are at the same temperature. It follows that the reproducibility and general accuracy of thermoelectric thermometry depend largely on the homogeneity—both chemical and physical—of the metals in the circuit. Any chemical inhomogeneities or physical strains which are present will generate a spurious thermal e.m.f. if exposed to a temperature gradient.

Useful accounts of the history, applications, and limitations of thermoelectric thermometry are given in *Temperature* **1** (1941) by Roeser p. 180), Scott (p. 206), etc., and in *Temperature* **4** (1972) by Hust, Powell, and Sparks (pp. 1525, 1569), Berman (p. 1537), and Zysk and Robertson (p. 1697).

Thermocouple materials

The article by Scott discusses the calibration of a large number of copper-constantan thermocouples against a platinum resistance thermometer over the range from 0° to -200 °C, and the intercomparison of these e.m.f.s with tabulated values for a representative copper-constantan thermocouple. The normal variation ranges from 0 at the ice point (the reference temperature is the ice point) to $\pm 50~\mu V$ ($\pm 100~\mu V$ in the most extreme cases) at $-200~\rm ^{\circ}C$. These deviations represent about $\pm 1~\rm per~cent$, so that errors of $\pm 1~\rm per~cent$ in estimating temperature might be expected in comparing any copper-constantan thermocouple with a standard table.

However, by using a formula of the type

$$E = at + bt^2 + ct^3$$
 for $-200 \,^{\circ}\text{C} < t < 0 \,^{\circ}\text{C}$

and determining the constants a, b, c by measuring E at three different temperatures, the values of t subsequently obtained by measuring E(t) at intermediate temperatures should not be in error by more than about $2 \mu V$, representing less than $0.1 \deg C$. The three calibration temperatures may be the oxygen point, the carbon-dioxide point, and a point in the region from -30° to $-50 \,^{\circ}$ C where the thermocouple may be calibrated in a stirred alcohol bath against an available resistance thermometer or liquid-in-glass thermometer. A slightly better fit is obtained by calibrating every $50 \deg C$ and producing a graphical tabulated error function to represent the difference between E (experimental) and E(t) calculated from the above equation.

Copper-constantan thermocouples become too insensitive for use below 20 or 30 K (see Fig. 4.17). An alloy of Au+2·1% Co achieved temporary popularity in the 1960s as its thermoelectric power versus copper or 'normal' silver (Ag+0·37% Au) was substantially larger, being c. $4 \mu V/K$ at 4 K compared with $1\cdot3 \mu V/K$ for constantan vs copper (see Fig. 4.17 and Powell, Bunch, and Corruccini 1961). However this alloy is metallurgically unstable and therefore varies much more with age and heat treatment than is desirable in a thermometer. Fortunately there are more dilute alloys which are stable and sensitive.

The extensive researches of Borelius *et al.* (1930) first revealed that many dilute alloys might be used for sensitive low-temperature thermocouples, particularly the monovalent metals copper, silver, or gold with small amounts of a magnetic solute such as iron or manganese or cobalt. Later it was shown that a few atoms per million of some of these solutes could carry a local magnetic moment in copper, gold, etc., and produce an anomaly at low temperatures both in the electrical resistance and in the thermoelectric power. Dauphinee, MacDonald, and Pearson (1953) suggested the use of some of the copper-rich alloys as thermocouples. Later gold + c. 0.03 per cent iron was used very successfully as a thermometer by Berman and Huntley (1963; also Berman, Brock, and Huntley 1964) at temperatures down to 1 K (see Fig. 4.17). Such dilute alloys are metallurgically stable provided that they are not heated in an oxidizing atmosphere.

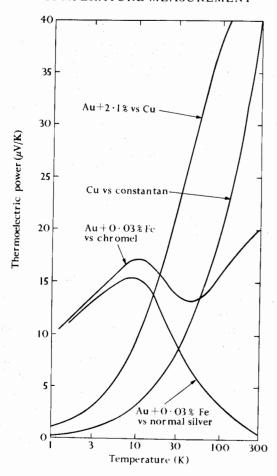


Fig. 4.17. Thermoelectric power of some thermocouples which are used at low temperatures. Data from Powell et al. (1961) and Berman et al. (1964).

This Au+0.03% Fe alloy is produced commercially by Tinsley and Company and alloys of gold with 0.02 at.% Fe and 0.07 at.% Fe are made by Sigmund Cohn in the United States; the variation of thermopower with composition is not very marked in this range (see review of Berman in *Temperature 4*, 1972). Calibration tables are given for 0.02 and 0.07% Fe alloys vs chromel, normal-silver, and copper from 1-280 K by Sparks

and Powell (1972) who also measured the variations (of \sim 1 per cent) in thermoelectric voltage for wires from different suppliers and different bars. Rosenbaum (1968, 1969) also gives data from 0.5 to 80 K on similar systems and Medvedeva, Orlova, and Rabinkin (1971) give data for a Au+0.07 at.% Fe alloy produced in the USSR, vs chromel. Table C in the Appendix of this book is abbreviated from Sparks and Powell (1972) and Sparks, Powell, and Hall (1968) for copper–constantan.

Chromel or KP (90 per cent Ni+10 per cent Cr) has some advantages over copper or 'normal' silver for the second leg of the thermocouple. As Fig. 4.17 shows, S for the AuFe vs 'normal' silver (and vs copper) decreases at temperatures above 20 or 30 K while for AuFe vs chromel, S remains $\sim\!15~\mu\text{V/K}.$ Also the low thermal conductivity of chromel can be an advantage in reducing heat leakage to the thermocouple junctions; copper has an additional disadvantage below 10 K in that minor changes in trace magnetic impurities (Fe, Mn, etc.) alter the thermopower very much.

As mentioned earlier, inhomogeneous lengths of wire in a temperature gradient can generate significant thermal e.m.f.s: a simple test is to take a length of wire, connect the ends to a potentiometer or digital voltmeter, pass the wire slowly through a glass U-tube immersed in liquid refrigerant and then discard wires which generate e.m.f.s of more than say 1 μ V. Giauque, Buffington, and Schulze (1927) describe such tests and report average e.m.f.s for constantan of 0.24 μ V in 0.5 mm wire and 1.8 μ V for 0.08 mm wire; the maximum e.m.f.s for these respective diameters were 0.7 and 3.1 μ V. They used copperconstantan thermocouples—originally calibrated from 15 to 283 K by reference to a hydrogen gas thermometer—as secondary standards at Berkeley for many years: the effect of inhomogeneities was partly cancelled by using five constantan wires in parallel, each of 0.25 mm diameter.

Similar tests by Sparks and Powell (1972) on chromel, constantan, and copper in liquid nitrogen and in liquid helium showed spurious e.m.f.s of $\sim 1~\mu V$. They also made thermocouples out of samples from different parts of a wire spool and from different spools to check the uniformity of the wires. Couples from different parts of the same spool immersed in nitrogen or helium gave e.m.f.s of 1 to 5 μV ; from different spools they averaged 20 μV

at each temperature for the alloys chromel and constantan, while copper gave $2 \mu V$ at 77 K and $20 \mu V$ in liquid helium.

TEMPERATURE MEASUREMENT

When using a thermocouple at low temperatures, there are considerable advantages in having the reference junction of the thermocouple also at low temperature, for example in liquid helium or liquid nitrogen. This can decrease the spurious effects arising from inhomogeneities when wires are brought out from a low-temperature cryostat to room temperature and into an ice pot. Suppose we are measuring a temperature of $T \approx 22 \text{ K}$ to ±0.2 K with a copper-constantan thermocouple; if one junction is in melting ice a total e.m.f. of about $6000 \,\mu\text{V}$ must be measured to $\pm 1 \mu V$. On the other hand, if measured with reference to a surrounding helium bath (4.2 K), then the total e.m.f. which must be measured to $\pm 1 \,\mu\text{V}$ is only about $60 \,\mu\text{V}$.

With small thermopowers care must be taken to avoid or to account for spurious thermal e.m.f.s, particularly those arising in the leads. This can be done with a superconducting reversing switch (Templeton 1955) or a superconducting shorting-bar (Berman and Huntley 1963). The reversing switch described by Templeton can be simplified slightly by using thermal switching rather than magnetic-field switching: the tantalum wires are wound onto small carbon resistors which can act as heaters to drive the tantalum coils normal when necessary.

Magnetic fields alter the thermopower particularly for the Kondo systems like AuFe at low temperatures (see for example Berman in Temperature 4, 1972; Chiang 1974). However if they are used in such a configuration that no temperature gradient occurs over the thermocouple leads which are in the magnetic field, then the thermal e.m.f. is field independent. Richards, Edwards, and Legvold (1969) showed that if the field region can be kept isothermal, no calibration changes will occur.

10. Temperatures below 0.5 K

These are accessible by the methods of magnetic cooling (see Ch. 9 and Hudson 1972) or using helium-3 in dilution refrigeration and Pomeranchuk cooling (see Ch. 8 and Lounasmaa 1974). The methods of measuring temperatures in this millikelvin region include some of the secondary instruments which we have already mentioned such as RhFe (unencapsulated) resistors, carbon resistors of some types, doped silicon, and also nuclear magnetic

resonance and nuclear susceptibility. Primary thermometers include y-ray anisotropy from oriented nuclei, melting pressure and viscosity of ³He, thermal noise, and paramagnetic susceptibility. Some of these will be discussed in relevant chapters on helium-3 systems and on magnetic cooling as they pose special problems, particularly of thermal contact.

11. Summary of temperature sensors 0.5-300 K

Secondary sensors which are commercially available (see Appendix) calibrated or uncalibrated, include the following:

- A. With sensitivity and stability of 1 mK:
 - (i) platinum resistance (encapsulated) for range T > 10 K,
 - (ii) RhFe resistance (encapsulated) for 0.5-300 K,
 - (iii) germanium (encapsulated) for 0.5-30 K. N.B. some may drift or jump.

All the above are expensive and are affected by magnetic fields.

- B. With sensitivity of 1-10 mK and stability of <100 mK:
 - (i) platinum resistors without capsules for T > 10 K,
 - (ii) carbon resistors, encapsulated or potted, for 0.5-100 K,
 - (iii) carbon-in-glass for 1-300 K, may be stable at 10 mK level,
 - (iv) capacitance (ceramic-glass SrTiO₃) for 0.5-60 K and T>70 K are independent of field H.
- C. With sensitivity of 10 mK and stability of 100 mK:
 - (i) p-n-junction diodes for 1-300 K,
 - (ii) thermocouples of AuFe for 2-300 K,
 - (iii) CLTS (manganin+nickel, usually 100 mK resolution) for 2-300 K.

A summary of temperature errors induced by high magnetic fields at low temperatures is given by Sample and Rubin (1977).

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CHAPTER V

HEAT TRANSFER

1. Introduction

A DETERMINATION of the physical properties of materials at temperatures considerably different from the ambient temperature requires some degree of thermal isolation of the material from its surroundings; the degree of isolation must be sufficient to meet the demands of temperature control, temperature measurement, and in the case of low-temperature research, the available refrigerating capacity of the coolant. In a measurement such as the determination of heat capacity by the adiabatic method, the sample must also be thermally isolated from its immediate environment—the cooling medium. These conditions imply that an important factor in the design of a successful cryostat is the ability to predict the degree of thermal isolation or in other words, to calculate the transfer of heat that will take place between the specimen and its surroundings; then materials and methods of construction must be used which will ensure this heat transfer being within or below certain allowable limits.

In general, heat may be transferred by conduction, convection, and radiation. In most low-temperature applications, thermal isolation is assisted by partial evacuation of gas from the interior of the cryostat so that convection is eliminated. Then effective heat transfer takes place by conduction through the residual low-pressure gas, conduction through the solids that interconnect the various parts of the cryostat, and by radiation. In addition such factors as Joule heating in electrical leads, eddy current heating, mechanical vibration, adsorption or desorption of gases may contribute to the heat transfer.

Of the three major processes responsible for heat conduction at low temperatures that due to conduction by solids can be estimated generally with a fair degree of accuracy: low-pressure gas conduction and radiation transfer may be estimated with rather less accuracy, the uncertainty depending on our lack of knowledge of the accommodation coefficient and emissivity respectively. However, it is usually possible to estimate an upper bound for the heat transfer by these processes and therefore ensure that materials, degree of high vacuum, etc., used are sufficient to meet the required demands.

The remainder of this chapter deals in some detail with the method of calculating heat transferred by these processes.

2. Conduction of heat by a gas

An elementary treatment on the basis of kinetic theory indicates that in a gas at normal pressures the thermal conductivity λ and viscosity η are given by (see, for example, Roberts and Miller 1960)

$$\lambda = \frac{1}{3}mln\bar{v}C_v, \quad \eta = \frac{1}{3}mln\bar{v},$$

where

m = mass of one molecule,

l = mean free path,

n = number of molecules per unit volume,

 $\bar{v} = \text{mean velocity},$

 $C_v = \text{specific heat per g.}$

Thus if ρ is the density,

$$\lambda = \frac{1}{3}\rho l\bar{v}C_{v}, \qquad \eta = \frac{1}{3}\rho l\bar{v},$$

and

$$\lambda = \eta C_v$$
.

Since the mean free path $l \propto 1/p$, both λ and η are seen to be pressure independent at least to a first approximation, and to depend on the temperature through their dependence on the mean velocity \bar{v} .

Experiment (and a more detailed theory) indicates that $\lambda = \text{constant } \eta C_v$ where the constant has a value of 1.5-2.5 for most common gases. λ and η increase monotonically with increasing temperature as T^n where the exponent n has experimental values in the range 0.6-0.9 for hydrogen, helium, nitrogen, and oxygen.

However, as we have pointed out before, the residual gas

pressure in a cryostat is nearly always reduced to a point where the mean free path becomes comparable with the dimensions of the system; at room temperature a pressure of 10^{-2} Pa is sufficiently low that the mean free path is ~ 1 m. At such pressures, the average molecule may travel from a hot wall to a cold wall without collision with another gas molecule, and the thermal conductivity becomes a function of the number of molecules present (and also their mean velocity), i.e. at low pressures $\lambda \propto n \propto p$.

For approximately parallel surfaces at temperatures T_1 and T_2 , the heat transferred, \dot{Q} , by conduction through a gas at low pressure p Pa is given by (see Kennard 1938):

$$\dot{Q} = \frac{a_0}{4} \frac{\gamma + 1}{\gamma - 1} \sqrt{\left(\frac{2R}{\pi M}\right)} p \frac{T_2 - T_1}{\sqrt{T}} \text{ mW/m}^2,$$
 (5.1)

where M is the molecular weight and γ is the ratio of specific heats of the gas, R is the gas constant in J/mol/K; a_0 is related to the individual accommodation coefficients a_1 and a_2 and the areas A_1 and A_2 of the two surfaces by

$$a_0 = \frac{a_1 a_2}{a_2 + (A_2/A_1)(1-a_2)a_1}$$

so that if $A_1 \simeq A_2$, then

$$a_0 = \frac{a_1 a_2}{a_1 + a_2 - a_1 a_2} \; ;$$

if also

$$a_1 = a_2 = a$$
, $a_0 = \frac{a}{2 - a}$
 $a_1 = a_2 = a$, $a_0 = \frac{1}{2}a$ for $a \to 0$
 $a_1 = a_2 = a$, $a_2 = a$

Accommodation coefficients are normally measured for the case of a wire at temperature T_2 slightly higher than a surrounding gas at temperature t_1 . In this case molecules colliding with the wire have an average energy corresponding to T_1 so that T in the denominator of (5.1) may be identified with T_1 . The molecules

leave the wire with an energy corresponding to a temperature T'_2 intermediate between T_1 and T_2 ; then

$$(T_2'-T_1)=a(T_2-T_1)$$

defines the accommodation coefficient a.

In many low-temperature applications the molecules may travel from one wall to the other without collision and it is impossible to identify T in (5.1) with either T_1 or T_2 . Also the value of p used in (5.1) must be considered very carefully, since at low pressures (under molecular or Knudsen conditions) the thermal transpiration or thermo-molecular pressure effect arises and the local pressure and temperature vary together as expressed by

$$p/(T)^{\frac{1}{2}} \times \text{constant}$$
.

Corruccini (1959) has examined this question of gaseous heat conduction at low pressures and low temperatures. He points out that p and T are associated in the derivation of (5.1), and that p is observed by a vacuum gauge usually at room temperature. Under low-pressure conditions $l \gg d$, the diameter of the tube connecting the gauge to the cryostat chamber, and if the system is in equilibrium, $p/(T)^{\frac{1}{2}}$ is constant. Therefore, if a value of p obtained from the gauge is inserted in (5.1), the appropriate value for T is the temperature at the pressure gauge.

Eqn (5.1) may be simplified to

$$\dot{Q} = 18 \frac{\gamma + 1}{\gamma - 1} a_0 \frac{T_2 - T_1}{\sqrt{(MT)}} p \text{ W/m}^2,$$
 (5.2)

and using

$$T = 295 \text{ K}.$$

$$\dot{Q} = 1.06 \frac{\gamma + 1}{\gamma - 1} a_0 \frac{T_2 - T_1}{\sqrt{M}} p$$
= constant $a_0 \cdot p \quad (T_2 - T_1) \text{ W/m}^2$, (5.3)

where the constant has approximate values of 2.1, 4.4, and 1.2 for helium, hydrogen, and air respectively. The chief uncertainty in calculating the heat conducted by a low-pressure gas lies in the accommodation coefficient a. As an upper limit a = 1, but experimental research has shown that with a clean metallic surface exposed to helium gas, a may be as low as 0.025.

Keesom (1942) has summarized earlier measurements of a for helium gas on surfaces of platinum, tungsten, and glass. These and later work (e.g. Thomas and Schofield 1955; Klett and Irey 1969) lead to values similar to those given by Corruccini (1959), namely $a \approx 0.3$ at 300 K, 0.4 at 80 K, and 0.6 below 20 K. It is only for surfaces which have been freshly degassed, for example a tungsten wire after flashing, that values of a < 0.1 are obtained.

For air and nitrogen on copper, Klett and Irey found $a \approx 0.7$ at 243 K and 0.8 at 77 K; for heavier polyatomic molecules, experiments indicate 0.8 < a < 1.0 but for the gases usually encountered in cryogenic design studies, a choice of $a \sim 0.5$ seems a good one.

3. Heat transfer through solids

The heat flow \dot{Q} through a solid of cross-section A under a temperature gradient $\partial T/\partial x$ is given by

$$\dot{Q} = \lambda(T)A \frac{\partial T}{\partial x}.$$

Thus, if the ends of a solid bar of uniform cross-section and length l are at temperatures T_1 and T_2 ,

$$\dot{Q} = \frac{A}{l} \int_{T_1}^{T_2} \lambda(T) \, dT.$$

 $\lambda(T)$ is the temperature-dependent thermal conductivity of the solid, of which some typical examples are shown in the graphs of Fig. 5.1. In Chapter XI are summarized experimental data (see also Table I in Appendix) of the thermal conductivity of the various typical groups of solids: (i) glasses, (ii) metallic alloys, (iii) pure metallic elements, and (iv) crystalline dielectric solids.

In the case of metallic alloys, e.g. brass, German silver, monel, stainless steel, available data enable us to give a fairly accurate estimate of $\lambda(T)$ at any temperature and therefore of the integrated heat conductivity $\int \lambda(T) \, dT$, provided that the alloy composition is not markedly different from that of alloys already investigated and that we know the physical state, e.g. strained or annealed. In the case of pure metallic elements, however, the conductivity at low temperature is very sensitive to small traces of chemical impurities and physical defects; but as discussed in Chapter XI, a comparatively simple measurement of the residual

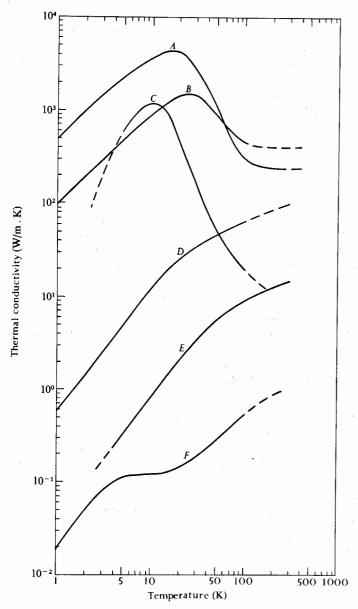


Fig. 5.1. Thermal conductivity of some solids, from data in Powell and Blanpied (1954). A, a metallic element, Al (high purity); B, a metallic element, Cu (electrolytic tough pitch); C, a dielectric crystal, quartz; D, an alloy, annealed brass (70 Cu, 30 Zn); E, an alloy, stainless steel; F, a glass, vitreous silica.

electrical resistance (normally at about $4.2 \, \text{K}$) enables a good estimate of the heat conductivity to be made.

The knowledge most often needed for practical cryogenic calculations is the effective heat conductance of a solid bar of a few common materials, with certain end temperatures. Commonly encountered pairs of end temperatures may be 300 (room temperature) and 77 K, 300 and 4.2 K, 77 and 4.2 K, 4.2 and 1 K. In Table 5.1 values are given for the mean heat conductivity,

$$\bar{\lambda} = (T_1 - T_2)^{-1} \int_{T_1}^{T_2} \lambda(T) dT,$$

for a number of commonly used materials, e.g. nylon, Pyrex glass, machineable-glass ceramic (Corning), AGOT graphite, a representative stainless steel, constantan, brass, phosphorus-deoxidized copper (representing the material from which many copper items are often made: pipe, some rod, and bar), and electrolytic tough pitch copper (representing the type of copper frequently used in spools of wire). The values in the Table and in Fig. 5.1 were based on the compilations of Powell and Blanpied

TABLE 5.1

Mean values of thermal conductivity expressed in W/m · K; values in brackets are extrapolated

	$T_2 = 300 \text{ K}$ $T_1 = 77 \text{ K}$		$ \begin{array}{c} \overline{\lambda} \\ T_2 = 77 \text{ K} \\ T_1 = 4 \text{ K} \end{array} $		$ \begin{aligned} \bar{\lambda} \\ T_2 &= 1 \text{ K} \\ T_1 &= 0.1 \text{ K} \end{aligned} $
Nylon	0.31	0.27	0.17	0.006	0.001
Pyrex glass	0.82	0.68	0.25	0.06	0.006
Machineable glass- ceramic Graphite (AGOT)	2	1.6	1.3	0·03 0·0025	0·004 0·0002
18/8 stainless steel	12.3	10.3	4.5	0.2	0.06
Constantan	20	18	14	0.4	0.05
(60 Cu, 40 Ni) Brass (70 Cu, 30 Zn)	81	67	26	1.7	0.35
Copper (phosphorus deoxidized)	190	160	80	5	(1)
Copper (electrolytic)	410	570	980	200	(40)

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(1954) and Childs, Ericks, and Powell (1973); some data below 1 K are from Lounasmaa (1974, p. 246) and those for the glass-ceramic are from Roth and Anderson (1976).

Values of λ or $\overline{\lambda}$ for most commercial glasses are within a factor of two of those given for Pyrex. Many disordered polymers or plastics lie within the same range of conductivity. Manganin approximates in behaviour to constantan and the inconel, monel alloys are intermediate between stainless steel and constantan.

The values in this table make it evident why alloys of the cupro-nickel family (copper-nickel, constantan, German silver) or of the monel and stainless-steel group are so frequently chosen for the tubes in a cryostat where low thermal conductivity is a requirement. Stainless steel and inconel have somewhat lower heat conductivities than the cupro-nickel alloys although the latter are often preferred due to the greater ease with which they may be soft-soldered.

4. Heat transfer by radiation

A perfect black body may be defined as one which absorbs all radiation falling upon it. For such a body the absorptivity a and emissivity ϵ are unity, and so its reflectivity

$$R = 1 - \varepsilon = 1 - a$$

is zero.

It may be shown (Roberts and Miller 1960) that for a black body at a temperature T the total radiant energy emitted per second per unit area is given by

$$E = \sigma T^4$$

where the constant σ , Stefan's constant, has an experimental value of $5.67 \times 10^{-8} \text{W/m}^2 \text{K}^4$. Such radiant energy is distributed over a range of wavelengths, the energy $E(\lambda) \, d\lambda$ emitted over a narrow interval λ , $\lambda + d\lambda$ being a function of λ and T. The function $E(\lambda)$ at any temperature T has a maximum value for $\lambda = \lambda_m$, and it may be shown that

$$\lambda_{\rm m}T = {\rm constant}$$
 (Wien's constant)

for which the experimental value is $2900 \,\mu\text{m}\,\text{K}$

Thus for

$$T = 300 \text{ K},$$
 $\lambda_{m} = 9.67 \mu\text{ m},$
 $T = 200 \text{ K},$ $\lambda_{m} = 14.5 \mu\text{ m}$
 $T = 77 \text{ K},$ $\lambda_{m} = 37.7 \mu\text{ m},$
 $T = 4.2 \text{ K},$ $\lambda_{m} = 690 \mu\text{ m}.$

Most calculations dealing with the radiant heat transfer in low-temperature equipment are not restricted to black bodies but deal with metallic surfaces whose emissivity may be anywhere between 0.01 and 1.0.

Most non-metallic surfaces, of which glass and perhaps baked varnishes are the most important from our viewpoint, do approximate to black bodies in that their emissivities are in the neighbourhood of 0.9. However, for a particular metallic conductor the emissivity or the reflectivity depends on the wavelength of incident radiation and the physical state of the surface.

The classical theory of Drude yields a relation between the reflectivity R, wavelength λ (μ m) and the d.c. electrical resistivity of the metal ρ (Ω m):

$$1 - \mathbf{R} = \varepsilon = 365(\rho/\lambda)^{\frac{1}{2}}$$

which at elevated temperatures is in agreement with experiment. At low temperatures, particularly for infrared radiation, the absorptivity is not as small as this theory predicts because of the anomalous skin effect. This effect occurs when the electron relaxation time (or mean free path) becomes long compared with the period of the incident electromagnetic wave. Reuter and Sondheimer (1948) calculated the effective increase of surface resistance at high frequencies assuming specular reflection of electrons at the surface; later Dingle (1952, 1953) calculated it also and by assuming diffuse reflection got quite good agreement with experiment, e.g. absorptivity a of 0.4 per cent for $14~\mu m$ radiation on copper at 4~K compared with a measured value of 0.6 per cent and a classical (Drude) theoretical value of 0.003 per cent.

Dickson and Jones (1968) compiled from the literature values of infrared spectral reflectance for a number of metals at low temperatures. These showed that for wavelengths of a few micrometres or more, electropolished or vacuum-deposited surfaces of Al, Cu, Ag, and Au all gave emissivities $\varepsilon \leq 0.01$ below 100 K.

For Sn, Pb, and a 70 Cu + 30 Zn alloy, $\varepsilon = 0.01-0.02$. In practical cryogenic problems of calculating radiant heat transfers, we are concerned with wavelengths of 10 μ m or more but the surfaces are often of uncertain condition. Some intelligent guessing at the state of the surface and the appropriate upper limit for ε is needed. As a guide Table 5.2 has some experimental values for common metals with surfaces in conditions varying from electropolished to highly oxidized. Other data may be found in the American Institute of Physics handbook, § 6 (McGraw-Hill, New York) and in volumes 7–9 of Thermophysical properties of matter (Plenum Press, New York).

For two plane parallel surfaces each of area A and emissivities ε_1 and ε_2 and at respective temperatures T_1 and T_2 , the

TABLE 5.2 Experimental values of emissivity

Material	Fulk, Reynolds, and Park (1955), 300 K radiation on 78 K surface	McAdams (1954), room tempera- ture	s Ramanathan (1952), 14 μm radiation on 2 K surface	Ziegler and Cheung (1957), 273 K radiation on 77 K surface
Al, clean polished foil	0.02	0.04	0.011†	0.043‡
Al, highly oxidized	_	0.31		
Brass, clean polished	0.029	0.03	0.018†	0.10#
Brass, highly oxidized		0.6	_	_
Cu, clean polished	0.015 - 0.019	0.02	0.0062-0.015	
Cu, highly oxidized	_	0.6	_	<u> </u>
Cr, plate	0.08	0.08		0.084#
Au, foil	0.010 - 0.023	0.02-0.03	_	
Ni, polished	-	0.045		_
Ag, plate	0.008	$()\cdot 02 - 0\cdot 03$	_	
Stainless steel	0.048	0.074	· —	
Sn, clean foil	0.013	0.06	0.013†	
Soft solder	0.03			0.047
Glass	_	0.9	-	

[†] These surfaces were electro-polished (Ramanathan).

heat transfer by radiation per unit time is

$$\dot{Q} = \sigma A (T_1^4 - T_2^4) \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2 - \varepsilon_1 \varepsilon_2}$$
 (5.4)

whence

$$\dot{Q} \simeq \sigma A (T_1^4 - T_2^4)$$
 for $\varepsilon_1 = \varepsilon_2 \simeq 1$.

In the case where $\varepsilon_2 \ll \varepsilon_1$, (5.4) reduces to

$$\dot{Q} = \sigma A (T_1^4 - T_2^4) \varepsilon_2. \tag{5.5}$$

Similarly, if $\varepsilon_1 = \varepsilon_2 = \varepsilon$, and $\varepsilon \ll 1$, (5.4) becomes

$$\dot{Q} = \sigma A (T_1^4 - T_2^4) \varepsilon / 2.$$

As discussed in Chapter II, a radiation shield is commonly used in cryostats and storage flasks to reduce the heat inflow and liquid evaporation. This shield is often a polished copper cylinder kept at a temperature intermediate between the ambient temperature and that of the experimental space being cooled by liquid air or by evaporating helium gas. It is useful to known how the temperature distribution on this shield varies with time, gas pressure, and emissivity. Dixon, Greig, and Hoare (1964) have measured distributions of temperature on a cylindrical shield made of phosphorus deoxidized copper, attached to a liquid-air chamber. Their shield of 0.16-cm thick copper was 60 cm long and 8 cm in diameter. It approached thermal equilibrium with a time-constant of about 1 h. After 3 h the temperature-difference along the length was c. 15 K for polished surfaces provided that the vacuum was better than $c.0.01 \,\mathrm{Pa}$; in a poor vacuum of $0.5 \,\mathrm{Pa}$ this amounted to nearly 40 K. Oxidation of the surfaces increased it by a factor of about 2.

5. Other causes of heat transfer

While the processes of heat transfer discussed in the preceding sections, viz. low-pressure gas conduction, heat conduction by solids, and radiation transfer, are those chiefly encountered, other less common but quite troublesome sources of energy often arise.

Joule heating

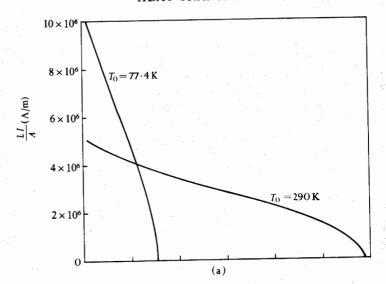
Joule heating in connecting leads and in resistance thermometers, giving rise to a heat input $\dot{Q} = I^2 R = V^2 / R$, is not difficult

[‡] These surfaces were neither highly polished nor heavily oxidized, but as encountered in normal practice (Ziegler). Ziegler observed that a thin layer of oil or Apiezon grease on a low emissivity surface raised the emissivity to 0·2 or 0·3. He also found that varnishes such as GEC adhesive No. 7031 and bakelite lacquer gave an emissivity $\varepsilon \approx 0.87$; similarly, Scotch tape (Sellotape) had an emissivity of about 0·88.

to estimate but may be overlooked as a source of temperature drift or temperature inhomogeneity in a cryostat. The opposing demands of low thermal conduction along electrical leads and insignificant heat dissipation in these same leads often present a problem. At temperatures below 7 K this has frequently been solved by using wires of a poor thermal conductor such as constantan, and tinning the surface with a thin lead coating; this becomes superconducting below 7 K and the wire remains a poor heat conductor.

As is discussed in a later chapter (XI), most alloys (excluding superconducting alloys) exhibit an electrical resistance which does not decrease appreciably as the temperature falls from room temperature to liquid-helium temperatures, but their heat conductivity usually decreases by a factor of 10-100. On the other hand, pure metallic elements have an electrical resistance which may fall by a factor of 100 or more as the temperature is changed from 300-4.2 K; over the same range the thermal conductivity of the pure metallic element normally increases as T falls below 100 K, passes through a maximum at a temperature in the vicinity of $\theta_D/20$ (say 10-20 K), and falls linearly towards zero at the absolute zero. As a result a piece of copper wire may have approximately the same heat conductivity at 4 and 300 K while its electrical resistance is different by a factor of 100; a wire of constantan may have approximately the same electrical resistance at 4 and 300 K but a heat conductivity which has changed by a factor of 100. It may be noted that at both low temperatures (~4 K) and high temperatures (~300 K) the ratio $\rho \lambda / T$ for most metals has a value which approximates to the theoretical Lorenz value of $2.45 \times 10^{-8} \text{ V}^2/\text{K}^2$.

With the development of superconducting magnets there is more frequent need to carry large currents $(10\text{--}100\,\text{A})$ into cryostats and therefore to optimize the size of current leads. McFee (1959) calculated the optimum dimensions for copper wires of normal electrical quality (resistivity ratio ≈ 100) assuming no heat transfer to the evaporating helium gas. The results in Fig. 5.2 show that for copper leads of length l and cross section A going from room temperature (or from 77 K) to a helium bath, the minimum heat inflow \dot{Q} is about 42 mW per ampere (or 9 mW/A). A review by Buyanov, Fradkov, and Shebalin (1975) gives rather similar figures for Al, Ni, Ag, and some alloys but



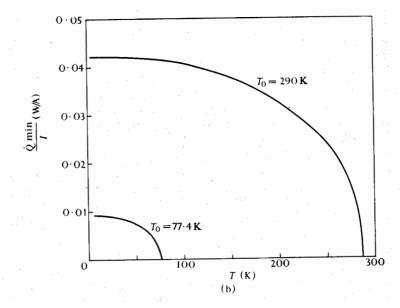


Fig. 5.2. Optimum size and heat input for leads of copper carrying current I from region at temperature T_0 to a lower temperature T. In (a) l/A is the ratio of length to cross-sectional area and in (b) \dot{Q} is the heat input (after McFee 1959).

shows that the optimum values of length/area differ greatly. For copper leads going from 290 K into liquid helium, lI/A should be 5×10^6 A/m; therefore if I = 20 A, l/A should be $2 \cdot 5 \times 10^5$ /m and so if $l = 0 \cdot 25$ m, the optimum A would be 10^{-6} m² corresponding to a single wire of 1 mm diameter or a bunch of 10 wires each of $0 \cdot 3$ mm diameter with heat leak $\dot{Q}_{\rm min}$ of $0 \cdot 8$ W.

The heat leak can be reduced considerably by changing the cross section at one or more intermediate temperatures (say 77 K) and optimizing the lead sizes for the different temperature intervals. Also heat transfer to the evaporating gas can be encouraged by using many strands of wire or by thermally anchoring the wires to a tube or sheet of metal exposed to the evaporating gas. Williams (1963) has shown how the heat leak can be reduced from say 9 mW/A to 1 mW/A per lead when operating at optimum current if there is good heat exchange. The review article by Buyanov et al. (1975) discusses this in more detail.

Gas adsorption

Another cause of temperature drift of concern to the lowtemperature calorimetrist is the adsorption or desorption of residual gas. The thermal energy required to desorb a layer of adsorbed gas from a surface is of the same order of magnitude as the latent heat of vaporization. As the temperature of the solid surface is raised, e.g. crystals in a calorimeter vessel, gas desorption begins and part of any electrical energy fed to the calorimeter is employed in this desorption process. Keesom (1942, p. 127) has given some adsorption data for helium gas on surfaces of glass and charcoal at low temperatures. Between 2 and 3 K glass adsorbs about $30 \times 10^{-6} \text{ mol/m}^2$ and the heat of adsorption is \sim 300 J/mol. The desorption of such a layer from 0.1 m^2 of glass needs energy of ~1 mJ. Thus in precision calorimetry it is undesirable to expose the sample or calorimeter to exchange gas at temperatures below about 10 K, because of the adsorption which occurs and subsequent slow temperature drifts which may be attributed to gradual desorption of the helium layer when the space is pumped to a high vacuum. This process has also been named as a contributing factor to 'heat leaks' in adiabatic demagnetization cryostats; when a salt pill is cooled to a temperature of $\frac{1}{100}$ K and is surrounded by a 1 K wall, helium gas (remaining from exchange gas used in cooling) slowly desorbs and becomes

adsorbed on the colder pill, transferring thermal energy in an amount which may cause a serious temperature rise, owing to the small heat capacities of the system.

The use of mechanical and superconducting heat switches has now become common in calorimeters and other cryostats requiring minimal heat leakages below 5 K. This avoids the need for helium 'exchange' gas and the annoying heat leaks which result from subsequent adsorption and desorption effects.

Helium film creep and thermal oscillations

Two annoying sources of heat can occur with liquid helium. One of these is due to the superfluid film and therefore is confined to liquid He II, that is to the normal isotope 4 He below the λ -point (2·17 K). The other arises from spontaneous oscillations which sometimes occur in columns of helium gas in narrow tubes.

When a dewar or chamber contains liquid He II, a mobile film covers the walls of the container up to a height where it is warm enough for it to evaporate. As it evaporates more helium flows up through this film so that the process leads to continuous loss of helium. The amount of this additional evaporation depends on the minimum perimeter of the walls covered by the film and the microscopic nature of the wall. For clean glass the flow rate (below 2 K) is c. 7×10^{-5} ml of liquid per s per cm of perimeter; this rate produces c. 3 ml of gas (n.t.p.) per min so that a mechanical pump of speed of 100 l/min would not be able to reduce the pressure below 3 Pa (≈ 0.02 Torr). Clean metal surfaces have film transfer rates about three times larger than that of clean glass, due probably to microscopic roughness. In practice, glass or metal surfaces are often 'dirty' due to adsorbed layers of air and may show transfer rates ten times that of clean glass (Bowers and Mendelssohn 1950). The result is that in small chambers containing pumped liquid helium it is difficult to reduce the pressure below, say, 100 Pa or about 1.2 K unless the film flow is reduced by having a small restriction in the pumping tube below the evaporation point (Ambler and Kurti 1952). This constriction may be 1 mm or even 0.1 mm in diameter but if too small it may be blocked more easily by impurities and make initial pumping-down intolerably slow. A suggested compromise is a 0.5-mm diam. orifice in the form of a piece of glass capillary tube a few millimetres long, sealed into the lower part of the pumping tube with epoxy resin.

Thermal oscillations in a tube (Keesom 1942, p. 174) leading down into a liquid-helium vessel can increase the evaporation rate by hundreds of cubic centimetres of liquid per hour. Their occurrence is rather unpredictable. Once they occur and are recognized they can be cured by altering the tube dimensions or inserting some form of damping (e.g. thread of cloth) in the tube. The necessary (but not always sufficient) conditions for these resonant oscillations to occur seem to be a diameter of less than 1 cm and a large temperature gradient with the bottom end of the tube being below $c.\ 20\ K$. Occasionally the oscillations themselves can be quite useful—witness the helium level detector produced by Clement and Gaffney, which was described above in $\ 2.3$ —although the associated inflow of energy is always a nuisance.

Mechanical vibrations

Mechanical vibrations can be a serious source of heat leakage in calorimetry and in precision thermometry at liquid helium temperatures, and in most experiments at millikelvin temperatures. Heating at the level of $0.1 \mu W$ and more can occur in an otherwise thermally isolated system due to being mechanically coupled to a building which itself is vibrating from elevators, nearby traffic, unbalanced machinery, etc. The effects were first noticed and measured by workers involved in magnetic cooling below 1 K (e.g. Cooke and Hull 1942; Darby et al. 1951). Later, Wheatley, Griffing, and Estle (1956) deliberately coupled a cryostat to a variable-speed motor and adjusted the vibration frequency from 0 to 13 Hz; they found at the maximum frequency, there was a leakage to their magnetic salt pill (mounted on a rather rigid support) of $0.4 \mu W$ compared with $0.015 \mu W$ when the motor was switched off. Fairly rigid suspensions inside a cryostat, e.g. graphite rods rather than nylon threads, are less susceptible to external vibrations because the resonant frequency is much higher than the frequency of most building or pump vibrations ($\sim 10 \text{ Hz}$).

As well as mechanical pumps being a nuisance, the action of mercury 'bumping' in a diffusion pump can produce vibrational heat leaks of $\sim 0.1~\mu$ W. Sorption pumps are a suitable alternative in some situations. Bubbling in cryogenic fluids is another

vibrational nuisance which in the case of helium can be eliminated by pumping below the λ -point.

To reduce the energy input from building vibrations, some degree of isolation is needed. The most complete is to mount cryostats on a pier in sandy soil in order to decouple it from the building. Otherwise use massive concrete blocks which themselves rest on isolating springs or wooden frames with their legs in sand-filled pipes or heavy plates on air-bag supports. The last-named can be simply a steel plate resting on an inflated rubber tube (from inside a small tyre) with enough mass in the plate and cryostat to reduce the natural vibration frequency well below that of the building. Another alternative is to do experiments at night without the annoyance of elevators, machinery, etc.! Lounasmaa (1974) and Mendoza in Experimental cryophysics (Hoare et al. 1961) discuss vibrations as well as other small heat 'leaks' which can upset millikelvin refrigerators.

Inadequate 'anchoring' of leads, etc.

This common source of heat inflow is really just another case of conduction by solids. Any lead wires, control rods, etc., which offer a flow-path for heat from room temperature to the experimental space need to be connected to a heat sink or guard-ring before reaching the experiment. If this thermal connexion is not adequate then annoying heating effects can arise. In calorimetry, heat conductivity measurements and in most experiments below 1 K, it is most important to guard against these heating effects by careful bonding of the leads to a surface which is at the temperature of the liquid bath. For electrical reasons it is impractical in most cases to solder the leads down: they must be cemented so as to preserve electrical insulation. If the wires are silk- or cottoncovered, a considerable length (e.g. 30 or 40 cm) should be tightly wound onto a copper post (high-conductivity copper) or cylinder which forms the heat sink and then cemented with a varnish such as G.E. 7031, Duco cement, etc. If the wires have only a coating of Formvar, Bicalex, etc., and no silk or cotton, then the heat transfer will be better and a shorter length need be anchored. But be careful that there is no slow reaction between the cement solvent and the coating which can later produce electrical breakdown. Better anchoring is achieved by cementing copper strips, say 3 mm wide by 40 mm long, onto the 'temporary' surface with nylon stocking as an insulator and using each strip as part of a lead. Also flexible copper laminates are available commercially (e.g. Sheldahl Ltd.) which consist of a thin plastic sheet with copper on each face which can be soldered to the surface and to leads.

Metallized ceramic discs can also be used in this same way, one side being soldered to a metal wall in contact with cryogenic liquid and the other side having the lead soldered to it. Alumina and sapphire heat sinks are commercially available.

Of course the most effective way of connecting leads thermally to the bath is to take them through a vacuum seal into the refrigerant but this sometimes presents high-vacuum problems. Designs for suitable epoxy-nylon-metal seals are discussed in § 10.4.

6. Example of heat-transfer calculation

As an illustration of the calculations that may be necessary in cryostat design, consider the magnitudes of the heat inflows from various sources in the following example (Fig. 5.3): A polished copper inner chamber of surface area 0.05 m^2 is supported by a German silver tube (2.0-cm diam., 0.3-mm wall thickness) inside a tarnished brass vacuum chamber in which the measured pressure (of helium gas) is 10^{-3} Pa; the length of the tube separating the two chambers is 6 cm. Twelve electrical leads (8 leads of 38 B. & S. gauge copper and 4 of 32 B. & S. constantan) enter the outer chamber through the pumping tube and are effectively thermally anchored on a copper bush at 77 K; the leads are then taken to the inner chamber, each lead having a length of about 12 cm between its points of attachment on the respective chambers.

We require to calculate the following.

- (i) Radiant heat inflow from the brass to the copper chamber.
- (ii) Radiant heat inflow down the German silver tube to the inner chamber when no radiation baffle is present.
- (iii) Heat conducted down the German silver tube from the outer to the inner chamber.
- (iv) Heat conducted down the electrical leads from one chamber to the other.

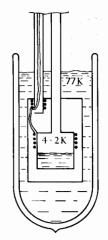


Fig. 5.3. Diagram of a cryostat.

- (v) Heat conducted through the low-pressure helium gas in inter-chamber space.
- (vi) And to examine whether Joule heating due to a current of 5 mA in the electrical leads is serious in view of the other heat inflows.

First,

(i) assuming that for tarnished brass $\varepsilon_1 \to 1$, and for polished copper $\varepsilon_2 \approx 0.03$, from (5.5)

$$\dot{Q}_{\rm r} = \sigma A (T_1^4 - T_2^4) 0.03$$

$$\approx 5.67 \times 10^{-8} \times 0.05 \times 0.03 \times (77)^4$$

$$= 3 \times 10^{-3} \,\text{W}.$$

(ii) Any calculation of the radiant heat reaching the inner space by 'funnelling' of room temperature radiation down the German silver tube must yield a very crude approximation to the true experimental result, at best. An upper limit $\dot{Q}_{\rm f}({\rm max})$ may be calculated easily, assuming 'complete funnelling', i.e. perfect specular reflection from the inner wall of the tube, so that all the radiation reaches the inner space.

$$\dot{Q}_{\rm f}(\max) = 5.67 \times 10^{-8} \times \pi \times (0.01)^2 \times (295)^4$$

= 0.135 W.

Alternatively, if we assume almost complete absorption of the radiation which reaches the inner wall of the tube, $\dot{Q}_{\rm f}({\rm min})$ is merely the radiation from a small solid angle subtended by the lower exit of the tube at its upper (room temperature) end. If the length of the tube be about 30 cm between 4·2 K end and that part at room temperature

$$Q_{\rm f}(\min) \simeq \frac{\pi (0.01)^2}{2\pi (0.3)^2} \times \sigma A (295)^4$$

 $\sim 10^{-4} \,\text{W}.$

In practice this minimum value for radiant heat inflow via the pumping tube may be approached by painting the inner wall of the German silver tube with an optical black paint, 'Aquadag', etc. More complete isolation from room-temperature radiation is usually obtained by means of a bend in the tube or insertion of a small radiation baffle. By this means the room-temperature radiation is adsorbed by the tube wall near the bend or at the baffle and transmitted into the liquid-nitrogen bath; the inner experimental space then only sees radiation emitted from a relatively small area of surface at 77 K which is transmitted by a direct path or successive internal reflections down the tube.

(iii) For the heat conducted by the German silver tube ($\bar{\lambda} = 12 \text{ W/m K}$)

$$\dot{Q}_{c} = \bar{\lambda} \frac{A}{l} \Delta T$$

$$= 12 \times \frac{2\pi \times 0.0003}{0.6} \times 73$$

$$= 0.275 \text{ W}.$$

(iv) The heat conducted down the electrical leads is given by

$$\dot{Q}_{c}^{*} = \dot{Q}$$
 (8 copper leads of 0·1 mm diam.)
+ \dot{Q} (4 constantan leads of 0·2 mm diam.).

From Table 5.1

$$\bar{\lambda}(Cu) = 980, \quad \bar{\lambda}(constantan) = 14$$

whence

$$Q_{\rm c}^* = 0.0385 \, \rm W.$$

(v) For gas conduction $\dot{Q}_{\rm g}$ is given by (5.3) which in the case of helium reduces to

$$\dot{Q}_{g} = 2 \cdot 1 p a_0 \Delta T \cdot W/m^2$$
.

Assuming that the respective surfaces are approximately equal and parallel, and that

$$a_{\text{max}} \simeq 0.5 = a_1 = a_2,$$

then

$$a_0 = 0.5/(2 - 0.5)$$

= 0.333.

Since $\Delta T = 73 \text{ K}$, $p = 10^{-3} \text{ Pa}$

$$\therefore \dot{Q}_g = 2 \cdot 1 \times 10^{-3} \times 0.333 \times 73$$

and since

$$A = 0.05 \text{ m}^2$$
$$\dot{Q}_g = 0.0025 \text{ W}.$$

(vi) (a) Eight copper leads of 38 B. & S. wire each have an approximate room-temperature resistance of $2.4 \Omega/m$. Assuming that $\rho_{293}/\rho_4 \approx 100$, $R(77 \text{ K}) \approx 0.46 \Omega/m$, and $R(4 \text{ K}) \approx 0.03 \Omega/m$.

If the mean resistance $R \approx 0.25 \Omega/m$, then the total heat produced by 5 mA is

$$8 \times (5 \times 10^{-3})^2 \times 0.25 \times 0.12 = 6 \times 10^{-6} \text{ W}.$$

A rough calculation based on a mean thermal conductivity of $1000 \, \text{W/m}$ K shows that the temperature rise in the wire will be $< 0.01 \, \text{K}$ at any point. If all the Joule heat were transferred to the inner chamber this would only amount to $6 \, \mu \, \text{W}$.

(b) In the case of the constantan wires (4 or 32 B. & S.), the resistance of each is about $14 \Omega/m$ and is fairly insensitive to temperature change.

Total Joule heat produced is

$$4 \times (5 \times 10^{-3})^2 \times 14 \times 0.12 = 1.7 \times 10^{-4} \text{ W}$$

and assuming $\bar{\lambda} = 14$ W/m K, temperature rise in the wire should be greater than 5 K.

Summarizing, we note that the major source of heat leakage is via the supporting tube, and provided that precautions are taken

to prevent room-temperature radiation entering the inner chamber via the tube this leak amounts to about $0.275 \, \text{W}$. Radiant heat of $10^{-3} \, \text{W}$ reaches the inner chamber from the surrounding 77 K chamber and heat leakage through the residual $10^{-3} \, \text{Pa}$ pressure of helium gas is less than $0.004 \, \text{W}$; by comparison a 5 mA current through each electrical lead could contribute a maximum heat inflow of about $100 \, \mu \text{W}$.

The total heat leak of about $0.28\,\mathrm{W}$ would evaporate nearly 400 ml of liquid helium per hour; this assumes that the cold evaporating gas does not play any useful role in cooling the wall of the German silver tube and thereby reduce the heat leak.

7. Heat transfer through pressed contacts

Elsewhere we make passing reference to the problem of heat transfer across the boundary between two solid surfaces in contact. This has a direct application to at least two practical cryogenic problems, namely to the design of mechanical heat switches (for example, as applied to calorimetry) and in the design of insulating supports for low-temperature equipment (as applied to the internal supporting members in large dewar vessels).

The first comprehensive investigation of thermal contact has been that of Berman (1956) who studied the thermal conductance of various solid contacts at liquid-helium and liquid-nitrogen temperatures, using loads of 50–250 lb. His results suggest that:

- (i) The measured thermal conductance is always greater than that calculated by the Wiedemann-Franz-Lorenz law from the measured electrical conductance. This discrepancy, often a factor of 100 or more, is as high as 10^5 when contact and measurement are made at 4.2 K. The only possible conclusion seems to be that the majority of the heat is carried across the interface by thermal waves rather than by electrons.
- (ii) The thermal conductance varies nearly linearly with the pressure, and hence is not sensitive to change in area for a given total load.
- (ii) At liquid-helium temperatures (1-4 K), the conductance varies at T^2 but becomes less temperature-sensitive at higher temperatures, the change in conductance between 64 and 77 K being only about 10 per cent.

- (iv) Some typical figures given by Berman for the thermal conductance of the contact between (a) two copper rods, (b) two 0.001 in. steel disks are:
 - (a) 1.02×10^{-2} W/K at 4.2 K; 32.5×10^{-2} W/K at 77 K;
 - (b) 0.54×10^{-2} W/K at 4.2 K; 26×10^{-2} W/K at 77 K;

in each case the contact was made at room temperature and the load applied was 100 lb.

Later measurements on metals by Berman and Mate (1958) were in substantial agreement but showed the conductivity to vary a little more slowly with temperature, as $T^{1\cdot3}$ for coppercopper and gold-gold. For sapphire-sapphire contacts under 100-lb load they found $\dot{Q}\approx 10^{-5}T^3$ W/K at liquid-helium temperatures. The most remarkable feature from a practical viewpoint was that the magnitude of the heat conductance for gold-gold contacts was about twenty times better than copper-copper whereas sapphire-sapphire was at least ten times worse (below 10 K). Therefore for good heat transfer in a mechanical switch, the contacts should be gold-plated. Conversely to achieve good insulation in a support system, hard ceramic contacts should be used; for example, a sapphire ball resting on a sapphire plate.

The experimental work on heat conduction through insulating supports by Mikesell and Scott (1956) is of less fundamental interest than Berman's experiments but of great practical significance in cryogenic design. Their work was concerned with the internal support of large dewar vessels by using stacks of thin disks. Although the mechanical strength of the stack is great, the thermal contact resistance between disks is such that the total thermal resistance of a stack may be a hundred times greater than that of a solid rod of the same material and dimensions. Mikesell and Scott found that the conductance of the stacks of disks could be decreased substantially by using a thin layer of manganese dioxide dust between each pair of plates.

Such stacked disks provide an excellent means of transmitting high pressures into a cryostat, as a stack can have very high compressional strength, and yet retain a low heat conductivity (see, for example, their use by Berman 1956).

Experiments on contact resistance also confirm the reasons for the frequent difficulties that are encountered in thermally anchoring electrical leads effectively at low temperatures. This boundary resistance is a common restriction on the flow of heat between dissimilar materials. It was ascribed by Little (1959) to acoustic mismatch between the materials, that is to a difference in phonon velocity between the media which affects the vibrational waves as it does electromagnetic waves traversing a boundary between materials of different refractive index. For the solid-liquid-helium interface, the term Kapitza resistance is used (reviews of Pollack 1969; Challis 1974; Snyder 1970) but its importance at low temperatures extends to metal–solder, solid–epoxy, solid–grease interfaces, etc. Lounasmaa (1974) has compiled values of the Kapitza resistance ($R_{\rm K}$) below 1 K for Cu–⁴He, Cu–³He, Cu–glue, Cu–Mylar, Al–Mylar, and many other combinations.

The heat transport is greatly increased if electron transport is made appreciable by using gold-gold contacts which have no oxide layer to reduce electron flow; also the use of a non-superconducting solder such as gallium (suggested by Reynolds and Anderson 1976 for $T > 1 \cdot 1$ K) achieves this.

8. Heat switches

General

The simplest and most commonly used heat 'switch' is still helium exchange gas. By changing the pressure of gas in the space between two walls from 10 Pa to 10^{-3} Pa the heat transfer between them is altered by many orders of magnitude. The chief drawbacks to this 'switch' are that (i) it takes a long time to turn it 'off' completely, particularly at liquid-helium temperatures, (ii) some gas always remains adsorbed on a surface and may be desorbed later and upset the energy balance, and (iii) at very low temperatures there is no gas left; even ³He has negligible vapour pressure below 0.1 K. Therefore various alternative switches have been evolved, viz.:

- (i) Mechanical switches which can be turned 'on' and 'off' easily but which generate some heat in the switching and are therefore most suitable above c. 0.5 K.
- (ii) Superconducting 'switches' for which the ratio of heat conductance in the 'on' position to the conductance in the 'off' position only becomes sufficiently high at temperatures below $\sim 1~\rm K$.

- (iii) Graphite 'switches' or links which represent a particular case of materials whose thermal conductivity varies rapidly with temperature; it is low enough at $\sim\!\!1\,\mathrm{K}$ to act as a thermal insulator but high enough at $10\,\mathrm{K}$ to conduct away thermal energy at an appreciable rate.
- (iv) Various other devices which make use of helium gas or liquid helium in tubes and can be turned 'on' or 'off' without too much delay.

Mechanical switches

These have become the accepted method of cooling calorimeters in the temperature region from 1 to 10 K; below this the heat evolved on breaking the contact becomes relatively large. The first type of mechanical switch described by Keesom and Kok (1933) and Ruehrwein and Huffman (1943) used the mating of conical surfaces for heat transfer. However, on breaking, these produce rather a lot of frictional heating and have not been used much at liquid-helium temperature. Two designs which are used down to 1 K are:

- (i) the jaw-type based on that of Webb and Wilks (1955) and refined by Manchester (1959) and Phillips (1959);
- (ii) the plate-type first used by Ramanathan and Srinivasan (1955) and Rayne (1956).

Of the examples of these which are described in the literature, the jaw-type have generally given less heating on breaking the contact but not so high a conductance when closed as the plate-type. Phillips (1959) achieved release energies of $10~\mu J$ by careful design of the jaws and by using rigid support for his specimen; the thermal conductance was of $\sim 10^{-3}$ W/K between 1 and 4 K; this might have been improved by gold-plating the jaws and the wire connected to the specimen.

Hill and Pickett (1966) have also described a switch rather similar to that of Manchester in which the jaws are gold-plated rather than covered with indium on the contacting surfaces. Their heat conductance was higher and varied less rapidly with T than did that of Manchester, particularly below 2 K. They found conductance varied as $T^{1.7}$ and was c. 10^{-4} W/K at 2 K which is still three or four times less than Phillips reported.

Other designs in which rather large loads could be applied to give a high conductance are described by Colwell (1969) and

Siegwarth (1976); the latter used jaws to clamp a number of gold-plated copper leaves together and achieved conductances from $0.1~\rm W/K$ at $2~\rm K$ to $1~\rm W/K$ at $15~\rm K$ with a $50~\rm kg$ load.

Birch (1975) has used the plate-type down to $0.3 \, \mathrm{K}$ and achieved a release energy of $10 \, \mu\mathrm{J}$ by eliminating any roughness and twisting action in the breaking of the contact. Birch has simply modified Rayne's switch (see Fig. 7.2) by ensuring that the push rod is in close contact with the main helium bath at some point and using a hydraulic system with small hand-pump to move the push rod. Contact with liquid helium is achieved by having the bellows down in the liquid. The contacting plates above and bleow the calorimeter are lapped flat and gold-plated to improve thermal conductance.

Aslanian and Weil (1960) have used a hydraulic control system in which the bottom plate-contact sits on the top of flexible bellows and is pushed upwards onto the sample by inflating with helium; they also report energies on release of c. 100 ergs.

Superconducting switches

The use of a superconducting link as a switch was first suggested by Heer and Daunt (1949), Gorter (1948), and Mendelssohn and Olsen (1950) as a result of experiments on the heat conductivity of superconducting elements. This switch depends on the fact that the thermal conductivity λ_n of a superconducting element in the normal state (induced by a magnetic field exceeding the critical field), is larger than its conductivity λ_s in the superconducting state. In the normal state, conduction electrons are chiefly responsible for the conductivity and at temperatures near or below 1 K, λ_n is limited by physical or chemical impurities so that $\lambda_n \propto T$. For example, consider a metal of residual electrical resistivity $\rho_r \simeq 10^{-3} \times 10^{-7} \ \Omega m = 10^{-10} \ \Omega m$; from the Wiedemann–Franz–Lorenz relation, $\lambda_n \sim 2.5 \times 10^2 \ T \ W/m \ K$ which is the electronic conduction of heat at low temperatures in the normal state of the metal.

In the superconducting state, at temperatures well below $T_{\rm c}$, only lattice waves contribute significantly and their conductivity $\lambda_{\rm s}$ is limited by grain boundaries. Casimir's theory of this and experiments (e.g. Berman 1976 and § 12.3) show that

$$\lambda_{\rm B} \sim 1.6 \times 10^3 \ DA^{\frac{2}{3}} \ T^3 \ {\rm W/m} \ {\rm K}$$

where D is the average grain size and A is taken from the heat capacity per unit volume at low temperatures, i.e.

$$C = AT^3 \text{ J/m}^3 \text{ K}.$$

Thus for Pb,

$$C \approx 100 \ T^3 \ J/m^3 \ K \quad (for \ T \ll \theta_D)$$

whence

$$\lambda_{\rm s} = 34 \times 10^3 \, DT^3 \, \text{W/m K}$$

so that if $D \sim 1$ mm,

$$\lambda_n/\lambda_s \approx 7T^{-2}$$

= 700 for $T = 0.1 \text{ K}.$

Hence in a case where the grain dimensions are about 0.1 cm, it is clear that $\lambda_{\rm n}/\lambda_{\rm s} \simeq 6T^{-2}$; for T=0.1 K this gives $\lambda_{\rm n}/\lambda_{\rm s} \simeq 600$. Experimental work below 1 K has confirmed that $\lambda_{\rm s} \propto T^3$ and that for high-purity wires of Pb, In, Sn the ratio $\lambda_{\rm n}/\lambda_{\rm s}$ may be from $10T^{-2}$ to $500T^{-2}$ K² (e.g. March and Symko 1965 or references in Lounasmaa 1974, p. 260; Berman 1976, p. 168). Therefore near 0.1 K the heat conductivity can be changed by a factor of 1000 or more by switching on or off a field of 0.1T produced in a small solenoid of niobium or niobium-titanium wire. Phillips (1959) and Martin (1061) have described their application to calorimetry.

Graphite switches

The word 'switch' is perhaps a misnomer for the use of a material which merely has a very rapid variation of heat conductivity with temperature. This can be used as mechanical support to help the initial cool-down of a system whose final temperature is to be so low that the conductivity of the link material then becomes negligible. Many types of polycrystalline graphite are useful for this. Their thermal conductivity varies approximately as T^3 and may have a magnitude of 10^2 W/m K at 100 K, 10^{-1} at 10 K, and 10^{-6} W/m K at 0.1 K (Berman 1952, 1958). Shore *et al.* (1960) first suggested the use of pitch-bonded graphite as a low-temperature support and a thermal shunt in parallel with a superconducting thermal switch: at liquid-nitrogen temperatures

it is an excellent conductor for cooling their paramagnetic salt but becomes an effective insulator at the lowest temperatures.

Later Pandorf, Chen, and Daunt (1962) showed that suitable carbon radio-resistors were quite effective as shunts in parallel with superconducting thermal switches. Their tests on Allen-Bradley and Ohmite resistors gave values of c. 0.1 W/m K at 10 K, and 5×10^{-4} at 1 K; they were not as high as pure graphite at temperatures above 10 K.

This behaviour is not confined to graphite. For any dielectric material at low-enough temperatures the conductivity $\lambda \approx a T^3$, the absolute magnitude being dependent on grain size and phonon velocity (or Debye temperature θ_D). Sufficiently fine-grained samples of the ceramics alumina, magnesia, beryllia, etc., may have $\lambda \approx 1$ W/m K at 10 K and therefore λ will be $\sim 10^{-6}$ W/m K at 0.1 K.

Zimmerman, Arrott, and Skalyo (1958) have found that mica condensers also will serve this purpose.

Other switches

The term 'switch' may also be applied to various tube devices in which gaseous or liquid helium acts as a medium of heat transfer. For example, the thermosiphon principle may be used with the particular gas condensing in the top end of the tube in contact with a cold heat sink and then dropping to the lower end where it evaporates in contact with the source or object to be cooled (e.g. Bewilogua, Knöner, and Kappler 1966). When cooled the gas and liquid can be pumped away.

Another device uses liquid He II in a tube. The liquid is a good conductor at temperatures near 1 K and can be easily displaced by a cylinder of Teflon which is a poor conductor (Shore 1960). Vilches and Wheatley (1966) have described the use of capillary tubes filled with liquid helium, for transferring heat to and from magnetic cooling salts (see § 8.5).

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CHAPTER VI

TEMPERATURE CONTROL

1. Introduction

CONTROL of temperature may be achieved by a variety of methods and with various degrees of efficiency, a desirable efficiency depending on the particular investigation for which a cryostat is intended. A measure of the efficiency is the width of the temperature region over which control can be maintained and the smallness of the temperature fluctuation achieved at any temperature in this region. In general terms temperature control demands an effective balance within the 'experimental space' between the supply and loss of thermal energy.

The various methods may be divided into two broad categories: first, those in which the experimental space (temperature T) is thermally linked (preferably by a 'poor' thermal link) to surroundings at a higher temperature, T_0 , and heat is continuously extracted from the experimental space; secondly, those in which the surroundings or a thermal reservoir to which the 'space' is loosely thermally connected, are at a lower temperature (T_0) than the desired control temperature, T, in which case heat is supplied to the 'space' to maintain control. Examples of the first are the use of controlled gas flow, gas desorption, controlled adiabatic expansion of a gas, and Joule–Thompson throttling; evaporation of a liquid under a controlled reduced pressure might also be considered to belong to this category.

In the second class belong the common methods of electrical heating by which a chamber or specimen is raised to a temperature above that of the surroundings by supply of electrical current to a resistance element, the current being controlled either manually or automatically in response to a temperature signal.

The two means most commonly used—vapour-pressure control and electrical heating—are discussed in §§ 2 and 3 below, followed in §§ 4 and 5 by descriptions of the 'controlled refrigeration' systems.

2. Control of vapour pressure

The relation between the temperature and the vapour pressure of a liquefied gas was discussed in Chapter IV (Temperature Measurement) and the importance of the vapour pressure of liquid helium, hydrogen, oxygen, etc., as secondary thermometers was stressed. Here we shall consider 'manostats' or pressure-control devices by which the vapour pressure of a boiling liquid may be controlled to within certain limits.

The usual arrangement (Fig. 6.1) has a manostat in the pumping tube from the liquid whose boiling pressure is to be controlled. The 'by-pass' valve enables the vapour to be pumped directly, e.g. when initially reducing the pressure over the liquid from atmospheric to near the control pressure, or when pumping to pressures below the lower limit of the manostat.

In the writer's experience, the most convenient pressure controller is that shown in Fig. 6.2 (after Kreitman 1964). A plastic or rubber sheet (<0.1 mm thick) moves up or down and thereby opens or closes a valve when the vapour pressure is greater or less than the control pressure P_0 . Changes in room temperature can cause the control pressure P_0 to drift but this tendency can be reduced by adding a large thermally-insulated ballast volume.

Another simple home-made manostat (Fig. 6.3) is that based on the Cartesian diver and described in detail by Gilmont (1951). In the glass version which is illustrated, P_0 is the control or

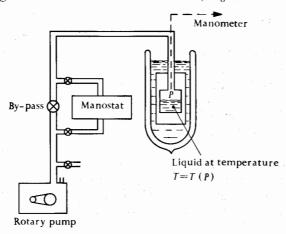


Fig. 6.1. Control of the pressure above a boiling liquid.

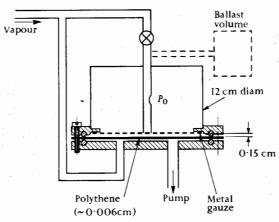


Fig. 6.2. A pressure regulator similar to that used by Kreitman (1964).

reference pressure under the diver and the valve consists of a smooth orifice in a glass rube which seats against a rubber pad (preferably gum rubber of 2-3 mm thickness). As discussed by Gilmont, the pressure P fluctuates with a small amplitude ΔP about P_0 and the ratio $\Delta P/P_0$ depends on the size of the orifice;

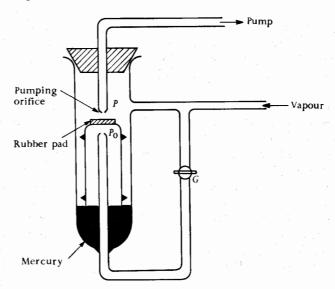


Fig. 6.3. A Cartesian manostat of glass.

with 1 mm diam. hole, the expected fluctuation is $c.\ 0.5$ per cent but is rapid and therefore masked for most purposes. Temperature control with the foregoing two manostats can easily be achieved to $\sim 1\,\mathrm{mK}$ at helium temperatures or 5–10 mK with liquid nitrogen, except at the lowest pressures (say <3 Torr or 400 Pa) where they are relatively less sensitive. The lower pumping speed of the Cartesian manostat can be a disadvantage. Another simple device with high pumping speed is that made by Walker (1959) from a very thin-walled rubber tube or 'sheath', the collapse of the tube walls forming the valve. This thin rubber perishes under ultraviolet illumination so it must be suitably protected.

Cataland, Edlow, and Plumb (1961) described a very stable manostat which is used in precision thermometry at some national laboratories, including the NBS: drift in the control pressure P_0 is avoided by using weights to control the pressure with reference to a vacuum. Thin-walled brass bellows respond to the difference between the set pressure and vapour pressure P by opening or closing a ball-bearing valve. Regulation at 4 K with 150 mm diam. bellows is better than 6 Pa (~ 0.05 Torr) over long periods.

Another stable (and more expensive) manostat has been made using a capacitance pressure sensor and operational amplifiers which activate solenoid valves to control the vapour flow (Fletcher 1977); pressure stability of better than 0.1 per cent is achieved with 4 He from 2 to 1000 Torr, corresponding to variations of <1 mK.

For very precise control of temperature of liquid-helium baths, it may be more simple to adjust and fix an appropriate pumping speed and then control by automatic electrical heating. Sommers (1954), Blake and Chase (1963) have described electronic controllers (see also § 3 below) designed for this purpose; they are activated by a carbon resistor in the helium bath, this resistor forming one arm of an a.c. Wheatstone bridge.

It should be noted that in pumping liquid-oxygen vapour, some care should be taken in choosing the type of mechanical pump and pump oil to use. Pumps of the Kinney type should not be used for oxygen as the explosion risk is great. The usual type of rotary vane pump has been used by the writer for pumping oxygen for many years, without any trouble, although it is

considered advisible by some authorities (e.g. Professor S. C. Collins, private communication) to replace the normal pump oil by tricresyl phosphate.

3. Control by electrical heating

As we have stressed before, regulation of temperature outside the ranges covered by the vapour pressures of available liquefied gases presents difficulties; the magnitude of these difficulties depends on the required degree of precision of the temperature regulation. The usual method is by controlling the supply of electrical energy to preserve a temperature T in the space which is above that of the surroundings (at T_0). As the loss of heat, $-\dot{Q}$, to the surroundings by radiation, conduction, etc., is a monotonically increasing function of $T-T_0$, so the electrical input, \dot{Q} must increase similarly with $T-T_0$. The situation is represented schematically in Fig. 6.4, where a temperature detector, e.g. thermocouple, or resistance thermometer, provides information by which manual or automatic regulation of the electrical current to a heater is determined.

Manual control of the heating current often meets the experimental demands, when physical measurements may be done quickly and when they are not very sensitive to temperature drift; particularly at low temperatures, where heat capacities are small and the time for establishment of thermal equilibrium is short, a correct adjustment of heating current may be found quickly.

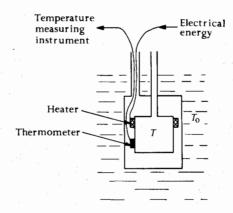


Fig. 6.4. Temperature control by electrical heating.

Unfortunately, any change in the heat loss to the surroundings—due to change in pressure of residual exchange gas, for example—must affect the temperature and await manual adjustment of the heating current.

Most automatically controlled heating systems used at low temperatures are based on continuous control, as opposed to the simple on-off type of controller operated by a bimetallic spiral or expanding mercury column which is often used as a thermostat at higher temperatures. Such continuous controllers are usually actuated by the signal from a thermocouple or resistance thermometer; they amplify this signal and feed it back into the electrical heater. The degree of amplification required depends on the sensitivity of the detector, i.e. the magnitude of the signal, and on the precision required in the control of temperature.

A comparison of a resistance thermometer and thermocouple thermometer as temperature detectors shows each to have certain advantages and disadvantages. By its very nature the resistance thermometer is itself a source of thermal energy which can be a serious disadvantage when it is desired to control T very close to T_0 . But resistance thermometers may be operated on a.c. and therefore supply an a.c. signal (e.g. out-of-balance e.m.f. when the detector is one arm of an a.c. bridge) which can be amplified more easily than the d.c. signal from a thermocouple. For temperatures in the range 4-20 K, a carbon resistance provides a very sensitive thermometric element; for the range from 20-300 K, a copper resistance winding or small platinum resistor (§ 4.6) is suitable. From 4-300 K, a CLTS (manganin+nickel resistor) or silicon diode can be used; also capacitance sensors can be used with an a.c. bridge over a wide range and are unaffected by magnetic fields. In a thermocouple detector there is negligible heat dissipation in the couple itself and Au+0.07 Fe:chromel will provide an adequate signal from 300 K down to liquid helium temperatures. Although a thermocouple is less reliable than some resistors as a reproducible precision thermometer, it can be stable for long periods of time when fixed in position in a cryostat and not subject to violent changes in temperature. The disadvantage is that a high-gain d.c. amplifier is required for precision control. Fortunately, reliable chopper-amplifiers for this purpose have been described and are now commercially available.

A good example of precision control by the thermocouple

method is that of Dauphinee and Woods (1955); the regulator shown schematically in Fig. 6.5 below is based on a chopper-type d.c. amplifier suitable for detecting thermocouple signals as small as 10^{-8} V. Choppers modulate the signal from a differential thermocouple; it is then amplified about 10^7 times and the output demodulated by further choppers, the input and output choppers being synchronous. The amplifier described is a fairly conventional low audio-frequency amplifier, preceded and followed by high-quality transformers. Low-noise electromechanical choppers suitable for such controllers are commercially available, e.g. in the Keithley nanovoltmeter. There are also many commercial controllers operating at the 0·1 K sensitivity level which can be activated by thermocouples as well as by resistance elements (Oxford Instrument Company and see Appendix). These may use JFET or photoconductive choppers.

Some other controllers have used d.c. signals and the galvanometer-amplifier principle. In one such, the d.c. signal is fed to a galvanometer and the light beam from this is chopped mechanically by a sector disc, then falls on a split photocell; the modulated output from the photocell is amplified, pass through a phase-sensitive detector, and fed to the heater (e.g. Gilchrist 1955). In another described by Rose-Innes (1973, p. 168), the light spot from the galvanometer illuminates a cadmium sulphide photoconductive cell whose resistance controls the current to the heater.

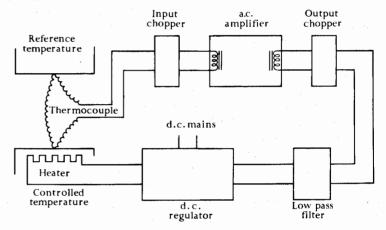


Fig. 6.5. The temperature regulator (after Dauphinee and Woods 1955).

In the writer's opinion, a.c. bridges are the best means of precision temperature control particularly since the growth of transistor technology has made their construction cheaper and quicker. In principle they all consist of a four-arm bridge with one arm being the temperature-sensing element, which is usually a resistance thermometer but can be a capacitance thermometer. Temperature changes in this arm produce a change in bridge signal which is amplified, phase-detected, power-amplified, and fed back into a d.c. resistance heater in the cryostat. Some care must go into the thermal coupling of the thermometer, heater, and other load to avoid 'hunting'. Control at the mK level from 4 to 150 K was achieved in one cryostat (White 1953) using a twoterminal 1000Ω manganin resistor wound non-inductively on the inner chamber of a cryostat with a $200\,\Omega$ constantan heater wound around the same chamber; this bridge-amplifier-detector system was based on controllers of Sturtevant (1938) and Penther and Pompeo (1941); Sommers (1954) and Blake and Chase (1963) have described similar ones.

With these two-lead thermometers, slow drifting occurs due to change in lead resistance with change in level of cryogenic fluid. This can be largely avoided by having a parallel compensating lead incorporated in the balancing arm of the bridge or by using a three-lead system. Bridges with greater stability and capable of controlling at the 0.1 mK level have been made using a four-lead resistance thermometer: that of Pickup and Kemp (1969) uses an a.c. version of the Kelvin bridge which is actuated by a carbon resistor (T < 20 K) and a copper or platinum resistor (T > 20 K).

The most recent version of this controller uses the bridge shown schematically in Fig. 6.6. The high-gain differential amplifier A_1 together with precision resistors R_1 , R_2 , R_3 , R_4 form a bilateral current source where the output I is not a function of voltage; the resistors are good commercial wire-wound with a temperature coefficient $<10^{-5}/K$. The current I flows through the 'unknown' (thermometer) resistance R_X , shown as a four-terminal connection with lead resistances r which are not required to be all the same. Amplifier A_2 is a voltage follower connected so that the point Q is at the potential of the tap on the linear divider (divider ratio α) representing the setting dials. The bridge balance is thus effectively independent of the lead resistances. A number of these bridge-controllers have been made at

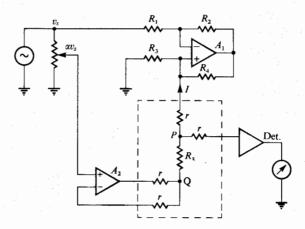


FIG. 6.6. Simplified diagram of a.c. bridge for a temperature controller: $R_1 = R_2$, $R_3 = R_4$, $I = v_s/R_4$, $v_0 = \alpha v_s$ and output $v_p = 0$ when $R_X = \alpha R_4$ (C. Pickup, private communication; Pickup and Kemp 1969).

the National Measurement Laboratory in Sydney and used for precise control of thermometer calibration cryostats (e.g. Plumb, Besley, and Kemp 1977); in this context 'precise' means better than $0.1 \, \text{mK}$ over many hours.

For very low temperatures (<1 K) where electrical noise is more important, the bridge described by Anderson (1973) may be more suitable. It also is a four-lead system with operational amplifiers but uses two ratio-transformer arms as shown schematically in Fig. 6.7.

 $R_{\rm S}$ is the reference decade resistor through which the current is automatically maintained constant, and $R_{\rm T}$ represents the resistance thermometer in the cryostat; its resistance is read directly in ohms from the null setting of the ratio transformer T_2 ; M is for monitoring the operational amplifier, F is a low pass filter, PS is a phase shifter, D a lock-in detector, etc.

Another interesting controller has been developed by Newrock, Wagner, and Rosenthal (1977) from those of Venegas and Finegold (1969) and Griffin (1975) which respond to either a resistance thermometer or to a capacitance thermometer which makes it very useful in high-magnetic field situations. They describe the short-term stability as being 0.1 mK with a carbon resistor and 1 mK with a strontium titanate capacitor; the long-term stabilities are respectively 1 mK and 3-5 mK.

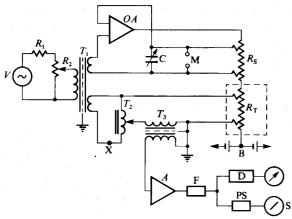


Fig. 6.7. Circuit of a four-terminal, low noise a.c. bridge (after Anderson 1973). Point B represents the common connection to the battery supply for the operational amplifier OA.

There are many descriptions of electronic controllers in the journals of scientific instruments; their control accuracy and ease of construction vary considerably but recent advances in transistor technology have made it much easier to construct precision controllers with a relatively few man-days of effort. Many commercial firms (see Appendix) also produce electronic temperature controllers but most are designed for control needs of ± 0.1 K.

4. Controlled refrigeration

By 'controlled refrigeration' we mean those methods by which an experimental chamber is maintained at a temperature below its general surroundings, using controlled expansion or desorption of a gas. Such methods have been most widely used to bridge the temperature interval between 4.2 K and that which can be attained with liquid hydrogen.

In the Clarendon Laboratory at Oxford, Simon expansion helium liquefiers were an integral part of a number of research cryostats; physical investigation of properties in the region between 4 and 10 K were done by carefully controlling the adiabatic expansion of the compressed helium gas (initially at 10 K and about 120 atm) so as to maintain temperatures of say 8, 7, or 6 K before the expansion and liquefaction is complete. The high thermal capacity of the compressed gas makes it relatively easy to cool to 7 K and maintain this temperature quite closely for a

period of many minutes. Examples of the use of this method of control are afforded by the work of Berman (1951) on thermal conductivity, and of MacDonald and Mendelssohn (1950) on electrical resistance.

Simon's desorption liquefier has also been used as an effective temperature controller in the range between 4 and 10 K (see, for example, Simon 1937). The process is very similar to that of controlled expansion, except that the helium-gas pressures involved are much smaller. Instead of controlling the expansion of the compressed helium gas, the rate at which the helium is pumped from its charcoal adsorbent is carefully controlled; the relatively large heat capacity of the adsorbed gas also acts as a thermal reservoir, the temperature of which is therefore insensitive to small changes in heat transfer. Measurements by de Haas, de Boer, and Van den Berg (1933–4) on electrical resistance, were made with the help of this method of maintaining steady temperatures.

Rose-Innes and Broom (1956) adapted this desorption principle to allow temperatures to be maintained from 4.2 K up to liquid-oxygen temperatures.

5. Flow method of control

A rather efficient method of regulating temperature was evolved by Swenson at the Massachusetts Institute of Technology (described in a paper by Swenson and Stahl 1954), a method in which both the latent heat of vaporization of a liquefied gas and part of the heat capacity of the gas are used to balance the heat inflow to an experimental chamber. The principles may be seen from Fig. 6.8 which illustrates a cryostat used for high-pressure investigations. Temperatures between 4 and 80 K were maintained in the experimental enclosure by drawing liquid helium from the reservoir through a $\frac{1}{8}$ -in thin-walled cupro-nickel tube to the heat exchanger. The exchanger consists of three concentric layers of $\frac{3}{16}$ -in. o.d. copper tubing, wound around and solder bonded to the copper-walled enclosure which is to be kept at constant temperature. The rate at which the liquid helium is drawn through this tubing is controlled by the setting of a fine needle valve in the pumping tube between the heat exchanger and a mechanical pump. When controlling the enclosure at some temperature T (>4·2 K), the liquid helium evaporates in the

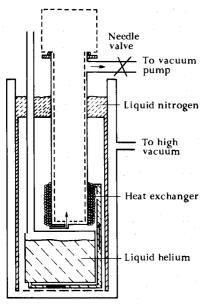


FIG. 6.8. Schematic diagram of a cryostat in which the temperature is controlled by the 'Swenson' method (after Swenson and Stahl 1954).

copper coil extracting about 84 J/mol from the system; it is warmed up to a temperature close to the control temperature T as it circulates through the coil, extracting further heat equal to about $20 \times (T-4\cdot 2)$ J/mol. It was found that to maintain steady temperatures of 30 K or less, the needle valve had to be adjusted very carefully to avoid too great a flow rate of the coolant. The addition of an electrical heater, e.g. carbon resistor in a copper sleeve, attached to the outside of the heat exchanger improved the control; the needle valve provided a coarse control and the heater current gave a fine adjustment.

Since Swenson's work, Klipping and his colleagues in Berlin have developed a number of flow cryostats which can be attached directly to a storage dewar (Klipping, Vetterkind, and Walentowitz 1965; Klipping, Schönherr, and Schulze 1970). Figure 6.9 is a schematic diagram based on the cryostat of Klipping *et al.* (1965) in which liquid helium or liquid nitrogen is sucked up through a transfer tube into a ribbed 'vaporizing' chamber which cools the experimental space above it; the gas then goes through a spiral copper coil to cool the shield. The flow rate is controlled

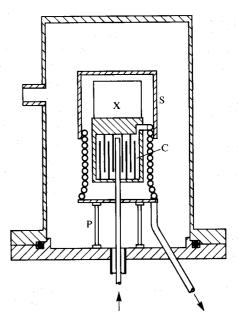


Fig. 6.9. Schematic diagram of a flow cryostat (based on Klipping et al. 1965). X is experimental space, C is the cooling chamber, S is a shield, and P is a supporting post.

by a solenoid valve in the pumping line which in turn is controlled by a carbon resistor or thermistor and an a.c. bridge-controller of the type discussed above in § 6.3. Klipping et al. (1970) noted that this form of cryostat did not give as good a thermal stability between 4 and 15 K as below 4 or above 15 K; temperature fluctuations are relatively greater in this range due to the small heat capacity of the chamber and the two-phase nature of the coolant, namely gas plus liquid droplets; they described a transfer tube with a valve in it to reduce the fluctuation.

A more elaborate and very stable cryostat was made by Plumb et al. (1977) for thermally cycling germanium thermometers, requiring 0·1 mK stability. They achieved this with a three-stage temperature control system: two shields were each refrigerated by helium flow controlled by a resistance-a.c. bridge-solenoid sequence and finally the copper thermometer block was controlled electronically by a similar a.c. bridge-controller (Pickup and

Kemp 1969); the three stages are weakly linked (thermally) by a stack of stainless steel washers or shims.

Some commercial firms (e.g. Oxford Instrument Company and Elscint Ltd., see Appendix) make small flow cryostats suitable for X-ray diffractometers, Mössbauer, infrared spectrometry, etc., which can be attached to a transfer tube and pumping system. Herbert and Campbell (1976) have described one of these, for Mössbauer experiments, which can be placed directly on top of a helium storage dewar. Controllers can be provided to operate them at the 1 or 0·1 K stability level. Solenoid valves which are proportional rather than on-off are now commercially available (e.g. Leybold-Heraeus).

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CHAPTER VII

INTRODUCTION TO CRYOSTAT DESIGN

1. General considerations

It is difficult to conceive of any single cryostat which is suitable for all possible physical measurements on a substance at all temperatures in the range we call 'low'. Even if possible, the complexity of such an apparatus would be considerable, to say the least. As a result it is necessary to formulate clearly the primary experimental problem to be tackled, and try to solve it as simply as possible, always consistent with the fact that a little extra difficulty in construction may allow a much wider range of usefulness or increased accuracy. Whether the primary aim is to measure the electrical resistance of an alloy, the X-ray lattice spacing in a solid or its heat capacity, a decision regarding the range of temperature over which measurements are needed is important in so far as the design is concerned.

With the aid of liquid refrigerants commonly available in a cryogenic laboratory, viz. liquid oxygen, nitrogen, and helium (and possibly liquid hydrogen), the following temperature ranges are immediately available by controlling the pressure at which the liquefied gas boils:

- (a) 1-4.2 K (liquid helium);
- (b) 54-90 K (liquid oxygen);
- (c) 63-77 K (liquid nitrogen);

(and (d) 10-20.4 K (by pumping liquid hydrogen to temperatures ranging from its normal boiling point to well below the triple point)).

Provided that vacuum pumps of the required speed are available, temperatures in these ranges can be attained within the liquefied gases boiling in a dewar and therefore in any experimental chamber immersed in the liquid. With a manostat connected on the pumping tube, they can be maintained with fluctuations of less than one part in a thousand; over much of each range, temperature fluctuations as small as one part in five thousand can be maintained for a long period of time. This

accuracy, of course, occurs in the temperature at the surface of the boiling liquid as calculated from the vapour pressure and does not mean that much larger temperature inhomogeneities cannot exist in the liquid itself, and particularly in the solid if pumped below the triple point.

If temperatures other than those within the accessible vapourpressure range of the available liquefied gases are required, other methods must be used. These other methods generally maintain temperatures within the experimental space that are above the temperature of the surrounding bath; then a balance between the loss of heat (by radiation, conduction, etc.) from the experimental chamber and the supply of heat from a manually or automatically controlled source to the chamber must be produced. The degree of ease or difficulty with which this balance, and therefore relative constancy of temperature, is produced depends ultimately on the type of physical investigation being pursued; for example it depends on whether a steady drift of 1 K/min or an irregular oscillation of 2 or 3 K in temperature is unimportant, or whether on the other hand the temperature must be maintained to ±0.005 K for an hour or more. This degree of difficulty not only depends on the type of experiment but also on the approximate temperature at which it is being carried out: at temperatures below say 20 K, heat capacities are small and the time required to attain thermal equilibrium is usually short, so that the response to the manual control of an electrical heater is quite rapid; but at 150 K equilibrium times are much longer and the difficulty of finding manually a particular heat input necessary to produce ultimate temperature equilibrium is more tedious.

Another important and related factor is whether adiabatic conditions are required. To illustrate this, consider a measurement of heat capacity or heat conductivity. In these measurements stray temperature drifts and spurious heat inputs to the specimen under investigation must be eliminated as completely as possible. The specimen or its immediate container must be in a high vacuum enclosure and the surroundings must be temperature controlled to varying degrees of constancy. On the other hand, a measurement of the Hall effect, electrical resistance, or magnetic susceptibility may be made in a short time with the specimen kept in equilibrium with its surroundings by the presence of exchange gas so that a slight change in temperature will

not affect the validity of the experimental value obtained, although it may make the precise temperature at which the value is obtained somewhat uncertain. Therefore before laying plans for a cryostat these questions must be answered:

- (i) Will results in the range from 1-4 K and 55-90 K give all the information needed, or are measurements, perhaps, only required at 90 K, 77 K, and 4.2 K?
- (ii) If the answers to these first questions are no, then how constant must the temperature be maintained and for how long at say 8 K, 40 K, and 115 K?
- (iii) Can the experimental space be kept filled with a lowpressure gas which will assist in preserving temperature equilibrium within this space?
- (iv) What form of access to the experiment is required, i.e. are ten or twenty fine copper wires as electrical leads all that are necessary, or do we need special windows for an infra-red or X-ray beam? Is some mechanical movement necessary in the experimental space, e.g. a mechanical switch or a suspension to a microbalance?

Having answered these questions—most of them with very obvious answers in a particular investigation—the problem of designing and making a suitable apparatus has to be faced. One of the major problems in this, apart from the obvious ones of available materials, workshop facilities, and a necessary mechanical lifetime, is that of heat transfer.

In any apparatus designed to operate at temperatures considerably different from its surroundings, and perhaps designed to measure properties which are strongly influenced by the inflow or outflow of heat and/or change in temperature, this factor is a vital one. As a result a large part of the success or failure of an apparatus to give accurate results can often be traced to the care taken in reducing stray heat inflows due to (i) conduction through low-pressure gas when the vacuum is not sufficiently good, (ii) radiation, (iii) conduction of heat along the tubes or electrical leads, or (iv) Joule heating or eddy current heating.

Chapter V deals with the calculation of heat inflows that may be expected and compares the magnitude of the heat transferred by radiation between surfaces of various emissivities with that conducted through low-pressure gas or conducted down electrical lead wires and supporting tubes.

The design and construction of laboratory cryostats are also dealt with in Chapter 10 of Hoare, Jackson, and Kurti (1961), by Rose-Innes (1973), and by Thornton in Chapter 20 of Advanced cryogenics (1971, Plenum Press, New York).

2. Cryostats for specific-heat measurements

Most specific-heat measurements at low temperatures have been made with the adiabatic calorimeter—originally introduced by Nernst and Eucken in 1910—and the ensuing discussion is restricted to examples of this type. In the simple form illustrated schematically in Fig. 7.1a the specimen S, with heater H and thermometer T (combined as one in some cases) attached, is suspended by nylon or cotton threads in an evacuated enclosure X, which in turn is surrounded by a liquefied gas A. The specimen may be in the form of a solid block of metal with T and H cemented to its surface or embedded in it; or the specimen may be in a solid, powder, or liquid form contained in a thinwalled calorimeter vessel of known heat capacity in which case T and H are usually attached to the calorimeter; a small pressure of helium exchange gas may then be used to ensure temperature equilibrium within the calorimeter. If the vacuum is sufficiently good and conduction down the leads is small, such a simple apparatus can adequately provide specific heat data over a quite wide range of temperature, provided that the temperatures of the wall X and the specimen S are not widely different, otherwise radiation and lead conduction become large. As a result this simplest form may be used at temperatures below 20 K, and at temperatures within the range of say 55-90 K covered by liquid oxygen, provided that $T_S - T_X$ is kept small. At temperatures above 20 K, an adiabatic shield in the space between S and X usually becomes necessary.

Silvidi and Daunt (1950) and Pearlman and Keesom (1952) have described comparatively simple cryostats of this type.

The second cryostat (Fig. 7.1b) is more complex than 7.1a in that it has an intermediate wall Z which is attached to the copper chamber B, and can therefore be controlled at temperatures different from that of the outer liquid bath A; either by reducing the pressure over a liquid in B or electrically heating the chamber B, its temperature and the temperature of Z can be controlled so

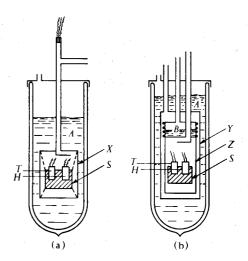


Fig. 7.1. Types of cryostat suitable for specific-heat determinations.

as to preserve only a small temperature difference between Z and the specimens.

An example of a cryostat of type (b), in which liquid can be drawn into the inner chamber B from the dewar bath itself, is illustrated in Fig. 7.2 (after Rayne 1956; also Birch 1975).

Liquid in the dewar A is at atmospheric pressure and can be admitted through the needle valve E into the chamber F. The vessel D is of brass and F is of copper, both being supported by thin-walled (0·1 and 0·2 mm wall thickness) German silver tubes from the top plate. In this cryostat both vessels are evacuated separately and the use of helium exchange gas at low temperatures is avoided by using a mechanical thermal switch similar to that described by Ramanathan and Srinivasan (1955). Quoting Rayne, 'within the working space, the specimen J is suspended by nylon threads from the disk K, which is thermally anchored to the bath F by a flexible copper strap L. Movement of the disk is made by a stainless steel tube M, connected to a bellows N which can be actuated by the screw mechanism P.... By lowering the disk and pressing the specimen against the flat bottom of the can, J may be cooled to the temperature of F. The avoidance of the use of exchange gas, particularly at liquid-helium temperatures, reduces the 'starting-up' time considerably and ensures that no heat leak through residual exchange gas can occur. Rayne used a

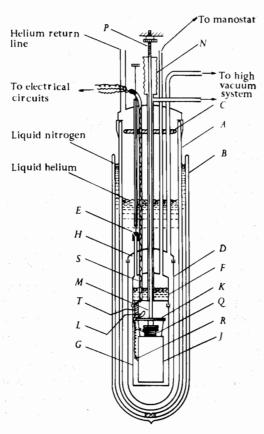


Fig. 7.2. Schematic diagram of cryostat (after Rayne 1956).

manganin heater wound on a copper former Q, screwed into the top of the specimen, and a 10- Ω Allen-Bradley carbon thermometer in a copper sleeve R for temperature measurement.

The most serious criticism that might be levelled at a specific heat apparatus of the general pattern of Fig. 7.1b is that at comparatively high temperatures where, for example, $T_{\rm A}$ may be 90·1 K, and $T_{\rm B}$ approximately 150 K, adiabatic conditions are not sufficiently well established. That is, due to radiation transfer and to heat flow along electrical leads, serious temperature inequalities may be produced between different points on the shield Z and thereby cause small temperature drifts in the calorimeter, sufficient to adversely affect high-precision

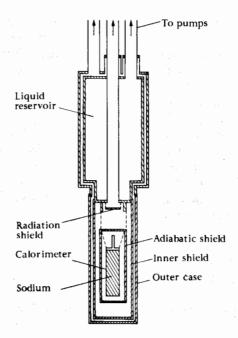


FIG. 7.3. A cryostat for specific heat measurements. Heaters and thermocouples are not shown (after Dauphinee, MacDonald, and Preston-Thomas 1954),

calorimetry. Two good examples of adiabatic calorimeters designed for use at temperatures up to room temperature, and to give values of specific heat correct to within about ± 0.2 per cent, are those of Dauphinee, MacDonald, and Preston-Thomas (1954) and Martin (1960, 1962). These are each rather like type 7.2b but have additional temperature-controlled copper shields interposed between Z and S. That of Dauphinee et al. shown in Fig. 7.3 has the shields controlled electronically in response to signals from a differential thermocouple.

Details of other calorimeters and the measurement techniques are reviewed by Hill, Martin, and Osborne (1967); heat switches used in calorimetry are also discussed in § 5.8. Some useful additional descriptions include those of Westrum, Hatcher, and Osborne (1953) dealing with the range 10–300 K; O'Neal and Phillips (1965), 0·1–4 K; Montgomery, Pells, and Wray (1967) with differential measurements on two samples from 1–4 K;

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Morin and Maita (1963) on small samples from 2-20 K; Lounasmaa and Guenther (1962) from 0·4-4 K; and Sellers and Anderson (1974) below 1 K without the use of a heat switch. Automatic data acquisition and computer control are described by Martin *et al.* (1973) and Joseph, Moody, and Whitehead (1976).

A common method of checking the precision of a calorimeter is to measure C_p on a sample of high-purity copper for which there is much tabulated data. Martin *et al.* (1973) discuss C_p for Cu and the small discrepancies which may arise from hydrogen impurities and differences in temperature scale.

3. Cryostats for measurement of thermal conductivity and thermoelectric power

In the solid rod shown in Fig. 7.4 the axial heat flow \dot{Q} is given by

$$\lambda(T) = \frac{\dot{Q}}{A} \frac{\delta l}{\delta T},$$

where $\lambda(T)$ is a function of T expressing the thermal conductivity of the material.

Thus the total heat conduction

$$\dot{Q} = \frac{A}{l} \int_{T_0}^{T_1} \lambda(T) \, dT.$$

If the rod is metallic (or a semiconductor), a thermoelectric potential difference is produced along the rod and the thermoelectric power with respect to the metal of which the potential leads 1 and 2 are made is $S = \delta V/\delta T$; the thermoelectric force,

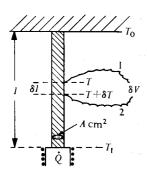


Fig. 7.4. Heat flow through a solid rod.

denoted by V or E, is

$$E = \int_{T_0}^{T_1} S(T) dT.$$

In principle and in practice the thermoelectric power S(T) may be determined either (i) by measuring δV and δT , where $\delta T \ll T$ and hence it may be assumed $S(T) \simeq S(T+\delta T)$; then, varying T_1 and T_0 , a series of values for S(T) may be obtained; or (ii) by keeping T_0 fixed and measuring the total thermoelectric force $E(T_1-T_0)$ as T_1 is changed; S(T) is then obtained by differentiating the curve E(T).

Similarly, in the case of thermal conductivity, an integrated conductivity is obtained by measuring \dot{Q} and T_1 for different values of \dot{Q} , and differentiating the resultant function $\dot{Q}(T_1)$ to obtain $\lambda(T)$. Alternatively, by keeping $T_1 - T_0$ small, values of δT and \dot{Q} are obtained at various temperatures and a graph of $\lambda(T)$ obtained directly from these.

Since the major interest in thermoelectricity has been practical thermometric interest in the thermoelectric e.m.f. E produced by a thermocouple junction with respect to a second junction fixed at a reference temperature (often $0\,^{\circ}$ C but sometimes $4\cdot 2$ or 77 K), the integrated quantity E is usually measured. This quantity has greater practical value and since it is normally a simple monotonic function of T, S can be derived by differentiation if required. In recent years, however, there has been an increased fundamental interest in thermoelectric power and many differential measurements giving S directly have been made (see, for example, Rumbo 1976). In these latter measurements the procedure is almost identical with the measurement of thermal conductivity except that a potential difference δE (= δV) must be obtained corresponding to δT and the heat flow \dot{Q} need not be known.

In thermal conductivity measurements, the interest has been a largely fundamental interest in $\lambda(T)$ and so the differential measurement giving $\lambda(T)$ directly has been used. Since $\lambda(T)$ is frequently not a simple monotonically increasing function of T but a rather complicated function, and also since δT can be measured with a fairly high degree of accuracy with a differential thermometer system, this yields more reliable results than the 'integral' method.

Most cryostats used between 1 and 100 K to measure $\lambda(T)$ or S(T) conform in principle to the two patterns shown in Fig. 7.5. In each a heater H_1 creates a temperature gradient along a rod-shaped sample and the gradient is measured by a pair of thermometers; this is a 'thermal potentiometer'. The heat sink at the cold end may be the main bath of liquid refrigerant as in (a) or a temperature-controlled enclosure as in (b). In the latter case, this 'enclosure' may contain pumped liquid which enters via a needle valve: ³He for 0.3-3 K, ⁴He for 1-4 K, O_2 for 55-90 K. The enclosure can be electrically heated (§ 6.3) to cover other temperatures or it may be controlled by a flow process such as the Swenson-Klipping methods described in § 6.4. Note that in the simpler arrangement of Fig. 7.5a, there can be a heater H_3 to warm the sample above the bath temperature, using a suitable thermal resistance between H_3 and the bath.

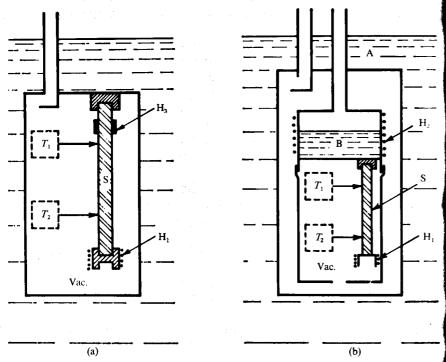


Fig. 7.5. Types of cryostat suitable for determination of thermal conductivity and thermoelectric power.

The accuracy of the thermal potentiometer depends on the thermometers (to give ΔT), knowledge of geometry (l/A), and there being negligible heat loss by radiation or conduction along leads so that Q is known. Some of the first accurate (\sim 1 per cent) measurements were made by de Haas and Rademakers (1940), Hulm (1950), and Berman (1951) using helium-filled gas thermometers which are connected by fine capillaries to a differential manometer—mercury or oil. These thermometers can be used over a wide temperature range above 1 K and are not affected by magnetic fields. However they are more cumbersome than the electrical temperature sensors which are now commonly used, namely carbon, germanium, or platinum resistors, AuFe thermocouples, etc. Some specific examples are described in the review article by White (1969) and the book by Berman (1976).

The problems and inaccuracies that occur in measuring $\lambda(T)$ are rather similar to those in calorimetry (§ 7.1). They arise from poor temperature control, thermal isolation, or temperature measurements. The additional factor which makes measurements of $\lambda(T)$ often less precise than C_p is that of the temperature gradient. The temperature gradient introduces radiation corrections which become important above 70 or 80 K, particularly when measuring poor conductors. This radiant heat transfer can be reduced by means of a close-fitting shield with a matching temperature gradient (Slack 1961; Ashworth et al. 1973). Also the measurement of the gradient ΔT usually requires two thermometers with precise calibrations rather than just one. Since the temperature difference ΔT may amount to only 10 mK (at helium temperatures), an uncertainty of ~ 1 per cent in ΔT means a resolution of 100 µK in each thermometer and a corresponding certainty concerning their relative calibrations. One method of reducing the difficulty is to keep T_1 constant when the heater H_1 is switched on; this can be done by using T_1 to activate the temperature controller rather than using a sensor on the heat sink (Cappelleti and Ishikawa 1973); then only T_2 needs to be calibrated. Rumbo (1976) achieved the same purpose by having an additional heater H_3 between T_1 and the sink (Fig. 7.6). When H₁ was switched off, H₃ was switched on and fed exactly the same heat \dot{Q} into the top of the sample, thereby preserving the same temperature difference between T_1 and the sink, T_B , so that T_1 was the same both when $T_2 - T_1 = 0$ and when $T_2 - T_1 = \Delta T$.

Rumbo (1976) and also Garland and Van Harlingen (1974) measured S and ρ for very pure metals as well as λ which necessitated measurement of very small voltage differences at liquid helium temperatures. They each solved the problem by a null method in which a superconducting Josephson device (SLUG) compared the voltage difference along the sample with that produced in a reference resistor (Fig. 7.6 from Rumbo 1976).

Other helpful descriptions of conductivity cryostats used above 1 K include those of White and Woods (1955), Lindenfeld and Pennebaker (1962), Holland and Rubin (1962), Klein and Caldwell (1966), Ashworth *et al.* (1973).

A cryostat for measurements of $\lambda(T)$ at temperatures down to $0.3 \, \mathrm{K}$ is illustrated in Fig. 8.4 (p. 206) in the chapter on ³He cryostats. In this, Seward and Narayamurti (1966) measured alkali halide crystals using matched carbon thermometers for determining T_1 and T_2 ; these were calibrated against a

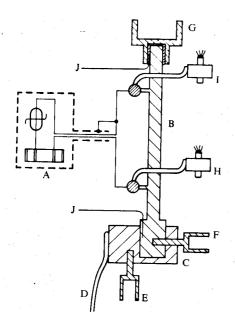


FIG. 7.6. Schematic diagram (after Rumbo 1976) showing specimen B, reference or standard specimen, and SLUG in the shielded enclosure A; thermometers I and H, and heaters G (equivalent to H₁), F(H₃), and E(H₂).

germanium thermometer on the heat sink. The latter is thermally linked via the copper C-piece to a liquid ³He chamber.

Other techniques, particularly applicable to the millikelvin temperature range with small power inputs, have been described by Anderson and his colleagues at Illinois (e.g. Zaitlin and Anderson 1974; Vorhaus and Anderson 1976; Roth and Anderson 1976).

4. Cryostat (1-300 K) for expansion measurements

This section will give some more specific details about the construction of a cryostat which is currently used at the National Measurement Laboratory (Sydney) for thermal expansion measurements (Fig. 7.7 and White and Collins 1972). Another cryostat, similar but for the inner experimental space, is used for conductivity measurements. The cryostat is immersed in liquid helium or in liquid oxygen. The inner enclosure is controlled to $\sim 1 \, \text{mK}$ either by pumping on liquid (He or O_2) in it or by electrical heating of the resistor H. T is a temperature sensor which activates an a.c. bridge controller (Fig. 6.6, p. 165) to supply the power to H as described in § 6.3.

The outer vacuum can is made of 67 mm o.d. brass tube (1.5 mm wall) and the inner is of 60 mm o.d. high-conductivity copper, also of 1.5 mm wall thickness. The outer can has a flange at the top with 1 mm diam. indium wire as a vacuum seal. The surfaces of the brass flange and brass plate are carefully machined flat and held together by Allen screws at 25 mm intervals around the perimeter. The copper inner can is attached below the chamber by a threaded joint with a little silicone grease on it. This remains vacuum-tight at low temperatures provided the pressure differential is small; usually both enclosures are at high vacuum but sometimes exchange gas (at $\sim 0.1 \text{ Torr or } 10 \text{ Pa}$) is admitted to one or the other.

The chambers are supported from the main top plate by pumping tubes of thin-walled stainless steel of $\sim\!10\,\mathrm{mm}$ diam., each of which is soft-soldered through bushes of brass or copper which are hard-soldered to the plates. These tubes have radiation traps at their lower ends and two of them carry electrical leads to thermometers, heater, etc. The leads are mostly of formvar-coated copper ($\leq\!0\cdot1$ mm diam.) which are thermally anchored at

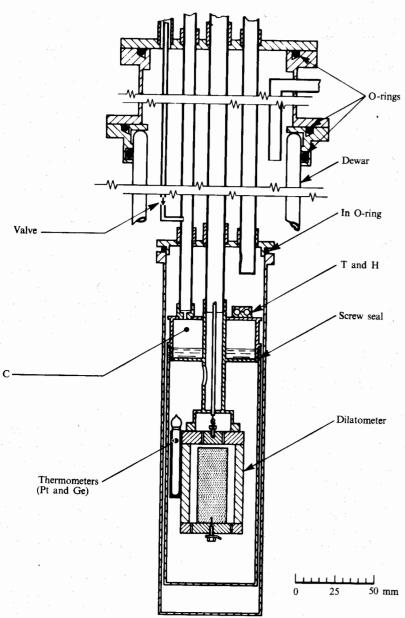
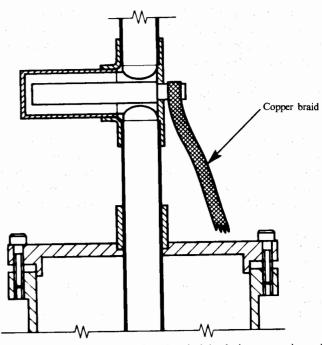


Fig. 7.7. Cryostat for thermal expansion measurements (§ 4 and White and Collins 1972) from 1-300 K. Upper part shows modular design of the top flange.



 $F_{1G.}$ 7.8. A thermal anchor-post for electrical leads in a pumping tube of a cryostat (§ 4).

the bottom of the respective pumping tube by wrapping them around the extension of the bush and cementing them with GE 7031. The coaxial leads to the capacitance dilatometer are of insulated constantan (0.2 mm diam.) in an earthed shield of 1.5 mm diam. stainless steel.

The valve for inlet of liquid from the dewar into the small inner chamber is a stainless-steel needle of 10° total taper seated in a brass or phosphor-bronze shoulder and is operated by turning a knurled head above the main top plate.

The thermometer elements, T, for activating the electronic temperature controller are a $56\,\Omega$ carbon (Ohmite or Allen-Bradley) and a small $50\,\Omega$ Rosemount platinum which together with a carbon heater H are held in a split copper clamp with vacuum grease to improve thermal contact.

The main top-plate is of brass with rubber O-ring seals so that the cryostat can be lifted out by disconnecting vacuum couplings and a multi-pin electrical connector. The top flange shown schematically in Fig. 7.7 is a modular design intended for glass dewars which are held and sealed by a rubber O-ring.

The electrical leads that go directly down a pumping tube to the inner enclosure can be thermally anchored to the main liquid bath in order that too much heat should not be conducted directly to the experimental space. Figure 7.8 shows a way of doing this, by having a copper anchoring post in a T-piece in the pumping tube and then cementing a few turns of these leads around the post; low-melting-point solder is used to seal the cover-tube over the post.

Before final assembly the copper and brass enclosures of the cryostat in Fig. 7.7 are all electroplated with gold to reduce subsequent tarnishing and radiation and also to improve heat transfer between contacting surfaces.

5. Cryostats for electrical resistance or Hall-effect measurements

From the cryogenic viewpoint electrical resistance and such quantities as magnetoresistance or Hall effect are among the properties whose measurement presents no great difficulties. For one thing such determinations are unaffected by exchange of thermal energy with the surroundings; the specimen may be kept in thermal equilibrium with a thermometer either by direct contact, by exchange gas, or by immersion of specimen and thermometer in a common refrigerating bath. Equally important is the fact that slow drifts in temperature of the specimen and its surroundings do not directly affect the determination as they do in calorimetric or thermal conduction measurements, except in so far as they introduce a small uncertainty as to the precise temperature of the specimen at the particular time that the measurement is made.

It is relatively difficult to measure the specific heat or heat conductivity of a solid at low temperatures, even when a comparatively crude estimate is required. But by merely attaching current and potential leads to a wire or rod and immersing it in a dewar of liquid helium, hydrogen, oxygen, etc., a reliable value of its electrical resistance may be obtained provided that there is a suitable electrical measuring circuit.

More generally, values of electrical resistance of a metal in wire or rod form are determined at certain fixed temperatures or over limited ranges of temperature by immersion in a series of liquefied gas refrigerants—boiling at atmospheric pressure or under controlled pressure.

For values over the whole range from about 1 K to room temperature, a cryostat of the type described in some detail in § 4 may be used. In this cryostat several specimens, in the form of wires or rods, are suspended in a strain-free manner from the copper pillar in the inner experimental vessel. To each specimen current and potential leads are attached, and the inner vessel is filled with a small pressure of helium exchange gas (~1 Torr) to preserve temperature equilibrium. By controlling the pressure over the evaporating liquid in the small inner chamber or by controlled electrical heating of this chamber, temperatures over the range 1 K to room temperature can be attained; temperatures are measured by the gas thermometers in the inner space, by the vapour pressure of the evaporating liquid, or with a platinum resistance thermometer in the inner space. At temperatures above, say, 170 K, a convenient alternative to the use of liquid oxygen (or nitrogen) in the dewar and electrical heating of the inner chamber, is the use of a well-stirred bath of alcohol or other low-freezing-point liquid, cooled by an immersed copper coil with a slow stream of liquid nitrogen passing through it.

Commonly available liquids which are used for such a low-temperature bath are methyl alcohol (melting point at $-98\,^{\circ}$ C), ethyl alcohol (melting point at about $-116\,^{\circ}$ C), and iso-pentane (melting point at $-160\,^{\circ}$ C). However, their highly inflammable nature may make it preferable to use a non-flammable mixture of organic liquids, if such baths are to be used frequently. As suggested by Scott (1941), a non-flammable eutectic mixture of carbon tetrachloride and chloroform may be used down to $-75\,^{\circ}$ C, and a five-component system (14.5% chloroform, 25.3% methylene chloride, 33.4% ethyl bromide, 10.4% trans-dichloroethylene, and 16.4% trichloroethylene) may be used to below $-140\,^{\circ}$ C.

6. Cryostats for optical and X-ray examination of materials

One particular avenue of research which the wide availability of refrigerants like liquid helium has encouraged is the measurement of optical properties of solids, e.g. infra-red and ultra-violet transmission; closely linked from the viewpoint of cryostat design are X-ray diffraction studies, whether they be an investigation of phase change or measurement of expansion coefficient from the measured lattice spacing. In all these cases, solids must be cooled,

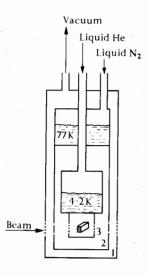


Fig. 7.9. Schematic diagram of the type of cryostat which may be used for optical or X-ray examination of materials.

maintained at specified low temperatures, and subjected to electromagnetic radiation, which must therefore have free access to and exit from the experimental region of the cryostat.

Usually temperature control need not be precise in experiments of this type as fluctuations of one or two degrees in temperature are unimportant. However, the necessity for providing unrestricted passage to a beam of infra-red radiation or X-radiation poses its own special problems.

A suitable type of cryostat is shown schematically in Fig. 7.9. The radiation beam in its passage from source to specimen must pass through three barriers: (1) the outer wall of the vacuum jacket which is at room temperature; hence the required type of window, e.g. beryllium or Mylar for X-radiation, silica for ultraviolet, or rock salt for infra-red radiation, may be cemented with epoxy or sealed with a flange and rubber O-ring; (2) the liquid-nitrogen-cooled radiation shield—usually of polished copper—which need not be vacuum-tight, as the regions on both sides of (2) may be pumped through a common line, and therefore holes or slits may be freely cut in to act as windows for the beam; (3) the final wall, which may or may not require a vacuum-sealed transmission window depending on whether the specimen must

be surrounded by exchange gas or can be supported in good thermal contact with the liquid-helium chamber to maintain temperature equilibrium.

Since the windows providing access for the beam must necessarily transmit some thermal radiation from surfaces at room temperature and at 77 K to the specimen, the latter must be in quite close thermal contact with the helium vessel if it is to be at a temperature within a few tenths of a degree of the helium bath. Experience has shown that with most pressure contacts and many cemented contacts the equilibrium temperature of a specimen may be many degrees above that of the low-temperature vessel to which it is fixed. This is particularly so in the case of solids which are poor thermal conductors, as their surface temperatures may be raised considerably by absorption of incident radiation. Of course, in the case of a solid metallic X-ray specimen which is solder-bonded to a heavy copper pillar, itself in contact with liquid helium, temperature equilibrium may be preserved quite well.

Temperature control

In the cryostat shown schematically in Fig. 7.9 the specimen can be brought to the approximate temperature of the lower liquid bath by having exchange gas in the inner enclosure (3) or by carefully cementing it to the copper post. However it is more difficult to control outside the temperature ranges of the bath, i.e. from 4-55 and above 90 K. One way of doing it is to separate the specimen or specimen cavity from the lower liquid reservoir by a metal post of carefully chosen material (e.g. brass) and suitable dimensions. Then with an electrical heater attached to the specimen or cavity, it can be controlled at temperatures above that of the liquid. This method has an obvious drawback if it is desired to operate from 1 K to room temperature; no single choice of connecting post is likely to allow control at both 5 and 40 K with liquid helium in the reservoir or at both 100 and 200 K with liquid oxygen, and yet preserve a relatively low rate of evaporation of refrigerant.

Another solution is to use a helium-gas-filled tube as a variable thermal resistance between the sample and the liquid rather than a fixed solid conductor. By varying the pressure of exchange gas in the tube, the thermal linkage can be altered easily and an electrical heater can be used to give temperature control.

Alternatively liquid and cold gas from the reservoir can be blown or sucked through a coil soldered to the sample-holder. This is a variant of the Swenson-Klipping form of temperature control (see § 6.5 for more details): usually a valve between the cryostat and the mechanical pump is manually or electrically operated to regulate the flow and the temperature. Instead of drawing liquid from a reservoir in the cryostat, it can be taken directly from a storage dewar, as in the commercially available 'continuous-flow' cryostats (e.g. Oxford Instrument Company). A good description of a home-made flow cryostat is given by Chhatwal and Chaudhuri (1974).

Most of the commercial cryostats or dewars for optical, X-ray, and neutron studies are of a modular construction, usually of metal in a form similar to that shown in Fig. 2.3b (p. 40).

Windows

Commercial cryostats are usually available with a variety of different windows, including a 'blank' so that the customer can make his own. Windows include vitreous silica and sapphire for ultra-violet transmission; Mylar for infra-red and X-rays; beryllium, aluminium foil and aluminized Mylar for X-rays and neutrons; and infra-red materials such as the Kodak Irtran series.

Methods of mounting vacuum-tight optical windows for low temperatures have been the subject of many articles in the pages of Cryogenics, Review and Journal of Scientific Instruments, etc.

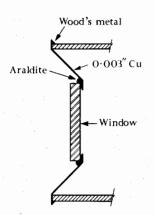


Fig. 7.10. An optical window for low-temperature use (after Roberts 1954).

One successful method of overcoming the problems of differential contraction is due to Roberts (1954), who cemented a thin flexible diaphragm of copper (0·1-mm thick) to his rock-salt window with epoxy resin. The outer edge of the copper shim (Fig. 7.10) is soldered to the copper chamber (Fig. 7.11). Warshauer and Paul (1956) described how a thin polyethylene window could be used and remain vacuum tight after repeated thermal cycling between 300 and 4 K; they milled a circular window from brass or copper and stuck the $0\cdot1$ mm polyethylene film to the flat surface around the aperature with silicone grease and clamped it with another brass plate.

For quartz or silica windows it is often necessary to avoid strain because of the optical effects. Gebhardt, Helbig, and Hümmer (1976) describe one way of avoiding this by cementing the window at its edge to thin-walled stainless steel tube (see also Bek et al. 1973; Loose et al. 1974; etc.).

Cryostats

In the infra-red absorption cell used by Roberts (1955) the specimen chamber is a copper tube with rock-salt windows. The tube can be filled with helium exchange gas (Fig. 7.11) to keep the specimen within $1 \, \text{K}$ of the cooling bath. The temperature is measured by a gas thermometer which occupies the annular volume V surrounding the radiation beam.

The method of construction used in Roberts's cryostat in which the two liquid chambers are directly above one another has advantages, in so far as the construction and maintenance of high vacuum-tight joints are concerned. The container B is of copper and A is of brass or copper; brass bushes are hard soldered into these containers and thin-walled cupro-nickel (or German silver) tubes are soft soldered through these. The radiation shield D should be of polished copper sufficiently thick-walled (say 1 mm) to ensure adequate heat conduction along it and be well soldered to chamber A; then temperatures within a few degrees of the liquid nitrogen in A should be maintained over the entire shield. A simple and effective alternative to polishing or plating the containers and shields is to wrap them with thin aluminium foil.

Another historic cryostat is that used by Barrett (1956) for X-ray diffraction studies of alkali metals at low temperatures. Illustrated in Fig. 7.12, it is a prototype of many later cryostates.

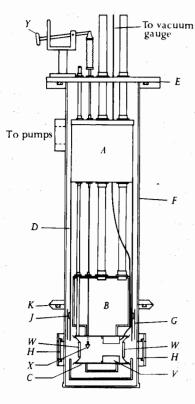


Fig. 7.11. Low-temperature absorption cell (after Roberts 1955).

Chamber 1 holds about 2 litres of liquid helium (or hydrogen, or nitrogen) which cools the specimen by conduction through the bar (9). The specimen can be changed by opening the O-ring joint between (3) and (4) and the joint (7).

Other 'window' cryostats include those of Brebner and Mooser (1902), Schoen and Broida (1962), Fitchen (1963), and Freeman (1971) for optical measurements; Mauer and Bolz (1961), and Croft and Thomas (1969) for X-ray work; and Abrahams (1960) for neutron measurements. Williams (1975) has reviewed Mossbauer systems at low temperatures. The firms listed in the Appendix make a wide variety of cryostats for all sorts of 'beam' studies and their catalogues are a useful source of information on methods of construction.

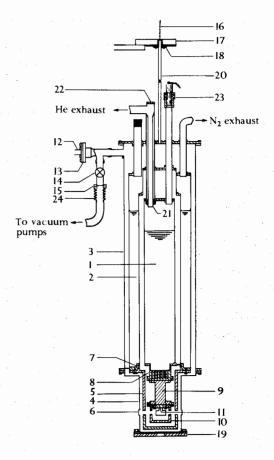


Fig. 7.12. A cryostat for X-ray diffraction studies (after Barrett 1956).

Richards (1964) has given an interesting account of Fourier-transform spectroscopy in the far infra-red which discusses the use of light pipes for bringing infra-red radiation into a cryostat. Instead of windows in the tail of the cryostat, a simple brass tube of ~ 1 cm diam. is very effective in funnelling long wave-length radiation from the top of the cryostat down to the bottom where an absorption sample and bolometer-detector are placed (see also short review of infra-red spectroscopy at low temperatures by Parkinson 1963).

7. Magnetic susceptibility cryostats

The many methods of measuring magnetic susceptibilities can be divided into two broad classes—static and induction methods. The latter involve a measurement or comparison of mutual or self-inductances. Using an a.c. inductance bridge or a ballistic throw method, they have been widely used for the measurement of susceptibilities of paramagnetic salts at temperatures near 1 K and below but have not been greatly used for absolute measurements at higher temperatures (see, however, inductance bridges of Maxwell (1965), Anderson, Peterson, and Robichaux (1970), and Cetas (1976).

Of the static methods generally used, those involving a weight determination and therefore classed as balance methods appear to be the most precise. The balance methods depend on the force exerted on a body placed in a non-homogeneous magnetic field; this force is measured by suspending the body from a sensitive balance. In the so-called Faraday method of measurement, a sample is used which is sufficiently small that the field B does not vary appreciably within the dimensions of the body, but is nevertheless sufficiently inhomogeneous to exert a measurable force given by

$$\mathbf{F} = \mathbf{M} \wedge \operatorname{grad} \mathbf{B}$$

where **M** is the magnetic moment. Hence, if χ_m is the mass susceptibility and m the mass, then

$$F_z = m\chi_m B_z \frac{\mathrm{d}B_z}{\mathrm{d}z}$$

is the vertical force exerted by an inhomogeneous field of strength B_z , and gradient dB_z/dz produced by a coil in the vertical or z-direction.

Apart from the Faraday method, that most commonly used is the vibrating sample system evolved by Van Oosterhout (1956) and Foner (1959). In this the sample is made to oscillate inside a coil system, designed so that the voltage induced is proportional to the magnetic moment of the sample. The so-called Foner Magnetometer is commercially available from Princeton Applied Research Corporation, Princeton, NJ.

The methods mentioned above and others are discussed in

detail in texts by Bates (1948), McGuire (1959), and Zilstra (1969)

Returning to the cryogenic aspects of the problems associated with susceptibility measurement by a balance method, we note two distinctive features:

- (a) the sample must be freely suspended with no mechanical constraint from a microbalance;
- (b) vibrations of the sample or balance should be avoided as much as possible.

The result is a narrow vertical tube in which the sample is suspended; the tube and balance (or part of them) are filled with exchange gas to keep the sample in temperature equilibrium with the nearby tube wall. The tube is then immersed in a dewar which, to ensure maximum field strength, is narrow in the region that is in the pole gap of the magnet. The requirement of no constraint prevents any thermometer being attached to the sample under investigation unless perhaps a thermocouple is attached to the sample and the two thermocouple leads form the suspension.

A common type of susceptibility cryostat is that illustrated schematically in Fig. 7.13 (cf. McGuire and Lane, 1949). The dewar containing liquid helium or liquid nitrogen may be pumped to control the temperature of the liquid bath if care is taken to avoid vibration from the mechanical pump being transmitted to the dewar and balance.

The chief problems arise when control of temperatures outside those covered by a liquefied gas is required. One method of controlling temperature at say 30 or 110 K has been used by Hedgcock and Muir (1960) and is illustrated in Fig. 7.14. The lower section of the sample tube is of copper of sufficient wall thickness to ensure a relatively small temperature gradient along the length of the specimen. This copper tube has an electrical heater and thermometers (carbon thermometer and a copper resistance thermometer) attached to it, and a heavy copper wire acts as a partial thermal link between the copper tube and the liquid in the wide tail of the dewar vessel. By carefully selecting the dimensions of this thermal link and varying the heater power, temperatures above that of the liquid refrigerant can be maintained around the specimen.

Other alternatives are to place a resistance heater in the

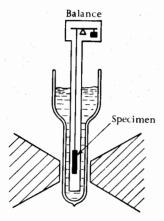


Fig. 7.13. Schematic diagram of a cryostat for susceptibility determinations.

bottom of the dewar to control the flow of evaporating cold gas past the experimental tail or to suck liquid through a small coil soldered to the copper tail, that is, a form of Swenson-Klipping flow cryostat (§ 6.4).

Radiation funnelled down the balance tube from room temperature can contribute to a serious temperature difference between the sample and its surrounding tube. Thin discs of aluminium or aluminized Mylar can be attached to the supporting 'fibre' to reduce this radiation.

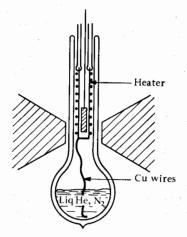


Fig. 7.14. A similar cryostat to that of Hedgcock and Muir (1960).

The suspension should be made of a poor heat conductor and be free of magnetic impurities. One common choice is silica, preferably the synthetic variety which is free of metallic impurities. Aluminium does not normally contain magnetic impurities and so is suitable for a suspension hook. Choice of materials is obviously most important when measuring specimens of relatively small magnetic susceptibility. To help in choosing materials which themselves have very small susceptibility, Salinger and Wheatley (1961) measured a number of common materials between 1 and 4 K.

They expressed their results in the form

$$\chi/\rho = B + C/T$$
.

Values for B and C (in units of 10^{-6} e.m.u. per g) are given in Table 7.1. To convert these to SI units (J/T² kg) multiply by 10^4 .

TABLE 7.1

Magnetic susceptibility $\chi/\rho = B + C/T$

Material	B (10 ⁻⁶ e.m.u./g)	C (10 ⁶ e.m.u./gK)
Pyrex tubing	1.6 ± 1	12±3
(Corning 7740)		
Silica	-1	~1
Nylon	-0.6 ± 1.5	0.3 ± 3
Epibond 100A	7 ± 13	0.1 ± 3
Mylar	50 ± 7	1.5 ± 6
Copper magnet wire	0.03 ± 1	0.01 ± 1.5
(Formex insulated)		
Brass	-180 ± 20	-30 ± 10
Stainless steel 316	312 ± 25	-105 ± 20
Stainless steel 321	100 ± 10	25 ± 10
Manganin	120 ± 10	-13 ± 3

8. Other cryostats

Many other physical measurements are performed at low temperature and they impose their own particular requirements on cryostat design. Some can be done in an experimental space of limited size with only a few electrical connexions to the outside world. Some may dissipate little heat and not need very fine temperature control.

For example, ultrasonic velocity and attenuation measurements can be done in the kinds of cryostats that we have discussed

earlier in this chapter. No peculiar cryogenic difficulties arise except perhaps the need to cement transducers onto crystals so they do not reflect ultrasonic waves too much nor crack at low temperatures: a variety of cementing materials have been used to make the seal including rubber solutions, Nonaq stop-cock grease, viscous silicone oils, alcohol, isopentane, and even methane. More details of the methods of measurements are given in reviews by McSkimin (1964), and E. R. Dobbs (Hoare, Jackson, and Kurti 1961, p. 254).

Microwave studies require a resonant cavity in the cryostat and need waveguides to connect this to the microwave source and detectors which are at room temperature. Precision-drawn stainless steel suitable for waveguides is available from sources such as Superior Tube Company, Norristown, PA. Naturally there must be a gas seal in the waveguide to prevent air travelling down into the cavity and condensing; pieces of mica sheet are commonly used as a seal at the junction of two pieces of waveguide. Bagguley and Owen (Hoare et al. 1961, p. 297) discuss some of the cryogenic problems of microwave measurements.

High pressures are often needed in conjunction with low temperatures in order to study the equation of state (P-V-T)of solids and also possible phase transitions. Since helium solidifies at less than 30 bars (3 MPa) below 2 K, there are no fluids available to transmit pressures in truly hydrostatic fashion. Fortunately solid helium and solid hydrogen each have low shear strengths and can be used for approximately hydrostatic transmission at pressures of 1 to 20 kb. Otherwise clamp and anvil techniques are used. These methods are reviewed by Swenson (1960), Levy and Olsen (1965), and Dugdale (1969). Other useful references include Lyon, McWhan, and Stevens (1967), Schirber (1970), and Webb et al. (1976).

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CHAPTER VIII

COOLING WITH HELIUM-3

1. Introduction

THE lighter isotope of helium, ³He, is obtained as a decay product of tritium and therefore is only available in relatively small quantities and is expensive. It has been sold through the Mound Laboratory of the Monsanto Research Corporation at Miamisburg, Ohio, at a price of about 30 cents per ml of gas. For research purposes it is liquefied in small quantities by contact with liquid ⁴He and *not* in a normal circulation liquefier of the type discussed in Chapter I.

The normal boiling point of 3 He is $3 \cdot 19$ K and the critical temperature is $3 \cdot 32$ K at a critical pressure of $1 \cdot 15$ atm (116 kPa). The latent heat and heat capacity of the liquid both vary with temperature but between $0 \cdot 5$ and 1 K they are approximately 1 J/ml and $0 \cdot 1$ J/ml K respectively. The density near 1 K is c. $0 \cdot 08$ g/ml. Monographs by Wilks (1967) and Keller (1969) give more details of the properties of 3 He as well as 4 He.

Near to their normal boiling points, the heat conductivity and viscosity of ³He and ⁴He liquids are rather similar in magnitude but whereas ⁴He has a superfluid transition at 2·17 K, ³He remains normal down to c. 2.6 mK. Below 1 K the vapour pressure of ³He becomes more than two orders of magnitude greater than that of ⁴He. A thermally shielded bath of liquid may be boiled under pressures of 10⁻³ Torr or less which correspond to temperatures of less than 0.3 K (see vapour pressures in Table A in Appendix). As a result, ³He has become widely used to provide an additional stage of cooling which encompasses the range from c. 0.25 to 1 K; this range was accessible hitherto only by using adiabatic demagnetization of a paramagnetic salt. Clearly a quietly boiling bath of liquid ³He is a more convenient cooling medium than a salt crystal with its attendant problems of magnetic field, thermal contact, temperature measurement, etc. (see Ch. IX). Many of the first ³He cryostats were discussed in a review by Taconis (1961) and some of their essential features are outlined in § 2.

A more powerful method which can produce temperatures of a few millikelvins is by adiabatic dilution of ³He in liquid ⁴He. This technique of refrigeration was proposed by London, Clarke, and Mendoza (1962) and proved practical by experiments at Leiden (Das, de Bruyn Ouboter, and Taconis 1965), Manchester (Hall, Ford, and Thompson 1966), and Moscow (Neganov, Borisov, and Liburg 1966). Although these first efforts did not produce temperatures much below 100 mK, they did reveal the problems arising in heat exchangers from instabilities and inadequate heat transfer, viscous heating, etc., so that later work in such centres as the Universities of Illinois, La Jolla, Cornell, Helsinki, Moscow, and Grenoble could produce temperatures as low as 3 mK. Some of these are discussed below in § 3 and more fully by Lounasmaa (1974) and Betts (1976) and in papers in the Proceedings of the International Cryogenic Engineering Conferences of 1974 and 1976 (ICEC 5, ICEC 6, published by IPC Science and Technology Press, Surrey, UK), etc.

An alternative to this usual dilution cycle was suggested and proved by Taconis et al. (1971) at Leiden, in which ⁴He is circulated rather than ³He. This cycle uses a 'superleak' as a filter in the circulation process and the thermomechanical or fountain effect as a pump. Temperatures as low as 10 mK have been reached by this method (§ 4).

Finally the adiabatic compression of liquid 3 He (Pomeranchuk 1950) has become a way of cooling to temperatures of ${}^{\sim}1$ mK, using the fact that the entropy of solid 3 He is greater than that of liquid 3 He below 0.3 K (see also Lounasmaa 1974, Ch. 4 and § 5 below).

2. ³He cryostats (evaporation cooling)

General principles

Figure 8.1 shows two conventional cryostats in schematic form in each of which there is a small ³He chamber attached to the experimental space. The pumping tube usually acts also as the condenser for initially producing the liquid ³He and therefore must be in thermal contact with a pumped ⁴He bath along part of its length. This ⁴He bath may be either the main dewar as in (a), or a separate chamber as in (b). This 1 K cooling stage can also be a copper plate cooled by a tube, soldered or welded to it,

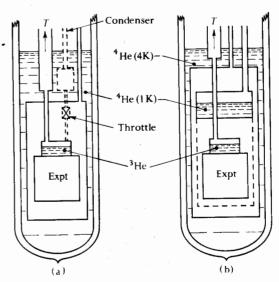


FIG. 8.1. Schematic diagrams of two alternative cryostats containing liquid ³He chambers. In (a) 'dashed' lines show how continuous circulation may be achieved.

carrying liquid ⁴He at a rate controlled by a suitable flow impedance. The latter can be a porous plug, a fine tube with a wire insert, or a pre-adjusted valve consisting of a small screw with a tapered seat. The 'cold-plate' technique is now widely used in dilution refrigerators for the 1 K cooling stage (see also Lounasmaa 1974, p. 7 and De Long, Symko, and Wheatley 1971).

There can be a separate condensing line, shown dotted in Fig. 8.1a which then allows continuous circulation of the ³He. This is necessary if the heat loads are large or experiments continue for a long time. If the gas is pumped by a system such as illustrated by Fig. 8.2 the high-pressure side of the pump is connected back to the condenser and liquid ³He slowly returns into the ³He chamber at a rate controlled by the throttle; this latter may be a valve, fine capillary tube, or porous plug. The other optional features shown dotted in Fig. 8.2 are the 'condensation' line and the mechanical pump (M.P.). The 'condensation' line allows gas to be pumped *from* the reservoir (Res.) through valves V_1 , V_2 , V_3 into the cryostat to accelerate the initial condensation of the ³He charge. The mechanical pump is not necessary if a diffusion pump is used which operates against a relatively high backing

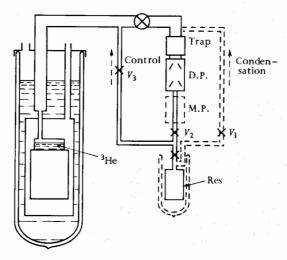


Fig. 8.2. Flow diagram of a ³He system. 'Dashed' lines indicate optional items.

pressure. For example, the 'Speedivac' type 2M4 made by Edwards and Company, Sussex, will operate against a maximum backing pressure of 35 Torr; this requires that either (a) the reservoir volume must be large enough that its pressure is below this, or (b) the backing side must be connected to a condenser immersed in the pumped ⁴He bath at a temperature of less than 2 K.

If a mechanical pump is included, it must be a model that is well sealed against gas leakage, such as that produced by the Welch Company, Chicago.

Another alternative is to use a sorption pump, that is to have an adsorber of charcoal or similar material contained in a vessel which is cooled by the ⁴He bath. The adsorbent is exposed to the gas evaporating from the ³He chamber. This system has been described by Eselson, Lasarev, and Shvets (1962, 1963) and provides large pumping speeds without vibration.

Examples

Some of the ³He cryostats have used the single condensation or 'single-shot' procedure rather than continuous circulation. The former is certainly more simple to make although the latter offers a greater cooling capacity for a given quantity of ³He.

Among the earlier cryostats, those of Roberts and Sydoriak

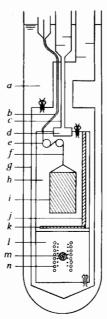


Fig. 8.3. A calorimeter cooled by liquid 3 He in the chamber d (after Seidel and Keesom 1958).

(1955) and Seidel and Keesom (1958) used the 'single-shot' while Zinoveva and Peshkov (1958), Reich and Garwin (1959), and Ambler and Dove (1961), all had continuous circulation of ³He.

Figure 8.3 (Seidel and Keesom 1958) shows a calorimeter which is cooled by ³He condensed in the space d. The specimen i can be lowered by the nylon thread f onto the copper plate k. The ³He vapour is pumped away through a 4-mm diam. tube c which enlarges before reaching the oil-diffusion pump. The refrigerating capacity near to the lower limit of $T \approx 0.3$ K is 5μ W. The temperature scale is established by means of a paramagnetic salt, m, of ferric ammonium sulphate.

Another single-shot cryostat used for thermal conductivity measurements down to 0.3 K is shown in Fig. 8.4 (Seward and Narayamurti 1966). The ³He chamber which is machined from copper has internal ribs to increase the area of heat transfer between liquid and metal. The salt used to calibrate the germanium thermometer (Ge) is a sphere of cerium magnesium

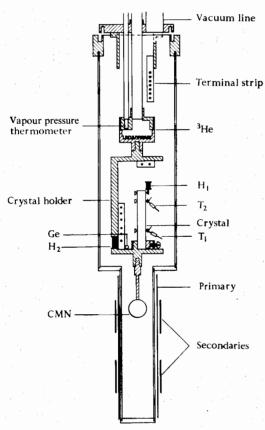


Fig. 8.4. A thermal conductivity cryostat cooled by liquid ³He (after Seward and Narayamurti 1966).

nitrate (CMN). The 'crystal holder' is a C-shaped piece of copper which thermally connects the platform holding the crystal to the ³He coolant.

Figure 8.5 shows a cryostat (Mate *et al.* 1965) in which the 3 He is pumped by adsorption on charcoal. K is a cage of copper gauze filled with 40 g of activated charcoal which can be raised or lowered into the cold region by a nylon line from the pulleys L. The 3 He chamber A is machined from solid copper and has a honeycomb structure to improve thermal equilibrium. An alternative construction is to put a tightly rolled cylinder of copper shim into the chamber and solder the bottom down. The sorption

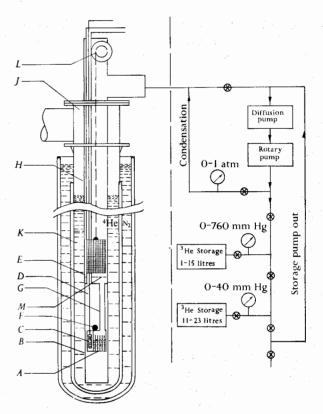


FIG. 8.5. A cryostat in which 3 He (in A) evaporates under reduced pressure, produced by the charcoal sorption pump (K) (after Mate et al. 1965).

pump has very high speed and so gives a lower temperature than rotary or diffusion pumps. Mate et~al. reached 0.28~K with a heat load of about $50~\mu\text{W}$. Further details of the use of sorption pumps for ^3He and ^4He may be found in papers by Eselson, Lazarev, and Shvets (1962, 1963), Shvets (1967), and Goldschwartz and Van der Merwe (1976).

3. ³He dilution

At the Low Temperature Physics Conference held in Oxford in 1951, H. London (p. 157 of the *Proceedings*) suggested that 'a valuable cooling process would ... make use of the entropy of mixing of ³He and ⁴He ... at very low temperatures the ³He can

'expand' by being diluted with ⁴He. The latter has negligible entropy below 1 K, while the entropy of the former is still appreciable.... Thus by a reversible adiabatic dilution ... the temperature would fall and at (say) 0.01 K the specific heat would still be appreciable.' Some years later the discovery of phase separation in liquid helium mixtures below 0.8 K and experiments on the osmotic pressure of ³He in liquid ⁴He resulted in London, Clarke, and Mendoza (1962) making more detailed proposals for designs of a dilution refrigerator. Following these, refrigerators were made by Das et al. (1965), Hall et al. (1966), and Neganov et al. (1966). Some of these first efforts were not completely successful but they proved that the dilution principle worked and paved the way to both commercial refrigerators which reach 20 mK or so (see Appendix) and to the present research models, some of which reach 3 mK.

Figure 8.6 is a schematic diagram from a comprehensive article by Wheatley, Vilches, and Abel (1968) on the 'Principles and methods of dilute refrigeration': ³He gas at a pressure of 20-30 Torr (~3 kPa) from the backing side of the pumping system enters the cryostat, is pre-cooled to 4.2 K, and then condenses in the 1 K cooling stage (pumped ⁴He). It then goes successively through a throttling impedance, heat exchanger attached to the still (or boiler), other heat exchangers and into the mixing chamber. There phase separation occurs with the lighter ³He-rich phase forming the top layer and some ³He diffusing across the phase boundary where adiabatic dilution causes cooling. It then diffuses through the quasi-stationary liquid ⁴He, via the heat exchangers to the still. This is electrically heated to a temperature of c. 0.6 K which evaporates the ³He preferentially as it has a much higher vapour pressure than ⁴He and then the ³He vapour goes to the pumping system through a tube of graded diameter.

Useful reviews include those of Wheatley et al. (1968, 1971), Radebaugh and Siegwarth (1971), and Lounasmaa (1974, Ch. 3). In the remaining part of this section we discuss some of the important features which emerge from these reviews, from original papers cited below, from published Proceedings of the conferences ICEC 3 to ICEC 6 (1970–1976, IPC Science and Technology Press, Surrey, UK), and unpublished proceedings of the 1976 EPS Study Conference on dilution refrigerators, held at the University of Lancaster.

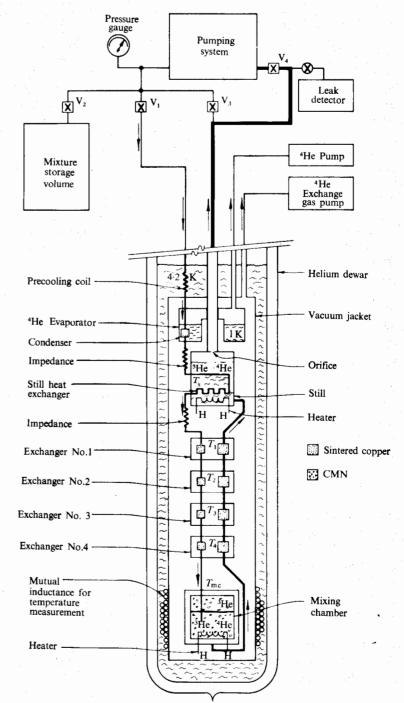


Fig. 8.6. Schematic diagram of a dilution refrigerator (after Wheatley et al. 1968).

Pumps

With the customary flow rates of 10^{-5} to 10^{-4} mol/s (equivalent to 1-10 ml of liquid helium per hour), a booster pump which can operate against a backing pressure of ~ 30 Torr is used alone or a diffusion pump plus a well-sealed mechanical pump (see Appendix for suppliers). A mechanical pump alone may be quite satisfactory unless high flows or very low temperatures (< 20 mK) are wanted.

1 K cooling stage

As in the ³He evaporation cryostats, this cooling stage may consist of a pumped chamber which is filled discontinuously with liquid ⁴He or a plate with a coiled tube thermally anchored to it. The heat transfer surface areas, particularly in the ³He condenser, should be increased by the use of sintered copper powder (see Fig. 8.6). Kraus (1977) and de Waele, Reekers, and Gijsman (1977) have described a dilution refrigerator without the pumped ⁴He bath, and use sintered copper heat exchangers to improve the heat transfer from the downflowing ³He stream to the evaporating ³He stream.

Impedance

This is necessary to keep the 3 He pressure in the condenser above the 15 or 20 Torr required for condensation; it is usually made by threading a closely fitting piece of wire (say, manganin) through a 0.2 mm i.d. tube of cupronickel or stainless steel tube and cutting it to the required length after flow testing at room temperature.

Still or boiler

It is usually made of copper, is well linked to the ³He input tube or heat exchanger, and has a small electrical heater (≤1 mW) attached to it. For best operation it is necessary to keep the ⁴He circulation as low as possible, preferably less than 10 per cent of the ³He circulation. To achieve this, He II film flow should be suppressed to some extent. Unless very low temperatures (<10 mK) are being sought, a small (1 mm diam.) electropolished orifice should suffice. More elaborate suppressors have been described by Wheatley, Rapp, and Johnson (1971), Kirk and Adams (1974).

Heat exchangers

Although not indicated as such in Fig. 8.6, the first exchanger below the still is usually a continuous tube-in-tube exchanger while the remainder are discrete units containing sinter or foil to maximize the area of heat transfer. Lounasmaa (1974) and the reviews of Wheatley et al., etc., describe methods of making such exchangers, e.g. filling tubes with pure copper powder of 40 µm particle size, heating first to 500 °C to degas, and then to 700 °C in a hydrogen atmosphere. More recent exchangers are described by: (i) Alvesalo et al. (1974) who use thin copper sheets with copper powder sintered onto them, (ii) Niinikoski (1971) whose extended exchanger consists of two tubes soldered together and wound into a spiral. Each tube is incompletely filled with copper sinter so that there is free passage for the liquid; the tubes are of different diameter with large tube for the dilute stream and smaller for the ³He-rich stream, and (iii) Frosatti and Thoulouze (in Proceedings of ICEC 6, p. 116, 1976) sintered silver powder onto silver foil (at c. 200 °C) which forms a boundary between two channels, the larger for ⁴He-rich phase and smaller one for ³He-rich. The two channels in Stycast epoxy are respectively about 4 and 1.5 mm in width and are sealed to the silver 'diaphragm' with epoxy resin.

Mixing chamber

These have been made of copper, brass, or epoxy depending on the need for screw-on connections, magnetic fields and eddy currents, etc. Note that because of the Kapitza boundary resistance the temperature of the chamber wall may be significantly higher than the minimum temperature achieved near the phase boundary.

Construction and operation

Because so many fine tubes are used in the refrigerators and they are easily blocked, it is advised *not* to use acid fluxes. Use silver solder or 'tin' with silver solder and then use resin solders or make all final joints with indium O-ring seals. A material commonly used for supporting the different parts of the refrigerator is pitch-bonded graphite which has a very low heat conductivity below 1 K (Fig. 9.8) and is reasonably strong. Machinable glass-ceramic (Corning) should also be suitable as its

somewhat higher conductivity is compensated by greater mechanical strength than graphite.

Apart from the reviews and papers mentioned above, descriptions of interest include also those by: (i) Anderson (1970): a relatively simple 50 mK refrigerator with a single coaxial heat exchanger, all of which can be made in a 'long weekend', (ii) Frosatti and Thoulouze (in Proceedings of ICEC 5 and ICEC 6) of two different Grenoble refrigerators, (iii) Roubeau (Proc. ICEC 6, p. 100) of a novel design, (iv) de Waele, Reekers, and Gijsman (Proc. ICEC 6, p. 112) of a double mixing chamber.

The development of heat exchangers with large effective areas for heat transfer, $A \sim 1 \text{ m}^2$, the reduction in viscous heating by having open flow channels in the exchangers, and increase in flow rate of ³He to $n_3 \sim 10^{-4}$ mol/s have all contributed to the more successful operation of dilution refrigerators. Temperatures in the mixer of less than 10 mK are commonplace and 3 mK or slightly less has been achieved in a number of 'fridges'. An empirical relation, $T_0^2 \approx 0.2 n_3/A$, has been quoted by Hall (Lancaster conference 1976) to connect the final temperature T_0 (K) with flow-rate n_3 (mol/s) and area of heat exchange A (m²).

4. Leiden 'superleak' refrigerator

Taconis and his colleagues at Leiden (e.g. Taconis et al. 1971; Pennings et al. 1976) developed the concept of circulating ⁴He rather than ³He in a dilution refrigerator. Figure 8.7 is a schematic diagram showing the mixing chamber M where cooling occurs, and the demixer D which is thermally linked to a 0.6 K bath of ³He which removes heat of demixing. M and D are connected by a tube which acts as a counterflow heat exchanger with ⁴He flowing down and ³He flowing upwards. There are no walls to present a Kapitza boundary resistance or viscous heating in this 'exchanger'. The superleaks S_1 and S_2 are stainless steel tubes packed tightly with jeweller's rouge which prevents liquid other than superfluid circulating. F is a tube for filling with the ³He-⁴He mixture. With a circulation rate of $n_4 \sim 10^{-3}$ mol/s, Pennings et al. have obtained temperatures as low as 10 mK at M.

5. Pomeranchuk cooling

Pomeranchuk (1950) predicted from a theoretical study of ³He that the entropy of the solid would be greater than that of the

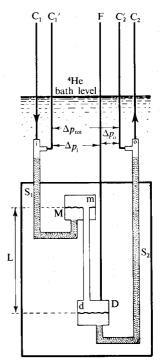


Fig. 8.7. Schematic diagram of the Leiden refrigerator (after Pennings et al. 1976).

liquid at sufficiently low temperatures and that therefore adiabatic compression of the liquid would produce a cooling effect. For some years the cooling could not be observed due to practical difficulties such as the low starting temperature needed, and frictional heating. Anufryev (1965) succeeded first in cooling 3 He from 50 mK to 20 mK and then followed work notably at La Jolla (e.g. Johnson and Wheatley 1970), Cornell (e.g. Sites *et al.* 1969, Halperin *et al.* 1973), and Helsinki (e.g. Alvesalo *et al.* 1974) which has produced temperatures of $\sim 1 \text{ mK}$. These have been most successful in studying the properties of 3 He itself as discussed by Lounasmaa (1974, Ch. 4) and Wheatley (1975).

Principles

The melting curve of 3 He has a deep minimum at T = 0.32 K where $P_{\min} = 2.93 \text{ MPa}$ compared with a melting pressure at 0 K of 3.44 MPa (Grilly 1971). This shows that a tube containing 3 He,

which passes from a region of $T < 0.32 \,\mathrm{K}$ to a region of $T > 0.32 \,\mathrm{K}$, will become blocked with a plug of solid at a point where $T \approx 0.32 \,\mathrm{K}$ when the pressure is increased above P_{\min} . Any further pressurization of the colder part of the tube or cell containing ³He must then be done by some other squeezing process and not via the capillary tube.

It also means that dP/dT is negative below 0.32 K and from the Clausius-Clapeyron relation

$$\frac{\mathrm{d}P}{\mathrm{d}P} = \frac{\Delta S}{\Delta V}$$

that entropy S (solid) > S (liquid) since V (solid) < V (liquid) at these temperatures.

As shown in Fig. 8.8 (from Lounasmaa 1974), the entropy of the solid from 0.3 K down to below 10 mK is close to R ln 2 and presumably arises entirely from the disorder of the nuclear spins $(I = \frac{1}{2})$; below 10 mK exchange interactions produce some

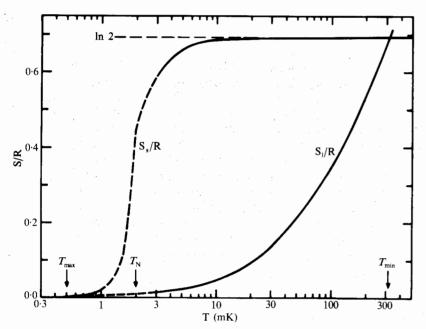


Fig. 8.8. The entropy of solid and liquid ³He along the melting curve (after Lounasmaa 1974, p. 61).

antiferromagnetic alignment which is complete near 2 mK. However the liquid of 3 He atoms is a Fermi liquid like the conduction electrons in a metal so that both their heat capacity and entropy are proportional to T. Thus the respective entropies are equal at $0.32~\rm K$ but S_1 falls below S_8 at lower temperatures and an isentropic or adiabatic compression of liquid 3 He beginning at say $T_0 \sim 30~\rm mK$ should produce a final temperature of $\sim 2~\rm mK$. Values of the entropy change during solidification lead to values for the cooling power which are an order of magnitude greater between 5 and 10 mK than for a dilution refrigerator of the same 'capacity', i.e. circulating the same number of moles per second as are converted into solid (Lounasmaa 1974, p. 67).

Cells

An example is shown in Fig. 8.9 from Osheroff, Richardson, and Lee (1972) of a Pomeranchuk cell which is precooled by the mixing chamber of a dilution refrigerator. Liquid ⁴He is compressed in the upper part to say 1 MPa and this is transmitted via the metal-epoxy shaft to the ³He with a pressure amplification effect. In this cell, the convolutions of the beryllium-copper bellows surrounding the ³He open during the compression and so do not crush the solid that is formed. A capacitance strain gauge measures the pressure in the lower chamber and the nmr signal from platinum measures the temperature.

6. Thermometry

Many of the thermometers used in ³He cryostats have already been discussed in Chapter IV, for example electrical resistors such as carbon, silicon, <u>Rh</u>Fe and capacitance elements. These are all useful secondary thermometers but suffer the problem of losing thermal contact below ~50 mK with the system whose temperature is to be measured.

The susceptibility χ of paramagnetic salts such as cerium-magnesium nitrate is a useful instrument particularly with the aid of SQUID detectors. For CMN in the form of a single crystal sphere, the χ -T relation is well established down to \sim 2 mK (see also § 9.3 for more details and references).

The nuclear susceptibility and nuclear magnetic resonance are widely used at millikelvin temperatures although the presence of iron impurities in say Pt must raise doubts about their reliability.

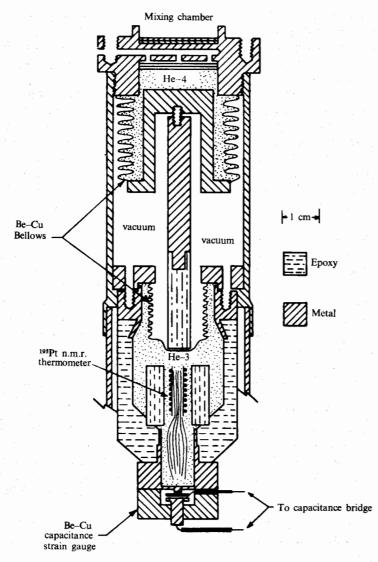


Fig. 8.9. A Pomeranchuk compression cell (after Osheroff et al. 1972).

As a primary thermometer, nuclear orientation measured by γ -ray anisotropy (see also § 9.3) works well as does noise thermometry.

Hudson et al. (1975) have reviewed the use of all these methods 'below 300 mK' in some detail and Lounasmaa and Betts each discuss the techniques in their books. Finally H. Hall (private communication) has suggested the viscosity of ³He measured with a vibrating wire as a reliable thermometer since viscosity $\eta \propto 1/T^2$.

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CHAPTER IX

ADIABATIC DEMAGNETIZATION

1. Introduction

At the beginning of this book it was pointed out that methods of cooling and entropy reduction are inextricably linked. Because the entropy or disorder of a gas is a function of volume as well as of temperature, the volume forms a useful physical variable by which the entropy of the gas can be reduced; if the initial alteration in volume V_1 to V_2 be made isothermally in a direction such as to reduce the entropy S, a subsequent adiabatic or isentropic change of V_2 to V_1 results in a drop in temperature.

To reach temperatures below that available by liquefying and pumping on helium, it is necessary to find some system which remains partially disordered and which can be ordered by a change in some available physical parameter. It was suggested by Giauque (1927) and independently by Debye (1926) that a disordered assembly of magnetic dipoles which may still occur in a paramagnetic substance at liquid-helium temperatures, should constitute such a system. Using the magnetic field B, as the variable quantity, successive processes of isothermal magnetization and adiabatic demagnetization should produce cooling. As is now well known, Giauque and MacDougall (1933) at Berkeley and de Haas, Wiersma, and Kramers (1933) at Leiden proved this experimentally; soon afterwards Kurti and Simon (1934) at Oxford also carried out successful demagnetizations.

Soon after this Gorter (1934) and Kurti and Simon (1935) suggested that temperatures of a microdegree might be attained by demagnetization of nuclear spins; however, the required starting condition that $B/T_0 \sim 10^3$ T/K made this technically impractical for some years to come. Eventually in 1956 Kurti *et al.* (1956) successfully demagnetized copper from initial fields of 2–3 Tesla and an initial temperature of 12 mK and achieved nuclear spin temperatures of about 20 μ K.

Analogous cooling processes have been demonstrated for an assembly of electric dipoles: application of an electric field to a

material containing a disordered array of electric dipoles decreases the entropy and when the field is switched off isentropically, a cooling or electrocaloric effect occurs (e.g. Hegenbarth 1965; Känzig, Hart, and Roberts 1964). In the case of a superconductor, adiabatic magnetization produces a marked cooling (e.g. Yaqub 1960). The history of magnetic cooling and some of the later developments have been given in monographs of Casimir (1940), Garrett (1954), Kurti (1952), Hudson (1972), Lounasmaa (1974), and in reviews by Ambler and Hudson (1955), de Klerk and Steenland (1955), de Klerk (1956), Mendoza (1961), and Little (1964).

The cooling process is illustrated in terms of entropy reduction by Fig. 9.1. This figure shows what is happening thermodynamically during the isothermal magnetization (change from B=0 to $B=B_1$ at T_0) and subsequent isentropic demagnetization (change from $B=B_1$ at T_0 to B=0 at T_1). We may also ask what happens to the alignment of the individual magnetic dipoles during these changes. First, let us consider the dipoles initially at T_0 as a non-interacting assembly, or more properly as an assembly with such a small interaction that the dipoles have no preferred orientation. If the paramagnetic ion has a total angular momentum J, then its moment may take up any one of 2J+1 directions with respect to the vanishingly small interaction field, the energy difference between adjacent orientations (or energy levels) being U, where U is assumed to be much less than kT_0 . The probability of the magnetic moment of an ion having a

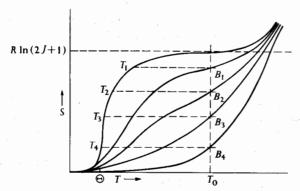


Fig. 9.1. Entropy of a paramagnetic salt used in cooling experiments (after de Klerk 1956).

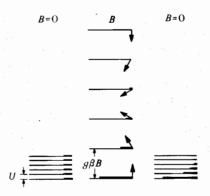


Fig. 9.2. Energy diagram of a paramagnetic ion (after Kurti 1952).

certain orientation is governed by the Boltzmann distribution, i.e. the factor $\exp(U/kT)$; since $U = g\beta B_{\rm int} \ll kT_0$, any of the 2J+1 orientations are equally probable. However, on applying a field B_1 such that $g\beta B_1 \ge kT_0$, the ions will go into the lower energy levels which correspond to dipoles pointing in the direction of the applied field (see Fig. 9.2). Here g is the Landé splitting factor

$$1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

and β is the Bohr magneton. In Fig. 9.2 the degree of occupation of the various energy levels (here J=5/2 so 2J+1=6) is indicated by the shading on the lines. On removing the applied field B_1 isentropically, the degree of order must remain constant but the difference U returns to its former small value. For this to occur the distribution functions involving $\exp(g\beta B_1/kT_0)$ ($B=B_1$ at $T=T_0$) and $\exp(g\beta B_f/kT_1)$ ($B=B_f\to 0$ at $T=T_1$) must be equal, hence the final temperature

$$T_1 = \frac{B_{\rm f} T_0}{B_1}.$$

Lest it be supposed that on reducing the external field B to zero, T falls to zero and thereby violates the third law, it should be remembered that the dipoles do interact, just as atoms in a gas interact and eventually condense into a liquid or solid state at sufficient low temperatures. So the small interactions (which may be represented as preducing an internal field, $B_{\rm int}$ or $B_{\rm f}$) cause the

fine splitting of levels by an amount U which is sufficient to give T_1 a finite value and prevent an 'attainability catastrophe'.

A further condition for effective magnetic cooling is that the non-magnetic entropy of the system should be small in comparison with the magnetic entropy $S_{\rm m}$, or more strictly in comparison with the possible reduction in magnetic entropy. This non-magnetic entropy comprises the vibrational entropy of the lattice, e.g.

$$S_0 = \int_0^{T_0} \frac{1944(T/\theta_D)^3}{T} dT = 648 \left(\frac{T}{\theta_D}\right)^3 \text{ J/mol K}$$

which is usually negligible at 1 K in comparison with $\Delta S_{\rm m}$.

Summarizing for the paramagnetic ion:

- (i) $S_m = R \ln(2J + 1)$ when B = 0,
- (ii) $\Delta S_{\rm m}$ should be appreciable in a field B, and
- (iii) we require $S_{\text{lattice}} \ll \Delta S_{\text{m}}$.

Experimentally the magnetic cooling process may be represented schematically by Fig. 9.3. The time spent at stage (b) must be sufficiently long for the heat of magnetization $Q = T_0 \Delta S_{\rm m}$ to be removed through helium exchange gas to the surrounding helium bath at temperature $T_0 \sim 1~{\rm K}$, i.e. for the magnetization to be effectively isothermal. (c) Represents the period during which the exchange gas is removed. Whether or not this exchange gas is removed completely, the process of demagnetization to a temperature $T_1 \ll T_0$ is sufficiently rapid that residual gas is adsorbed onto the cold surface of the salt pill.

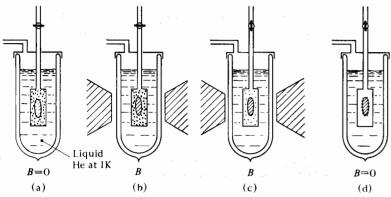


FIG. 9.3. Schematic diagrams of the experimental procedure used in magnetic cooling.

Provided that liquid helium and suitable pumps, dewar, magnet, etc., are available, cooling to 0·1 or 0·01 K can no longer be considered a particularly difficult or exclusive art, thanks to the pioneering efforts at Berkeley, Leiden, Oxford, and Cambridge. However, the problems of knowing what temperatures are attained by demagnetization, of maintaining those temperatures for appreciable periods, and of ensuring that the temperature at one point in a salt pill is also the temperature at another point or in some attached specimen are formidable.

2. Paramagnetic salts

Salts suitable for magnetic cooling must contain paramagnetic ions which have a non-zero resultant angular momentum or magnetic moment. The interaction between the magnetic ions (dipole-dipole or exchange interaction) should be sufficiently small that the energy level splitting U is much less than kT at 1 K; but in a field of one tesla the splitting $g\beta B$ should be greater than kT. In addition, it is desirable that any higher energy levels should be already so high in zero external field that their influence on the distribution function is negligible, i.e. they should be 'quenched'.

Then we may assume that the entropy and magnetic moment M are functions of B/T only, e.g.

$$M = \text{constant } B/T$$
 (Curie's law)

or magnetic susceptibility $\chi = {\rm constant}/T$ down to a temperature $T \sim \theta = U/k$. When temperatures in the neighbourhood of this characteristic temperature θ are reached, thermal energies have become comparable with the residual splitting or interaction energies, so that Curie's law is no longer obeyed; θ is the approximate limit of cooling and is also near the maximum of the magnetic specific heat anomaly. At temperatures appreciably above θ , the ion interaction is negligible and the magnetic specific heat $C_{\rm m} = {\rm constant}/T^2$.

Suitable magnetic ions come largely from the transition elements and the rare earth elements; that is, from those elements in which the atoms have a residual magnetic moment due to an unfilled but partially shielded inner shell. Of these, the most commonly used have been Ce, Gd, and Nd among the rare earths and those transition elements with an unfilled 3d shell, viz. Cr, Mn, Fe, Co, Ni; certain cupric salts have also been found useful.

These elements, present in the form of magnetic ions, are normally used in mixed salts in which the interaction is reduced by the presence of non-magnetic ions and water of crystallization. For transition elements the energy levels of interest are generally the spin levels as the orbital magnetism—if present—is quenched by the crystalline electric fields, i.e. Stark splitting of the orbital levels such that the energy gap between them is much greater than kT at 1 K. The magnetic moment due to electron spin is not directly affected by these electric fields but only via a coupling of the orbital and spin momenta.

The properties of a number of the most commonly used salts for which magnetic cooling experiments, susceptibility measurements, specific heat measurements, and paramagnetic resonance studies have provided data, are given in reviews by Cooke (1955), Ambler and Hudson (1955), de Klerk (1956), Hudson (1972), etc. For example, in the case of ferric ammonium alum, the chemical formula is FeNH₄(SO₄)₂.12H₂O. The ground state of the ferric ion is ${}^6S_{\frac{5}{2}}$ from which 2S+1=6 and therefore the total spin entropy $S_m=R$ ln 6. The susceptibility closely follows Curie's law with a Curie constant of $4\cdot 39$ emu/mol and resonance studies give $g=2\cdot 00$. Measurements of specific heat show

$$C/R \simeq 0.013_5/T^2$$
.

Some of these salts are listed in Table 9.1 with values for the temperature T_1 reacted by adiabatic demagnetization from $T_0 \approx 1.1$ K, $H_1 = 0.5T$ (de Klerk 1956). Values of the Néel temperature T_N , Curie Constant c, and heat capacity constant, $b = C_m T^2/R$, are from Hudson (1972, p. 110).

A property of obvious interest when using a salt as a cooling medium is its specific heat. Not only is this a fairly direct criterion of the splitting of the energy levels, and hence of the temperatures which may be obtained by demagnetization, but it also governs the warming-rate of the salt arising from a given 'heat leak'. If the electrical resistance of a material is to be measured near $0.1\,\mathrm{K}$, it is pointless to use a cooling salt such as cerium magnesium nitrate which has a single maximum in the specific heat below $0.01\,\mathrm{K}$ and hence a very small heat capacity between $0.1\,\mathrm{m}$ and $1.0\,\mathrm{K}$.

The specific heat curves shown in Fig. 9.4 have been plotted from data given by de Klerk (1956) in his review. Not shown is

TABLE 9.1

Magnetic cooling salts: T_1 is temperature reached from $B_1 = 0.5T$, $T_0 = 1.1 \ K$; T_N is Néel temperature; $b = C_m T^2/R$ and Curie Constant c in emu/g-ion. (Note: c in J/T^2 g-ion = $10 \times c$ emu/g-ion)

Salt		$T_1(K)$	<i>T</i> _N (K)	c emu/g-ion) ь
Cr(NH ₃ CH ₃)(SO ₄) ₂ .12H ₂ O	CMA	0.21	0.016	1.83	0.018
CrK(SO ₄) ₂ .12H ₂ O	CPA	0.20	0.009	1.84	0.017
$CuK_2(SO_4)_2.6H_2O$		0.099	0.05	0.445	5.7×10^{-4}
FeNH ₄ (SO ₄) ₂ .12H ₂ O	FAA	0.090	0.026	4.39	0.013
Gd ₂ (SO ₄) ₃ .8H ₂ O	GS	0.28	0.182	7.80	0.32, 0.37
$Mn(NH_4)_2.(SO_4)_2.6H_2O$	MAS	0.165	0.173	4.38	0.032
$Ce_2Mg_3(NO_3)_{12}.24H_2O$	CMN	~0.01	0.0015	$C_{\parallel} \sim 0$	6.6×10^{-6}
				$C_{\perp}^{"}=0.317$	

that for cerium magnesium nitrate, for which $C/R \simeq 6 \times 10^{-6} \ T^{-2}$; this may be compared with $C/R = 0.018 \ T^{-2}$ for chromium methylamine alum.

As suggested above, these properties may be altered by diluting a paramagnetic salt so as to increase the distance between magnetic ions, thereby decreasing the magnetic interaction and hence the splitting of the lower energy levels. As de Haas and Wiersma (1935) found, dilution of chromium potassium alum with aluminium potassium alum allows much lower values of T_1 to be obtained provided that B_1 is increased. But dilution also reduced the magnetic entropy S_m so that the total heat capacity per unit volume is reduced and likewise the capacity of the salt for cooling other objects is reduced.

As we shall discuss further in §§ 4 and 5 below, the cooling salt is usually mounted in a cryostat in one of four forms: (i) single crystal, (ii) powder compressed into a semi-solid rod, (iii) loose powder packed into a glass, plastic, or metal container to which can be added glycerol, oil, or helium to improve the heat transfer, (iv) a solid cylinder formed by mixing the salt with epoxy resin. Thermal contact to the salt can be made by growing the crystal around a wire (silver) grid or by including fine metal wires in the pressed (or cemented) rod. Most of these salts must be protected against loss of water of crystallization. It is usually advisable to store 'salt pills' in a refrigerator or in liquid nitrogen and to avoid

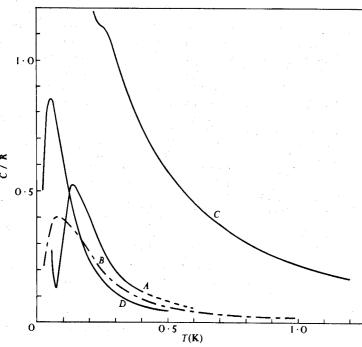


FIG. 9.4. Heat capacity of some salts used in magnetic cooling. A, chromium methylamine alum; B, chromium potassium alum; C, gadolinium sulphate; D, ferric ammonium sulphate.

pumping a vacuum in the space around them until they have been cooled well below room temperature. Some paramagnetics which are not hydrated have been used for cooling but they have not won general acceptance for use below 0·1 K: they include the double fluorides such as (NH₄)₃CrF₆ (Ambler and Hudson 1956), acetyl acetonates (Daunt and Pillinger 1955), ruby (Heer and Rauch 1955), and some rare-earth alloys (Parks 1963).

3. Temperature measurement

Relationship between temperature and magnetic susceptibility

For paramagnetic salts there is an observable magnetic property, the susceptibility, which is temperature sensitive and provides a thermometric parameter. We may define a temperature scale T^* such that the observed volume susceptibility is related to

it by

$$\chi = c/T^*$$

where c is the Curie constant, since it is known that for a non-interacting assembly of magnetic dipoles (and for most magnetic cooling salts at temperatures $T \sim 1 \text{ K} \gg \theta$) the magnetic susceptibility varies inversely as the absolute temperature. However, even at temperatures $T \gg \theta$ we cannot put $T^* = T$ due to the complicating influence of the shape-dependent demagnetizing field and the Lorentz internal field—due to magnetic interactions.

Following de Klerk (1956), Hudson (1972), etc., the local or internal field in the salt, $B_{\rm loc}$ can be related to the external applied field $B_{\rm ext}$ by

$$B_{\rm loc} = B_{\rm ext} + (4\pi/3 - \varepsilon)M/V$$

where $4\pi M/3 V$ is a dipole interaction field deduced by Lorentz; ε is the demagnetizing coefficient which decreases as the length/diameter ratio of the salt pill increases. For a spherical pill, $\varepsilon = 4\pi/3$ and so

$$B_{\rm loc} = B_{\rm ext}$$

and

$$\chi_{\rm loc} = \chi_{\rm ext}$$
.

Kurti and Simon introduced a quantity $T^{(*)}$ defined as

$$T^{(*)} = c/\chi_{loc}$$

so that for a spherical pill, $T^{(*)} = T^*$. More generally

$$\chi_{\rm loc} = \frac{\chi_{\rm ext}}{1 + (4\pi/3 - \varepsilon)/V}$$

so that

$$T^{(*)} = \frac{c}{\chi_{\text{ext}}} \{ 1 + (4\pi/3 - \varepsilon)\chi_{\text{ext}}/V \}$$
$$= T^* + (4\pi/3 - \varepsilon)c/V$$
$$= T^* + \Delta.$$

Provided $T \gg \theta$, we may assume $T^{(*)} = T$ for most paramagnetic salts used in cooling experiments.

Therefore

$$\chi_{\text{ext}} = \frac{c}{T - \Delta} = \frac{c}{T - (4\pi/3 - \varepsilon) fc/V};$$

here f is a filling factor which may be required, in the case of loosely packed salt pills, to take account of their density being appreciably less than the density of a single crystal. For example, let us consider potassium chrome alum. From Kurti and Simon (1938a) the Curie constant per cublic centimetre is 0.0066 so that if a pill has an approximately spheroidal shape, ratio of length to diameter of four, and density about 97 per cent of the single-crystal density, then

$$\Delta = (4\pi/3 - 1) \times 0.0066 \times 0.97$$

= 0.019₅,

so that the measured susceptibility $\chi \propto (T - 0.02)^{-1}$.

Before considering the discrepancies between the thermodynamic temperature and the 'magnetic' temperature which may occur at temperatures below 1 K let us consider the usual methods of measuring the susceptibility.

Susceptibility measurement

Although the balance method (see Chapter VII) of measuring susceptibility was used in Leiden in their early experiments on demagnetization, this has been superseded by the inductance bridge. A simple form of this is the ballistic bridge (Fig. 9.5a) which is now partly of historic interest.

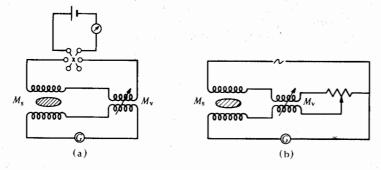


FIG. 9.5. (a) Ballistic bridge; (b) a.c. Hartshorn bridge.

In the ballistic method, a measured current supplied by an accumulator is reversed through the primary coil of a mutual inductance M_s around the salt pill; this induces a current pulse through the secondary which is measured by the deflexion of a ballistic galvanometer G—usually of period 10 to 20 s. The primary of $M_{\rm s}$ consists of a few hundred turns of copper wire wound onto the tail of the helium dewar and therefore immersed in liquid nitrogen, or it may be wound on the outer jacket of the experimental chamber and be in liquid helium; the secondary coil of some thousand or more turns of fine copper wire lies inside the primary. Part of the inductance may be cancelled by the variable inductometer M_v which is external to the cryostat. As discussed by de Klerk in his review (1956) practices differ: M_v may be used to create a null method whereby changes in the setting of M_{ν} record the relative change in susceptibility of the salt pill; or M_{ν} may be set so that the ballistic deflexion δ is approximately zero at say 4 K and as the temperature is lowered δ is recorded as a function of temperature.

In the latter case

$$\delta = \text{constant } \chi + b = \frac{a}{T - \Delta} + b.$$

The constants a, \dot{b} which depend on the coil geometry and on the Curie constant are determined by plotting δ against the reciprocal of $(T-\Delta)$ in the range from 4 to 1 K, and then extrapolated at lower temperatures to obtain a value of $T^* = T^{(*)} - \Delta$. It is common to wind two portions of the secondary of M_s in a region well above and well below the salt pill and wind them in opposition to the central portion. These are designed to cancel out the ballistic deflexion (or a.c. signal when using a bridge) in the temperature range where the salt's susceptibility is small.

The a.c. methods have become generally adopted because their sensitivity can be made greater and because of the availability of commercial components including ratio-transformers and phasesensitive detectors. Versions of the Hartshorn bridge, shown schematically in Fig. 9.5b, are widely used (see for example Hudson 1972); details of individual bridges are given by de Klerk and Hudson (1954), Maxwell (1965), Anderson, Peterson, and Robichaux (1970), Cetas and Swenson (1972), and Cetas (1976). The ultimate in detector sensitivity is provided by the SQUID

(Lounasmaa 1974, Ch. 7; Giffard, Webb, and Wheatley 1972) and allows the use of very small quantities (~mg) of paramagnetic salt as far as temperature sensing is concerned.

Care must be exercised with a.c. methods to avoid stray heating either from relaxation effects in the salt or eddy currents in metal parts. The former can be made negligible by working at low frequencies since the heat absorption amounts to $\frac{1}{2}B_0^2\omega\chi''$ where B_0 is the amplitude of the alternating field, ω is its angular frequency, and χ'' is the complex part of the susceptibility. Eddy current effects are reduced both by using sensitive bridges that require small alternating fields and by avoiding the use of continuous sheets of good-conducting metals; the latter may involve using shields of coil-foil (Anderson, Salinger, and Wheatley 1961) which are made by winding fine copper wire onto a mylar-covered former, covering the wires with cement (e.g. GE7031); after baking and removal from the former, the sheets of fine wire can be made into thermal shields, etc. (see e.g. Cetas 1976).

T-T(*) relations at low temperatures

In the liquid-helium region above 1 K, the temperature T is assumed to be that of the surrounding bath with which it is in thermal contact. Therefore a good estimate of T can be obtained from the helium vapour-pressure or from a calibrated secondary thermometer. Then if the susceptibility (or a related measurable parameter) is given by

$$\chi = c/(T - \Delta) + a$$

the constants can be determined in this range 1-4 K and, as long as $T^{(*)} = T$, can be extrapolated to lower temperatures. However once $T \to \theta$, the interaction 'temperature' between the spins, this equality breaks down and some absolute method is needed to relate $T^{(*)}$ to T.

In the traditional thermodynamic method we define, from the second law,

$$T = \frac{\mathrm{d}Q_{\text{rev}}}{\mathrm{d}S} = \frac{\mathrm{d}Q_{\text{rev}}/\mathrm{d}T^{(*)}}{\mathrm{d}S/\mathrm{d}T^{(*)}};$$

it follows that by a series of demagnetizations from a known field B and known temperature T, and an allied series of specific heat

determinations (warming the salt to determine $T^{(*)}$ as a function of Q), the numerator and denominator in this equation may be determined. Hence the relation between $T^{(*)}$ and T may be found for a particular salt.

Both the principles and the practice of the determination of the thermodynamic scale below 1 K have been discussed at length by Kurti and Simon (1938b), Cooke (1949), and in the reviews by Ambler and Hudson (1955), and de Klerk (1956). Figure 9.6 illustrates the principles of the determination. At temperature T_0 (in the liquid-helium region), the difference in entropy ΔS of the salt in fields B_1 and B_2 may be determined theoretically from the properties of the salt or directly by measuring ΔQ_0 ; heat ΔQ_0 is evolved in changing from B_1 to B_2 and may be determined from the quantity of helium evaporated. If two isentropic demagnetizations from B_1 and from B_2 to B=0 take the salt to temperature T_1^* and T_2^* respectively, the difference in entropy is still ΔS between the positions A' and B'. Alternatively, by supplying heat ΔQ to the salt, it may be warmed from the temperature T_1^* to T_1^* and hence the difference $_{1*}T_{2*} = \Delta Q/\Delta S$ may be found in degrees kelvin. This implies a knowledge of ΔQ which must be obtained by calibration of the heating source (γ -ray heating or a.c. electrical heating) at a temperature in the vicinity of T_0 ; here the salt is known to obey Curie's law and hence the thermodynamic temperatures are known. By a series of demagnetizations, a fairly accurate picture of the $T-T^*$ relation may be obtained.

Hudson (1972, Ch. V) has collated $T - T^*$ data for a number

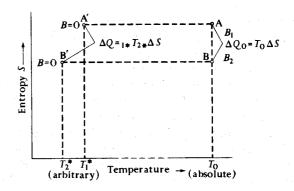


Fig. 9.6. Establishment of a thermodynamic temperature scale below 1 K (after Kurti 1952).

of important salts including CMN, CPA, CMA, and FAA. For CMN which is the most widely used thermometer salt below 1 K, T and $T^{(*)}$ differ by less than 1 per cent down to 6 mK for both single crystals and powder specimens (see also review by Hudson et al. (1975) of thermometry below 300 mK).

Surprisingly the equality seems to persist down to 2 or 3 mK for powder samples of CMN—witness the discussion by Hudson (1969) of the 'Delta Campaign'. For these other three salts, the difference between T and $T^{(*)}$ becomes significant at temperatures of 0.4 to 1 K. The use of paramagnetic salts such as CMA, MAS, and GS in establishing temperature scales above 1 K is discussed above in § 4.3 (also, for example, see Cetas (1976)).

Other thermometers

Apart from the measurements of electronic susceptibility discussed above, there are numerous other primary and secondary methods of measuring temperatures below 1 K. Among the primary thermometers discussed more fully by Lounasmaa (1974, Ch. 8) are:

- (i) anisotropy of γ-rays emitted from oriented radioactive nuclei such as ⁵⁴Mn or ⁶⁰Co (see also Weyhmann 1973 and Steyert in *Temperature*, **4**, 1253. Instrument Society of America, Pittsburgh, 1972),
- (ii) Mossbauer effect measurements of similar oriented nuclei (Taylor in *Temperature*, **4**, 1259, 1972),
- (iii) Brownian noise in a resistor using SQUID detectors (Kamper in Temperature, 4, 349, 1972),
- (iv) properties of ³He including melting pressure and viscosity. Secondary thermometers include some which have already been described in Chapter IV for use above 1 K and which can be used also down to $T \sim 10$ mK. These are carbon resistors, particularly the Speer brand (Anderson in *Temperature*, 4, 773, 1972), germanium resistors (some Cryocal unencapsulated), <u>Rh</u>Fe resistors (unencapsulated) and electrical capacitance. The other important thermometer which needs a calibration point is nuclear susceptibility. This can be used by measuring the static susceptibility with a SQUID magnetometer or by nuclear magnetic resonance, whether continuous or pulsed. Lounasmaa (1974) and Symko (in *Temperature*, 4, 1239, 1972) review the relative merits and problems which include impurity effects and relaxation times

(see also Walstedt et al. 1965). The nuclear spin-lattice relaxation time τ varies inversely as T and for some 'popular' metals is given by

$$\tau = 1 \cdot 1/T$$
 s/K for Cu;
= $0 \cdot 09/T$ s/K for In;
= $0 \cdot 03/T$ s/K for Pt.

More details of these methods can be found in the books of Hudson and Lounasmaa, and in descriptions of individual cryostats mentioned earlier in Chapter VIII and below in § 9.4.

4. Cryostats

Introduction

For effective cooling by demagnetization certain provisions must be met in the cryostat:

- (i) It must allow the salt to be cooled to $\sim 1 \, \text{K}$ by thermal contact with a pumped liquid-helium bath.
- (ii) At the salt there must be an adequate magnetic field to reduce the entropy appreciably, and thermal contact must be maintained to allow the heat of magnetization $(Q = T_0 \Delta S_m)$ to be transferred to the helium bath.
- (iii) Before demagnetization this thermal contact must be broken, and after demagnetization thermal contact must be sufficiently bad that the leakage of heat to the salt pill is small compared with its heat capacity.

Traditional cryostats

The two cryostats illustrated in Fig. 9.7a and (b) are of particular historic and technical interest. In the first figure ((a) of a Leiden cryostat) the ellipsoidal salt is mounted on a glass pillar within a small vacuum jacket, also of glass. The secondary coil of the mutual inductance is wound onto the vacuum jacket and is in the liquid helium contained by the inner dewar. The primary coil, wound onto the tail of the helium dewar, is immersed in the liquid hydrogen or liquid nitrogen of the outer dewar. Helium exchange gas is used in the vacuum jacket for cooling the salt pill and afterwards pumped away. In later versions (e.g. Mess et al. 1969) the cooling salt, say CPA, is separated into two segments, the main salt pill and a thermal gaurd pill half-way along the supporting rod.

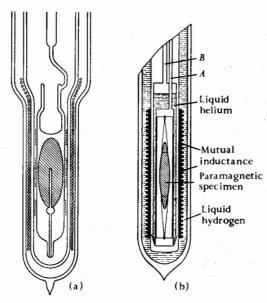


Fig. 9.7. Demagnetization cryostats. (a) Leiden (after Casimir, de Haas, and de Klerk 1939); (b) Oxford (after Kurti 1952).

The NBS installation (de Klerk and Hudson 1954) uses a very similar demagnetization cryostat, and in both Leiden and the NBS the cryostat is suspended from a long rotatable arm so that the whole cryostat may be moved out of the poles of the magnet after demagnetization.

In the Oxford pattern (Fig. 9.7b) the salt pill is tautly suspended by silk or nylon threads inside a cylindrical metal cage; this cage fits into the German silver vacuum chamber which is sealed at the bottom by a greased cone and socket joint.† Formerly all these Oxford cryostats had a small Simon expansion liquefier in the upper part of the apparatus. The mutual inductance is wound onto a former of cloth-bonded bakelite or similar insulator, which fits over the outside wall of the vacuum case and is therefore surrounded by liquid hydrogen. The liquid helium is

pumped through tube B and exchange gas is admitted and removed through tube A. It should be noted that if metal chambers surround the salt these should be of a metal such as German silver which does not become ferromagnetic at low temperatures. When an a.c. induction method is used for determining susceptibility it is preferable to use glass throughout the 'tail' assembly.

Modern cryostats

Changes from these traditional patterns have been largely the introduction of 'superconducting' (lead or tin, § 5.8) heat switches between the salt and liquid helium, occasional use of 3 He instead of 4 He in the final cooling pot to give $T_{0} \approx 0.3$ K instead of 1 K, epoxy resins for construction of heat shields, and salt containers and finally superconducting magnets in place of the bulky electromagnets which were used prior to 1960. Methods of making these cryostats are illustrated in papers by Mess *et al.* (1969), Vilches and Wheatley (1966), Collan, Krusius, and Pickett (1970), Kobayasi, Shinohara, and Ono (1973), and in books of Hudson (1972) and Lounasmaa (1974).

Salt pills

The pressed variety may be easily made by partially filling a cylindrical hole in a steel block with the powdered salt, the bottom end of the hole being closed by a short length of steel rod which is free to slide in the hole. With a sliding steel piston inserted above the salt, a hand-operated or hydraulic press is then used to form a compact pill. The pill can then be pushed out fairly easily, although fracturing can occur during the removal which has led to the occasional use of a split-steel block, in which the two halves are bolted together during the pressing operation. A little vacuum grease mixed with the powdered salt in a pestle and mortar before pressing often results in a stronger pill. With reasonable care, such salt pills may be ground or filed to a required shape and then surface-sealed with nail varnish or other cement to retard dehydration. Strong well-bonded pills can be made by mixing the powdered salt with a cold-setting epoxy resin or other plastic; thermal contact with the salt is facilitated by including copper wires or foil in the mixture. Geballe and Giauque (1952) have described a technique of shaping salt pills into ellipsoids of revolution.

[†] As sealing agent for such a ground joint high-vacuum greases such as Apiezon L or Apiezon K are frequently used, but it has been found that fluids which form glasses may be more satisfactory. Hudson and McLane (1954) describe the use of an alcohol-glycerine (2 parts glycerine and 1 part of n-propyl alcohol) mixture which gives leakproof joints in the helium region, provided that it is cooled slowly to liquid-nitrogen temperatures.

Alternatively, large single crystals of many paramagnetics may be grown from solution and can be formed onto a metal mesh or gauze in the process, e.g. onto silver, gold, or platinum gauze (Dugdale and MacDonald 1957; Wheatley, Griffing, and Estle 1956).

5. Heat transfer and thermal equilibrium below 1 K

Introduction

Two major problems in carrying out measurements of physical properties at temperatures below 1 K are those of maintaining the temperature of a specimen sensibly constant and uniform, and knowing what the temperature is. Obviously this is particularly the case when the specimen under investigation is neither the cooling salt itself nor a paramagnetic salt whose temperature can be inferred from a susceptibility measurement. In most investigations on the properties of paramagnetic salts, the primary problem is to ensure a small heat leak and hence slow warming-up rate so that they are in thermal equilibrium during readings; they provide their own thermometer. But when investigating physical properties of materials which do not act as cooling agents themselves, the additional problem arises of thermal contact with the cooling agent and with the primary thermometer—the salt.

As we discussed in Chapter V, the heat leakage is due largely to (i) radiation, (ii) residual gas conduction, (iii) conduction through solid supporting rods, wires, etc., (iv) gas desorption or adsorption, and (v) mechanical vibration.

Another annoying source of heating which is important in the millikelvin region (where nanowatts are significant) is pick-up from local radio and TV stations. The only completely effective solution is a shielded building or shielded room, which is expensive.

Lounasmaa (1974, Ch. 9) gives an excellent review of the problems of thermal contact and isolation below 1 K. Many of the experimental studies were carried out by Wheatley and Anderson and their colleagues at the University of Illinois (e.g. Wheatley, Griffing, and Estle 1956; Anderson, Reese, and Wheatley 1963; Vilches and Wheatley 1966; Anderson, Folinsbee, and Johnson 1971).

Radiation

In so far as radiation is concerned, the heat leak is negligible if the salt is surrounded by a metal wall near 1 K, provided that no radiation from surfaces at higher temperatures can enter the 'salt' chamber via pumping tubes. In glass demagnetization cryostats, radiation protection is necessary in the form of a coating on the glass chamber which is at or near 1 K. Wheatley et al. (1956) found that an adsorbent film of 'Aquadag' and layer of aluminium foil was efficient; with this protection, rather than chemical silvering, a flashlight beam did not noticeably change the normal heat leak of 13 nW from other sources. Anderson et al. (1971) showed that suitably coated Mylar was an efficient radiation trap but that coil-foil was not.

Gas adsorption

It seems dubious whether residual gas conduction and adsorption can be separated as heat-transfer factors, when a salt pill or specimen is at 0.01-0.1 K and is surrounded by a 1 K enclosure. However, the dependence of heat-leak rate on the exchange-gas pressure† and pumping time before demagnetization is quite marked. Exchange-gas pressures of $\sim 10^{-4}$ Torr appear to be too small for the heat of magnetization to be removed efficiently, and exchange-gas pressures of 10⁻² Torr are rather large as they result in large heat leaks (after demagnetization) even when pumping times of more than 1 h are used. This is partly due to adsorption of helium on the surfaces at 1 K, which cannot be completely removed by pumping but which transfers slowly to the salt pill after demagnetization; such effects are much less marked with glass than with metal cryostats. The effect of adsorbed exchange gas is most noticeable when salt pills or specimens have to be warmed up again to 0.5 or 0.6 K for the purpose of physical measurements, as the vapour pressure of liquid helium is relatively high ($\sim 10^{-4}$ Torr) at such temperatures, and the vacuum deteriorates rapidly due to desorption from the walls of the pill. In the experiments of Wheatley et al. (1956) with a glass cryostat, they confirmed that a suitable exchange-gas pressure is $\sim 10^{-3}$ Torr and to ensure minimum heat leak later, a pumping time of about

[†] For methods of removing heat of demagnetization, i.e. heat transfer, without the use of exchange gas, see discussion on heat switches in § 5.8.

2 h is needed. With a pumping time of 1 h the heat leak 10 min after demagnetization was 30 nW compared with 4 nW when pumped for $2\frac{1}{4}$ h.† For many experiments, such small heat leaks are an unnecessary luxury and a pumping of a few minutes followed by demagnetization (and the resulting adsorption of exchange gas on the salt pill) may be all that is necessary.

Heat conduction through supports

Conduction in solids is discussed in more detail in § 12.4 and § 5.3 and data for some materials which are used in cryogenic apparatus are given in Table I in the Appendix. Here we are concerned with the behaviour below 1 K where the experiments of Wheatley, Anderson, and others at Illinois and Pohl at Cornell have contributed much of the data: Figure 9.8 shows the solids used in millikelvin cryostats. Sources of data are as follows: Anderson et al. (1963) for epoxy (Epibond 100A) and manganin; Roth and Anderson (1976) for MGC (Corning machinable glass ceramic), graphite (AGOT) and borosilicate glass; Zeller and Pohl (1971) for nylon and Teflon; Childs, Ericks, and Powell (1973) for stainless steel, brass, sapphire; Locatelli, Arnaud, and Routin (1976) for sintered alumina. Data and references for many other materials can be found in the compilation of Childs et al. and in Lounasmaa (1974, Ch. 9).

For most of the 'amorphous' solids such as Pyrex, silica, epoxies, plastics, etc., $\lambda(T)$ has a plateau value of ~ 0.1 W/m K around 10 K but below 1 K, λ varies as T^n where $n \sim 2$. For crystalline dielectrics, λ varies roughly as T^3 over a wide range of low temperatures because the conductivity is limited by boundary scattering at these temperatures and therefore reflects the temperature dependence of the heat capacity of the phonons. Thus the values shown for a sapphire crystal are representative of a rod of a particular diameter; a fine-grained rod of sintered alumina (see Fig. 9.8) may have a conductivity 100 times smaller.

Manganin and stainless steel are examples of high-resistance alloys for which approximate values of λ can be calculated from the electrical resistivity ρ using the Wiedemann-Franz-Lorenz relation

$$\lambda = LT/\rho$$
, $(L = 2.45 \times 10^{-8} \text{ V}^2/\text{K}^2)$.

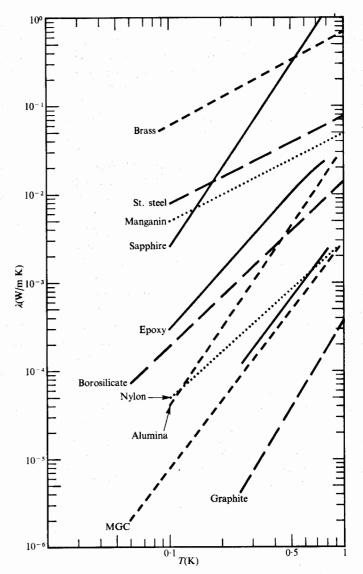


Fig. 9.8. $\lambda(T)$ of some solids used in cryostats below 1 K.

[†]To achieve such small heat leaks a second 'guard-ring' salt pill was attached to the supporting glass tube.

Since ρ is sensibly constant at low temperature, $\lambda \propto T$ if we neglect the phonon contribution.

Likewise the conductivity λ of pure metallic elements (in the normal state) also varies as T at low temperature but may be 10^4 to 10^5 times larger than for manganin or stainless steel. In the superconducting state, at temperatures well below $T_{\rm c}$, the heat conduction occurs via the phonons and therefore varies as T^3 as in a dielectric crystal. Thus $\lambda_{\rm s}/\lambda_{\rm n} \propto T^2$ and the increasing difference between $\lambda_{\rm S}$ and $\lambda_{\rm n}$ as T falls is the basis of the superconducting heat switches (see also § 5.8) used frequently in millikelvin refrigerators.

Mean values for $\lambda(T)$ between 1 and 0·1 K were also given above in Table 5.1 for solids used in cryostat construction. For example, the average $\bar{\lambda} \sim 10^{-3}$ W/m K for nylon, 6×10^{-3} for Pyrex glass, and 2×10^{-4} W/m K for graphite (AGOT), therefore for a rod 100 mm long and 1 mm in diameter, $l/A \sim 10^5$ m⁻¹ and so the heat flow along the rod with ends at 1 K and 0·1 K would be respectively 10 nW for nylon, 60 nW for Pyrex, and 2 nW for graphite.

This heat-leakage down supports may be reduced by using a 3 He cooling stage at c.~0.3 K or by using a double-pill technique, mounting the second 'guard-ring' pill of a paramagnetic salt at a point on the supporting tube or thread. In a further refinement, Dugdale and MacDonald (1957) thermally connected a light metal shield to the 'guard' salt so that a copper-plated German silver shield (at $T \approx 0.5$ K) surrounded the other 'salt' pill or specimen being investigated. In this case not only is conduction down the supporting tube or thread reduced, but heat leaks due to gas conduction or adsorption are reduced also; by such means heat leaks have been reduced to ~ 1 nW.

Vibrations

The results of investigations of mechanical vibrations as a source of heat inflow have been discussed in Chapter V. Suffice it to say that, with glass supports, the natural period of vibration is sufficiently high that normal laboratory or pump vibrations do not set the pill into vibrations of large amplitude, although heat leaks of a few ergs per minute might be traced to such a cause. With salt pills suspended by threads, the resonant period is often much closer to or identical with the period of some local vibrations and

may result in heat inputs of hundreds to thousands of ergs per minute; to counteract this, taut suspension threads, efficient damping of the pump vibrations and isolation of the cryostat from pumps and building vibrations may be used.

Thermal contact and equilibrium in the salt

As most heat leaks to a salt are to the surface or to points on the surface, and any heat leaks arising from an attached specimen are also to isolated regions within the salt pill, their effect on the temperature equilibrium of the salt pill is important.

For a single crystal of an insulator we may assume fairly rapid establishment of thermal equilibrium; the thermal conductivity at these low temperatures is due to lattice waves of fairly long wavelength and is limited by crystal or grain boundaries. The Casimir expression for λ_B as a function of grain size, θ_D , T, etc., is fairly well obeyed for many crystals at liquid-helium temperatures (e.g. reviews by Berman 1976, and § 11.3). The first measurements below 1 K by Kurti, Rollin, and Simon (1936) for a ferric ammonium alum crystal of 7-mm diam. showed

$\lambda \approx 2.5 \text{ mW/m K}$ at 0.07 K

and for a potassium chrome alum crystal of the same size

$\lambda \approx 10 \text{ mW/m K}$ at 0.18 K.

These values are a little smaller than Casimir's expression predicts but confirm that these salts are sufficiently good conductors that temperature gradients within the crystal will be small unless, either the heat leaks are intolerably large, i.e. $\dot{Q} > 1~\mu W$ or the temperature is very low, i.e. $T \le 1~m K$.

In salt pills made of compressed powder, the conductivity will be correspondingly smaller as it is limited by grain size. In fine-grained material there may be a serious lack of thermal equilibrium at the lowest temperatures unless metal foil, wire, or gauze are included in the pill. If this pill is to be used to cool another material, then such metal inserts are useful for making thermal contact between the pill and the object to be cooled. The contact or boundary resistance between a metal and salt crystal becomes of extreme importance.

Beginning with Mendoza (1948) there have been many measurements of the boundary resistance or conductance between salt crystals and metal fins, metals and liquid helium, etc. Vilches and Wheatley (1966) summarized many of these for the range 0.04–0.3 K as follows:

(i) for chrome potassium alum (CPA) to copper (coil-foil or copperplate) with apiezon 'N' grease in between:

$$\dot{Q}/A \cdot \Delta T = 250 T^3 \text{ W/m}^2 \text{ K},$$

- (ii) CPA-copper (coil-foil) with silicone grease: $40T^3 \text{ W/m}^2 \text{ K}$,
- (iii) CMN-CMN crystal with GE7031: 14T²⁻⁴ W/m² K,
- (iv) FAA-quartz crystal with apiezon 'J' oil: $100T^{2\cdot7}$ W/m² K,
- (v) FAA or CPA-liquid ⁴He: 200T³ W/m² K,
- (vi) Cu-liquid ${}^{3}\text{He}$: $500T^{3}$ W/m 2 K,
- (vii) Cu-liquid ⁴He: 200T³⁻⁴ W/m² K.

Lounasmaa (1974, Ch. 9) has updated this compilation and presented it in useful graphical form, by plotting the boundary (Kapitza) resistance $R_{\rm K}AT^3$ (units of ${\rm K^4m^2/W}$) against T. He includes values for metal–Mylar sandwiches glued with Epibond; for example, the conductances for Cu– and Al–Mylar are approximately given by $2000T^3~{\rm W/m^2}~{\rm K}$.

What is apparent from these various experiments on heat contact between the salt and embedded fins? Above about 0·1 K, as Mendoza suggested in 1948, the temperature of a specimen should be within a few hundredths of a degree of the temperature of the salt, provided that the specimen is connected via a good thermal link (copper wires) to extended fins which are firmly embedded in a compressed salt pill or are bonded to a single crystal. This presupposes that heat leaks to the specimen are maintained at a level of the order of 10 nW or less. An interesting means for maintaining low temperatures despite an appreciable heat input is that of 'incomplete demagnetization'; this was originally suggested and used by Kurti.

In this procedure the salt is first demagnetized to a field of, say, $0.1 \,\mathrm{T}$. During the course of the experiment, the field is slowly reduced from $0.1 \,\mathrm{T}$ at a rate sufficient to keep the salt temperature sensibly constant; this takes advantage of the relatively large specific heat of the salt in a magnetic field.

6. Two-stage cooling, cyclic magnetic refrigeration, and nuclear demagnetization

Thermal switches and two-stage processes

The demagnetization processes described in this section consist of two stages in 'series' which must be linked by a heat switch. Various types of switch were discussed earlier in § 5.8. We may illustrate schematically the use of a thermal switch in a 'two-stage' magnetic cooling process (Fig. 9.9) and examine its application to three particular problems: (i) two-stage cooling involving electron paramagnetics, (ii) cyclic magnetic refrigeration, (iii) nuclear demagnetization. As illustrated, L_1 and L_2 are thermal links, which when 'closed' allow heat flow; S_1 and S_2 are cooling salts.

In case (i) a two-stage demagnetization may be used to obtain temperatures of $\sim 0.001\,\mathrm{K}$ with comparatively small magnetic fields, e.g. $0.5\,\mathrm{T}$. A salt S_1 with a comparatively high characteristic temperature θ is magnetized with L_1 closed; L_1 is opened and S_1 is demagnetized to obtain a temperature of about $0.1\,\mathrm{K}$. Salt S_2 of much lower θ (e.g. diluted salt) is in a magnetic field during this procedure and is therefore magnetized at $T_0 \sim 0.1\,\mathrm{K}$. L_2 is now opened and S_2 is demagnetized to give a final temperature $T_1 \sim 0.001\,\mathrm{K}$.

In (ii) S_2 is a salt which acts as a thermal reservoir and is kept cool by cyclic removal of heat to S_1 and from S_1 to the helium bath: with L_1 closed, S_1 is magnetized; then after opening L_1 , S_1 is demagnetized and L_2 is closed to partially cool S_2 . Subsequently L_2 is opened and L_1 is closed and the process is repeated. Once the system has reached equilibrium, and provided that the

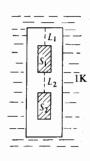


Fig. 9.9. The use of thermal switches in two-stage cooling processes.

heat leak to S_2 is small in comparison with its heat capacity, its temperature will oscillate with small amplitude about a mean temperature T with the period of the magnetic cycle.

In principle the nuclear cooling (iii) is similar to (i) but S_2 is now a nuclear paramagnetic while S_1 remains an electronic paramagnetic.

Two-stage cooling of electronic paramagnetics

Considering these processes in a little more detail, the first was ably demonstrated by the experiments of Darby *et al.* (1951) in which a final thermodynamic temperature of about 0.003 K was obtained with a field $B \approx 0.42 \text{ T}$; with $B \approx 0.9 \text{ T}$, they reached $T \approx 10^{-3} \text{ K}$ and maintained the temperature below 0.01 K for about 40 min.

The experimental arrangement and warm-up rate after demagnetization from $0.9\,\mathrm{T}$ is shown in Fig. 9.10. In these experiments L_1 was helium exchange gas and L_2 a superconducting thermal link of lead wire 3 cm long and $0.3\,\mathrm{mm}$ diam. The consecutive processes of demagnetizing S_1 (iron ammonium alum), opening link L_2 , and then demagnetizing S_2 (diluted mixed crystals of potassium chrome alum and potassium aluminium alum in the

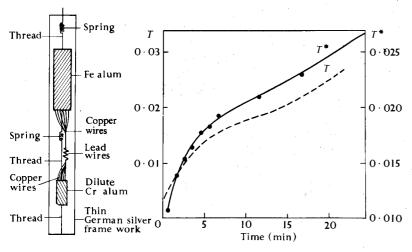


Fig. 9.10. Diagram of the arrangement used by Darby et al. (1951) in a two-stage cooling experiment; the temperature of the dilute chromium salt after demagnetization is shown in the graph (T^* = magnetic temperature, T = thermodynamic temperature).

ratio of about 20:1) were achieved by gradual lowering of the magnet.

Cyclic magnetic refrigeration

An interesting development in cryogenics was the construction of the first cyclic magnetic refrigerator at Ohio State University (Heer, Barnes, and Daunt 1954, Daunt 1957). This could maintain temperatures in the range $0.2-1.0\,\mathrm{K}$ by continuous extraction of heat. A few copies were made commercially by the Arthur D. Little Corporation but were soon superseded when ³He became available in sufficient quantities to use as a refrigerant for this temperature range.

However this refrigerator is still of interest as a prototype for later designs which use superconducting solenoids (see Zimmerman, McNutt, and Bohm 1962, for details of a refrigerator with superconducting magnets) and different cooling salts to maintain temperatures below those reached by liquid ³He.

Nuclear demagnetization

The limiting temperature which may be reached by demagnetizing a system of magnetic spins is determined by the interaction between the spins. Nuclear spins have magnetic moments which are two thousand times smaller than those of electronic spins, so that this interaction is reduced and temperatures can be reached which are a thousand times smaller than with electronic spins. The chief technical difficulties are the requirements of a low starting temperature and a high magnetic field, since a value of $B/T_0 \sim 10^3 \, \text{T/K}$ is needed to ensure appreciable spin alignment; also short relaxation times are needed between the nuclear spin system and conduction electrons, lattice, etc.

The first cooling by demagnetization of nuclear spins was reported by Kurti et al. (1956) who achieved spin temperatures of $\sim 20~\mu \rm K$. The nuclear stage (equivalent to S_2 in schematic diagram of Fig. 9.9) was of copper in the form of 1500 enamelled wires, each of $0.1~\rm mm$ diameter to reduce eddy-current heating. The wires, tied in a bundle, were folded over four times at the lower end to constitute the nuclear 'salt' and embedded at their top end in the electronic paramagnetic salt (S_1) ; this was chrome potassium alum mixed with some glycerol and water to promote thermal equilibrium and improve heat transfer to the copper wires, and was held in a Perspex container. The heat link L_2 thus

consists of the copper wires themselves in order to avoid the complexity of a magnetically operated heat switch for these preliminary experiments. This whole assembly of $S_2 + L_2 + S_1$ was mounted inside a double-walled brass tube, the top part of which contained 25 g of manganous ammonium sulphate cooled by the initial demagnetization (when S_1 is demagnetized). The lower part of the double-walled shield was kept in good thermal contact with the manganous salt by liquid helium and thin copper wires between the brass walls.

In later experiments liquid ³He was used to cool the heat shield and spin temperatures of a few microdegrees were achieved from starting conditions of $B/T_0 = 200 \, \text{T/K}$ (e.g. Kurti 1963). However lack of a thermal switch between the copper and the electronic stage plus the relatively long spin-lattice relaxation time τ for copper meant that the electron or lattice temperatures did not fall significantly. The nmr thermometry experiments of Waldstedt *et al.* (1965) showed that for copper $\tau \approx 1.1 \, \text{T}^{-1} \, \text{s/K}$.

Symko (1969) inserted a superconducting heat switch of 0.5 mm diam. tin wire between his electronic cooling stage (CPA in a slurry with glycerol) and the nuclear stage: in one case the latter was a bundle of fine enamelled copper wires and in a second case he included fine indium powder and tap grease as a paste between copper wires. With starting conditions of $B_0 = 3.2$ T, T = 12 mK, and final field B = 40 mT, he achieved a spin temperature in the Cu–In mixture of 0.2 mK for Cu spins and ~ 1.7 mK for In. The latter should equal the electron temperature for In since τ is small.

Berglund *et al.* (1972) used a dilution refrigerator as the primary cooling stage and 70 000 fine (0.05 mm diam.) insulated copper wires for the nuclear stage, separated by a tin heat-switch. Starting from a field of 5 T and 16 mK and with a final field of 72 mT they observed a minimum spin temperature of 0.54 mK after 90 minutes and calculated a minimum electron temperature of ~ 0.5 mK. Further details are given by Lounasmaa (1974), Hudson (1972), and in original papers by these authors.

It would seem that with presently available magnets of >10 T and improved dilution refrigerators which give $T_0 \le 5$ mK, nuclear refrigeration should give real temperatures of ~ 0.1 mK or less provided heat leaks can be minimized and relaxation times maximized in the same experiment.

7. Magnets

Magnetic fields play an essential role in the cooling processes which were discussed in this chapter. Magnets and cryogenics are also interdependent in other areas: magnetic fields are necessary to the solid-state physicist who studies either the motions of free electrons in metals at low temperatures where thermal scattering is reduced, or the spin-energy levels of bound electrons and nucleons. In return, low temperatures produce the superconducting state in some metals and its convenient corollary, the superconducting magnet.

The various types of magnets which are used in cryogenics may be classified as follows:

- (i) the iron magnet which has a ferromagnetic core of high permeability, has relatively small power requirement, and gives a field which is limited by the saturation magnetization of the iron;
- (ii) the normal coil magnet whose field is only limited by the available electric power, removal of Joule heat, and the mechanical strength of its components;
- (iii) the pulsed coil in which the limiting field is set more by mechanical strength than by power or heating;
- (iv) the superconducting coil which avoids both power and heating problems completely but is limited by the critical field of the superconducting components.

These magnets have been discussed in some detail in the monographs by de Klerk (1965), Parkinson and Mulhall (1967), and Montgomery (1969); and reviews by Chester (1967), Wood (1971), and Lubell (1972) on superconducting magnets and Carden (1976) on high-field electromagnets.

Iron-core magnets

The magnetization of iron becomes saturated when the domains are fully aligned which requires a field of c. 2 T. Fields which are a little greater than this can be obtained with iron magnets by careful shaping of the pole-faces in order to concentrate the field locally. Fields of between 4 and 5 T have been reached with pole gaps of 2 cm in the large electromagnets at Leiden (14 tons in weight), Bellevue near Paris (nearly 100 tons), and Uppsala (37 tons). Further refinements in the design of the yoke and pole-faces have allowed fields of nearly 4 T to be

reached in a 2-cm gap in magnets of only 2 or 3 tons weight, for example in that made by the Arthur D. Little Corporation and designed by Bitter and Reed (1951).

With the advent of superconducting magnets, the rather massive iron-core electromagnets have largely gone out of favour. But there continues to be a need for more modest iron-core magnets which produce fields up to say 1.5 T for nmr and esr measurements and in situations where liquid helium is not regularly available (see Appendix for some suppliers).

Normal coil magnets

A study of the field-power characteristics of iron-core magnets and normal solenoids (Bitter 1962) shows that below 2–3 T the iron magnet is more effective for a given power, but above 3 T the iron-free solenoid wins. For such a solenoid the field \boldsymbol{B} and power dissipation \boldsymbol{W} are related by the Fabry formula

$$B = 10^{-6} G (W \eta / a_1 \rho)^{\frac{1}{2}}$$

where η is the filling factor for the winding, ρ is the electrical resistivity, a_1 is the inner radius (all expressed in SI units); and G is a dimensionless factor depending on shape of winding and current distribution and lies usually between 0.15 and 0.25. Assuming $G \approx 0.2$, $\eta \approx 0.7$, and $\rho \approx 2 \times 10^{-8} \Omega$ m, then

$$B = 1.2 \times 10^{-3} (W/a_1)^{\frac{1}{2}}$$

so that for $a_1 = 50$ mm, 5 MW will give a field of 12 T and 1 MW is needed to produce 5 T. Such power loads are not inconsiderable so that fields in this range are now usually produced by superconducting magnets. It is in the region above 15 T where normal solenoids, with either continuous or pulsed operation, are necessary (e.g. Carden 1976).

Pulsed coil

In the BS days, that is 'before supermagnets', pulsed operation of magnet coils provided a very useful source of high fields without the necessity for large generators. Presumably they will continue to be useful for attaining fields above the limit of supermagnets, and applying them to experiments which can be performed during the brief life of the pulse.

Kapitza pioneered the use of high-pulsed fields by using batteries (chemically stored energy) and generators with large flywheels (mechanically stored energy) to provide a large pulse of electric power. More recently storage capacitors have been used also for this purpose (de Klerk 1965). Olsen (1953) has described how a small copper coil immersed in liquid helium achieved fields of nearly 20 T by discharge of a 3000- μ F bank of condensers, charged to 300 V.

Superconducting magnets

The pioneer efforts of G. B. Yntema, S. H. Autler, J. E. Kunzler, and others showed that some 'hard' superconductors could carry appreciable currents in the presence of magnetic fields 5 T or more. These materials included ductile alloys such as NbZr, NbTi, MoRe, and compounds of the β -wolfram structure such as Nb₃Sn, V₃Ga, etc.

Since some of these have become commercially available in the form of wires (alloys) or tapes (compounds), they have become widely used for winding solenoids where relatively high fields are required. They have the obvious disability of needing liquid helium or at least refrigeration to below 10 K and some show small remanent field effects amounting to 1–10 mT. For some years, the available wires also exhibited 'flux-jump' instabilities but these have been largely overcome by use of multifilaments embedded in copper, aluminium, etc. Some of the review articles that deal with problems and their solutions are by Montgomery (1963), Chester (1967), Lubell (1972), and in the proceedings of cryogenic engineering conferences (e.g. Adv. cryogen. Engng, Plenum Press) and applied superconductivity conferences.

Materials. Among the alloys NbZr has now been largely replaced by Nb plus 50–70 per cent Ti. The latter alloys have $T_{\rm c} \approx 10~{\rm K}$ and critical fields of near 10 T: the alloys with lower Ti content carry more current at high fields whereas the materials of higher concentration are better at lower fields. The commercial multifilament wires usually contain 20–500 individual filaments of $\sim 0.1~{\rm mm}$ diam. in a copper matrix, the ratio of Cu to superconductor being 2:3 in most cases (See Lubell 1962 and Appendix for suppliers). The multistrand nature of the superconductor and the copper (or silver or aluminium) coating allows for

redistribution of the currents if there is a local flux-jump or if a small length of superconductor becomes normal.

Nb₃Sn and V₃Ga are available in the form of flexible ribbon coated with copper or silver and in widths varying from 1 to 13 mm. Values of T_c are respectively 18 and 14.5 K and operating fields can exceed 15 T (e.g. Lubell 1972).

A survey of available materials was made by Cattams for the journal *Cryogenics* (12, 356) in 1972 which listed about 10 suppliers of wire or tape and a range of prices depending on composition, number of filaments, etc. Most lay between 1 and 5 cents per ampere-metre.

Coil construction. For the highest fields, that is to obtain fields close to the maximum, it is usually better to buy a ready-made magnet from one of the many suppliers (see Appendix) as a large part of the cost lies in the wire which they buy in quantity; they also have the winding jigs and experience with joining the superconductors. However there are occasions where a homemade coil is needed to fit a particular cryostat or to be wound onto an existing cryostat chamber. If so, bear in mind that the former should be a rigid material whose expansion coefficient is not too different from the wire, e.g. RCA suggest stainless steel for large coils. The winding should be firm because any movement induced by electromagnetic forces may cause quenching of the current. Mylar sheet can be used between layers to guard against breakdown and the coil can be 'plotted' in epoxy resin to give added strength and stability after winding; the 'potting' or filling is best done with the aid of a sealed furnace which can be evacuated and then pressurized slightly to fill the coil with resin.

Junctions between the superwire and copper current-leads can be made by either (a) soldering to the copper- or silver-plate if there is any on the wire, (b) cleaning and ultrasonically tinning the wire with indium after which it may be soldered, clamped, or crimped to copper pieces attached to the current leads, or (c) just cleaning the wire and clamping it between copper plates or crimping it in a copper tube to which the leads have been soldered; contact is improved by gold-plating the clamping surfaces or in the case of crimped tubes by cleaning and tinning the inside. Satisfactory junctions between two superwires can usually be made by cleaning, and crimping them side by side in a copper

tube. Avoid placing the junctions in a high-field region. More details of winding and joining are given by Gugan (1963), Laverick (1965), and in the instruction sheets distributed by some wire manufacturers.

Operation. The early NbZr coils did not always perform as well at temperatures below 4.2 K as at the normal boiling point of helium but the evidence on the later copper-clad NbTi coils shows a marked improvement on cooling. Biltcliffe et al. (1972) obtained improvements of 20–25 per cent in the quenching field of NbTi on cooling to 2 K enabling them to produce fields in excess of 10 T.

If the coil is provided with a superconducting 'shorting' switch, then it may be operated in the persistent mode which allows a very steady field to be maintained; also the current from the external source can be cut off, which stops Joule heating in the leads. The 'shorting' switch can consist of a metre or so of the superwire which is in thermal contact with a heater (carbon resistor) which can drive the wire normal to 'open' the switch.

For most laboratory-scale magnets, the current needed is 50–100 A which can be supplied by a transistor circuit (e.g. McAvoy 1963, and commercial suppliers), preferably one in which the current may be swept from zero to $I_{\rm max}$ at a very steady rate.

The leads which carry current to the magnet in the cryostat should be of optimum size to minimize the combined effect of Joule heating and heat conduction. This was discussed in an earlier chapter (\S 5.5) and it was pointed out that selection of optimum lead size also depends on two rather uncertain factors: first, the heat transfer from the leads to the evaporated heliumgas stream, and second the duty cycle of the magnet. A usual compromise for magnets needing a maximum of 25 A is to use a bunch of 10 or 12 copper wires of 34 B. & S. gauge (each 0.016-cm diam.) or a single wire of c.0.06-cm diam.; the use of many fine wires exposed to the helium gas gives better heat transfer.

Obviously if we use seven-strand cable for our magnet with $I_{\rm C} \approx 200~{\rm A}$ or Nb₃Sn tape with $I_{\rm C} \approx 100~{\rm A}$, the selection of optimum leads becomes more important. It is desirable to anchor the leads thermally with liquid air and to use two different sizes for the section from room temperature to 80 K and from 80 to 4 K.

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CHAPTER X

VACUUM TECHNIQUES AND MATERIALS

1. Introduction

It is clear from a consideration of heat transfer that one of the most important requirements in low-temperature research is that of maintaining a high vacuum. Whether this vacuum be in a space around the refrigerant liquid or in an enclosure within the liquid, pressures of 10^{-4} Pa ($\sim 10^{-6}$ Torr) or less must often be maintained to ensure thermal isolation or thermal equilibrium. The general techniques of producing high vacua have been discussed in many books including Dushman (1962), Yarwood (1967), Roth (1976), Holland, Steckelmacher, and Yarwood (1974), and Barrington (1963). Here we shall merely point out some features of a suitable pumping system and summarize the equations for the pumping speed of tubes and orifices, so that pumps and pumping-tube dimensions may be chosen which are commensurate with one another and which may meet such practical requirements as the removal of exchange gas from a cryostat.

These books (also Roth 1966) discuss the common methods of making seals, e.g. metal-glass seals, sealing cements, solders, etc. In low-temperature work some special problems arise as many cement seals and rubber gasket or rubber O-ring seals are no longer practicable for vacuum-tight assemblies. In § 3 of this chapter a brief account and discussion is given of available low-melting-point solders which are particularly useful in making vacuum-tight joints which can be cooled and can also be 'broken' and remade fairly readily. Some other types of vacuum seals and cements as well as the use of metal-glass seals at low temperatures are described later in the chapter.

2. Vacuum technique

High-vacuum system

In most low-temperature equipment, a vacuum system is required to produce and maintain pressures of the order of 10^{-4} Pa

in a relatively small chamber. As there are or should be no permanent gas leaks into the chamber (cf. a nuclear accelerator or ion source into which a small regulated leak of hydrogen, deuterium, or helium is maintained), pumping speeds are not of primary importance in maintaining a low pressure. However, in many cases a small pressure (say 10 Pa) of helium gas may be admitted to the chamber for purposes of obtaining thermal equilibrium. The time required for the subsequent removal of this exchange gas will depend on the effective speeds of the pumps and connecting tubes; unless an unusually short time of the order of seconds is required for this removal, the pumping speed of the system need only be of the order of a litre per second, i.e. much smaller than the speeds of hundreds or thousands of litres per second required in ion accelerators. It is fortunate that pumping speed requirements are rather modest, since the design of an experimental cryostat usually restricts the possible size of pumping tubes which connect the experimental chambers (enclosed as they are in a dewar vessel) to the pumping system. A conventional pumping system is illustrated in the schematic diagram of Fig. 10.1. Pure helium for use as exchange gas (or for filling gas thermometers) is kept in the flask; this can be replenished by taking helium gas from a cylinder through a liquid-nitrogencooled charcoal trap or using evaporated helium gas from a liquid-helium storage dewar.

 G_1 and G_2 are vacuum gauges for determining the approximate pressure in the system. G_1 is conveniently a discharge gauge in which a high voltage from a Tessla coil produces a visible discharge at pressures from 1 to 1000 Pa or higher depending on the gas present. The character of the discharge is determined by the gas pressure and type of gas. With a little experience, helium gas (giving a pinkish discharge turning pale green at lower pressures), nitrogen (reddish), oxygen (straw yellow), carbon dioxide (whitish blue), and water or organic vapours (bluish colour) can be distinguished. For measurement of lower pressures (the function of G_2 in Fig. 10.1) a number of different types of gauge can be made or obtained from manufacturers of highvacuum equipment. Among those commonly used are (i) the thermionic ionization gauge with a lower limit of 10^{-7} Pa (ii) the mercury McLeod gauge which has a lower limit of about 10⁻⁴ Pa and does not register the pressure of condensable vapours, (iii)

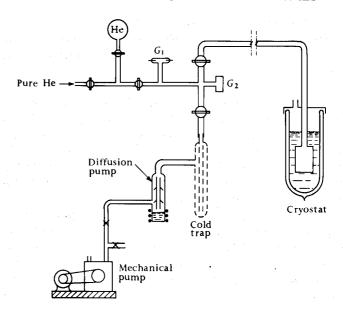


Fig. 10.1. Schematic diagram of a pumping system.

the hot-wire Pirani gauge with a lower limit of 10^{-1} Pa (iv) the Philips (or Penning) cold cathode ionization gauge which is available with a lower limit of 10^{-4} Pa. Of these the Philips gauge has many advantages in range, simplicity, and reliability of operation but its sensitivity varies somewhat with the composition of the gas present so that it only provides an approximate measure of the pressure; the usual calibration supplied with a commercial model is approximately correct for air. Whichever gauge is used, a record of the pressure in the cryostat chamber is only obtained if the gauge is in a position close to the chamber, i.e. if the resistance of the pumping line (reciprocal of its pumping speed) is much less between the point of attachment of the gauge and the chamber than it is between this point and the throat of the diffusion pump. A further problem arises when the cryostat chamber is surrounded by liquid helium as the vapour pressure of gases other than helium will be negligible at this temperature. When the system is in equilibrium, and if there is no helium leak into the cryostat, the gauge may register a much higher pressure than exists in the cryostat chamber; the gauge is at room temperature, and is exposed to gases and vapours arising from the

nearby tube walls, tap grease, back diffusion through the pump, etc., but these gases (other than helium) do not affect the static pressure in the chamber which is at liquid-helium temperatures. As Garfunkel and Wexler (1954) have pointed out, one of the only reliable means of measuring the helium-gas pressure in such a chamber, which may be as low as 10^{-7} Pa, is to connect a helium mass spectrometer leak detector on the high-pressure side of the diffusion pump and determine the rate at which helium gas is being 'ejected' by this pump.

The choice of metal or glass for the pumping system depends partly on the desired pumping speed and on individual preference as well as the availability of materials.

If large pumping speeds and hence large pumping tubes are required, metal tubes and large-bore metal valves-necessarily rather expensive or difficult to make—are needed. If neither a large pumping speed nor a mechanically robust system is necessary and a competent glass-blower is available, the entire pumping system (excepting the rotary mechanical pump) may be constructed relatively quickly from glass.

In Fig. 10.1 a cold trap (usually liquid-nitrogen cooled) is shown in dashed lines. With a mercury diffusion pump, this trap is necessary to reduce the ultimate vacuum below the vapour pressure of mercury (~10⁻¹ Pa) at room temperature. In an oil-diffusion pump the ultimate pressure without a cold trap varies from 10^{-2} to 10^{-5} Pa depending on the type of oil used and the design of the pump. Oil-diffusion pumps are, however, rather less robust in operation due to the danger of cracking the hot oil by exposure to air, and they generally require a somewhat lower backing pressure for efficient operation; while many mercury diffusion pumps operate satisfactorily with a maximum backing pressure of $\sim 10^2$ Pa, most oil diffusion pumps require that the backing pressure be kept to $\sim 10 \, \text{Pa}$.

These questions are discussed in much greater detail in the standard texts on vacuum technique by Yarwood, Dushman, etc.

Pumping speed

The pumping speed of an orifice is expressed as the volume of gas passing through the orifice per unit time measured at the usually expressed in litres per second. When the mean free path of

the gas molecules is appreciably greater than the dimensions of the orifice or width of pumping tubes, so-called Knudsen conditions apply, i.e. the molecules diffuse without being affected by the presence of other gas molecules. Since the mean free path is inversely proportional to pressure and in most gases at room temperature is 1 m for a pressure of 10⁻² Pa, the condition for Knudsen flow is seen to be usually satisfied at the pressures produced by a diffusion pump, unless the dimensions of the pumping tubes and orifices are very great.

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Under such high-vacuum conditions, the pumping speed or volume of gas escaping per unit time through an orifice is given by

$$S = 3.6 \times 10^4 A \sqrt{(T/M)} \, \text{l/s}$$

where A is the area in m^2 , T is temperature, and M is molecular weight. Hence for air at 295 K

$$S = 11.7 \times 10^4 \, \text{l/s m}^2$$
.

Thus we may expect the pumping speed at the throat of a diffusion pump to be partly controlled by the available area of the annular aperture through which the gas diffuses before it is entrapped by the streaming vapour of the pump. In fact the efficiency of diffusion pumps is rather less than unity so that the effective speed for air is given by

$$S_p = \text{speed factor} \times A \times 11.7 \times 10^4 \text{ l/s}$$

where the 'speed factor' has a value of about 0.4 for a good oil diffusion pump and 0.2-0.3 for a mercury pump.

In the case of a cylindrical pumping tube for which the length $l \gg d$ (the diameter), the speed or conductance is given by

$$S_{\rm L} = 3.82 \times 10^4 \sqrt{\left(\frac{T}{M}\right)} \frac{d^3}{l} \, \text{l/s},$$

here d and l are in metres.

For air at 295 K this reduces to

$$S_{\rm L} \simeq 10^6 \frac{r^3}{l}$$
 (radius $r = \frac{1}{2}d$)
= $\frac{r_{\rm mm}^3}{l_{\rm mm}} 1/s$.

For helium gas, M=4 and therefore the speed of an orifice, pump, or tube is $\sqrt{(\frac{29}{4})} \approx 2.7$ times greater than for air. If a section of the pumping tube is at a low temperature T the speed of this section will be reduced proportionately to $T^{\frac{1}{2}}$ due to the lower kinetic velocity of the gas molecules at this temperature; this refers to the speed measured at the pressure existing in the cold tube, not to the mass flow or equivalent room-temperature speed which is increased as $T^{-\frac{1}{2}}$. Otherwise it might appear that for a cryostat pumping system, tubes of larger bore are required for the colder section than for the room temperature section. This is, of course, not the case, as a detailed analysis shows, since the pressure of a given mass of gas being taken through the system will be proportional to the temperature at any point assuming it is in equilibrium. Garfunkel and Wexler (1954) have calculated the effective room-temperature speed S_r for a number of tubes of differing diameter in series, under molecular flow conditions.

If we wish to calculate the time required to reduce the pressure in a volume V from P_1 to P_2 , where the limiting low pressure that may be reached is P_0 , time t is given by

$$t = \frac{V}{S} \ln \frac{P_1 - P_0}{P_2 - P_0};$$

and if we assume that $P_0 \ll P_1$, P_2 ,

$$t = 2.3 \frac{V}{S} \log_{10} \frac{P_1}{P_2}.$$

For example, suppose P is initially 100 Pa (~ 1 Torr) in a volume of 11 and P_2 is to be 10^{-3} Pa, then if $S_p = 5$ l/s and $S_T = 0.5$ l/s

$$\frac{1}{S} = \frac{1}{5} + \frac{1}{0.5}$$
$$= 2.2$$

and

$$t = 2.3 \frac{1}{1/2.2} \log_{10} (10^5)$$

= 25 s.

In practice the time required would be longer than this as the speed S_p of the diffusion pump would be small until the pressure

was reduced to $\sim 10^{-1} \, \text{Pa}$. From the initial pressure of 100 Pa down to $10^{-1} \, \text{Pa}$, $S_{\rm p}$ would be largely governed by the speed of the backing pump and the tubing connecting the backing pump to the diffusion pump.

At sufficiently high pressures that the mean free path is very much less than the lateral dimensions of the pumping tubes, we may assume normal laminar flow governed by Poiseuille's equation. In the intermediate region, usually corresponding to a pressure of 1 to 10 Pa, the mean free path and the lateral dimensions are comparable and precise calculation of the effective conductance of a tube is difficult.

We stated that the speed of a diffusion pump is controlled by the rate of diffusion of gas molecules through the throat of the pump into the vapour stream. In a rotary mechanical pump an oil-sealed eccentric rotor revolves in a cylindrical cavity 'sweeping' out the gas from the high pressure or entry side to the exhaust side at a speed depending on the number of revolutions per unit time and the volume of the space between the rotor and the fixed cylinder. In a pumping system, such as shown in Fig. 10.1, the speed of the mechanical pump can be much smaller than that of the diffusion pump. For example, if the speed of the diffusion pump is $S_p = 50 \text{ l/s}$ at a pressure of 10^{-2} Pa ($\sim 10^{-4} \text{ Torr}$) and it requires a backing pressure of 10 Pa, then the speed of the mechanical pump need be only

$$S_{\rm M} = \frac{10^{-2}}{10} \times 50 = 0.05 \, \text{l/s}$$

= 3 l/min:

it is advisable to increase this figure a few times to allow for the restricting effect of the tubing between the pumps. Backing pump speeds are often expressed in litres per minute or cubic metres per hour.

It should be emphasized that in designing a pumping system, consideration should be given to the matching of the pumping speeds of the various components; therefore an approximate estimate should be made of the speed of the proposed pumping tubes between the diffusion pump and the cryostat. It is pointless to make or buy a large 200-l/s diffusion pump, when it is to be connected by a length of 100 cm of 2-cm bore tubing (speed $S_L = r_{mm}^3/l_{mm} = 1 \text{ l/s}$) to the vacuum chamber of a cryostat; the

total speed or conductance is the reciprocal of the sum of the reciprocals of the individual speeds, i.e. the resistances are additive so that $S = (\frac{1}{200} + \frac{1}{1})^{-1} \approx 1$ l/s in this example. Likewise it is rather wasteful to use a 450-l/min mechanical pump to back an 8-l/s diffusion pump as a 50-l/min mechanical pump is just as effective.

An illustration of the dependence of pumping speed on pressure for some common mechanical and diffusion pumps is given in Fig. 10.2. With dry air the one- and two-stage mechanical pumps should give ultimate vacua of about 1 and 10⁻² Pa respectively. This assumes that no condensable vapours are present which may contaminate the oil. Mechanical pumps do not remove condensable vapours efficiently unless they are fitted with a gas ballast system, i.e. an automatic system which injects gas every cycle to aid in 'sweeping' away the condensable vapours. A diffusion pump does pump condensable vapours although the speed will vary with the molecular weight of the vapour. The mercury-diffusion pumps 1M2 and 2M2 will yield an ultimate vacuum of about 10^{-4} Pa ($\sim 10^{-6}$ Torr) if used with a cold trap, The oil diffusion pumps 1O2 and 2O3 may give an ultimate vacuum (without cold trap) of 10^{-3} to 10^{-4} Pa, depending on the type of oil and the heating power used.

Most of the major manufacturers (e.g. Leybold-Heraeus, Balzer, Edwards, Veeco, etc.) publish useful booklets showing speed curves, construction, oils, etc., for their pumps. It is important when pumping oxygen with a mechanical pump, particularly of the rotary piston type, to use a safe fluid such as tricresyl phosphate.

The principal oils used in diffusion pumps are the Apiezon A, B, and C hydrocarbons produced by the Shell Company, Octoil, Amoil, and Octoil-S by Bendix Corporation, and the silicone oils by Dow Corning Corp. The silicones are most resistant to oxidation but can decompose in the presence of electrical discharges and hot filaments and give undesirable insulating deposits.

Low-temperature leaks

Cryogenic apparatus does not usually require a pumping system of high speed. By necessity the size of the connecting tubes into a cryostat limits pumping speed severely. This limitation means that leaks, if present, will be a serious problem. Often they

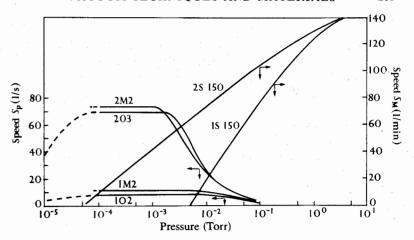


Fig. 10.2. Speeds of some commercial pumps (Edwards and Co., London) for dry air at room temperature. 1S150, Speedivac rotary pump: 1-stage; 2S150, Speedivac rotary pump: 2-stage; 1M2, mercury-diffusion pump: 1-stage; 2M2, mercury-diffusion pump: 2-stage; 1O2, oil-diffusion pump: 2-stage; 2O3, oil-diffusion pump: 3-stage.

will be serious not only because of low pumping speeds but because the leaks will be exposed to liquid refrigerants at low temperatures, which makes the leak rates much greater. Leakhunting is usually done at room temperature with a mass spectrometer or by cruder means, and may show no sign of a leak; and yet when the vacuum chamber is covered with liquid helium, a leak may become all too obvious but difficult to locate with any precision. The most annoying leaks are the λ -leaks which only appear when liquid helium II surrounds the offending part. The superfluid helium will creep through fine cracks of $0.1 \mu m$ or less in diameter at a rate which makes it impossible to maintain a sufficiently high vacuum for many experiments, e.g. calorimetry. Yet at room temperature the leak rate may be so small that a mass spectrometer detecting 10⁻¹⁰ Torr l/s will not give any indication of a leak. Such leaks as this are not uncommon in silver-solder joints which have been overheated, or in porous brass plates or in copper which contains oxygen and becomes slightly porous after heating. They can be avoided by careful selection of materials and soldering techniques. Croft (1963) included such leaks in his interesting review of 'Cryogenic difficulties'.

3. Solders

The most commonly used solders may be divided into three main classes: hard solders, soft solders, and low-melting-point solders. The latter have a frequent application in low-temperature equipment as they provide a means of making and breaking a vacuum joint without raising the temperature of the adjacent metals to more than about 100 °C. More detailed information on the composition of hard and soft solders than is given below may be obtained from physical tables or a standard handbook such as the *Metals Handbook* (American Society of Metals, Cleveland, Ohio).

Hard solders

These solders generally melt between 600° and 1000°C and are nominally a Cu–Zn brazing alloy with added silver; those having around 50 per cent silver content have the lowest melting points. They are generally used with a borax or boric acid flux, the two components being commonly mixed to a paste.

Such fluxes are readily available commercially from firms which supply hard solders, e.g. Handy and Harmon of Conn., Johnson Matthey of London, and Eutectic Corp. of New York. The most commonly used alloy is 'Easy Flow' which melts at about 630 °C and contains 50 per cent Ag, 15·5 per cent Cu, 16·5 per cent Zn, and 18 per cent Cd. Note that the cadmium can produce toxic fumes.

Another which is cadmium-free contains 45 per cent Ag, 30 per cent Cu, and 25 per cent Zn, melts over the range 675–745 °C, and is specified by the American Society of Testing Materials as ASTM Grade 4. Others are listed in the Metals Handbook, e.g. 8th Edition, Vol. 1 (1961, American Society of Metals) and in Roth (1966). After soldering it is very important to remove all traces of the borax flux with hot water, brushing, acid, and more water. In some installations such cleaning is difficult and an alternative technique is to solder with a silver/copper alloy containing phosphorus (e.g. Sil-fos from Johnson Matthey) while keeping the interior of the copper pipes filled with a 10 per cent $\rm H_2 + 90$ per cent $\rm N_2$ gas mixture.

Soft solders

Soft solders are generally tin-lead alloys, the eutectic mixture of 63 per cent Sn, 37 per cent Pb having a melting point of

183 °C. Mild fluxes such as rosin, rosin in alcohol, or a paste of petroleum jelly, zinc chloride, and ammonium chloride are often used in radio soldering. When a flux with a stronger cleaning action is required as in many metal-metal junctions, a zinc chloride solution is formed by dissolving zinc in hydrochloric acid. For soldering to stainless steel excess hydrochloric acid is desirable or a strong solution of phosphoric acid may be used. Commercially available fluxes include 'Baker's Fluid' (Baker's Soldering Fluxes, Middlesex, England), Kester Soldering Salt (Kester Solder Co., Chicago, Illinois) and a stainless steel soldering flux (Dunton Company, Rhode Island).

The solders include:

- 37.5% Sn, 60% Pb, 2.5% Sb—melting over a range from 185°-225°C; this is generally used for joining lead pipes and cable sheaths.
- 40-45% Sn, 60-55% Pb—these are very ductile solders, melting over a range from about 183°-230 °C and used generally in radio soldering.
- 50% Sn, 50% Pb—a good general-purpose solder melting from 180°-225 °C.
- 60% Sn, 40% Pb—a high-quality general-purpose solder melting from $183^{\circ}-191^{\circ}C$.
- 100% Pb—pure lead is sometimes useful because of its higher melting point of 327 °C.
- 50% Sn, 32% Pb, 18% Cd—the addition of cadmium reduces the melting point in this alloy ('low-temperature solder') to 145 °C.

In cryostat construction, particularly when using fine tubes which can be easily blocked, complete removal of the acid flux is important. Many people now prefer to avoid soldering fluxes altogether by arc-welding under an argon or helium atmosphere. Lounasmaa (1974, p. 7) makes this point strongly in writing '... an all-welded stainless steel design must be preferred.... Tensions and corrosion, caused by acid flux, are absent'. However this welding of thin stainless steel does require a skilled practitioner.

Low-melting-point solders

These solders, some of which melt well below 100 °C, are alloys of bismuth with the elements lead, tin, cadmium (and

indium in some instances). Like pure bismuth, those alloys containing a high percentage of bismuth (usually more than about 50 per cent) expand on solidification. The alloys are rather weak and brittle and should be used for joints or seals where they are not subject to stress, particularly bending stress. If used in a situation illustrated by Fig. 10.3a with copper or brass, then Wood's metal (or other low-melting-point alloy) should give a completely satisfactory vacuum-tight joint, unaffected by repeated cooling to liquid-helium temperatures. It is advisable with these solders, particularly those with melting points at 100 °C or less, to 'pretin' the metal surfaces which are to be joined, with a soldering iron beforehand. These alloys do not generally 'tin' when at or just above their liquid points. Therefore parts should be pretinned before assembly using sufficient heat to activate the flux (zinc chloride solution, Kester's soldering salt, Baker's fluid are satisfactory).

Wood's metal and other low-melting alloys are made and sold in most industrial countries under various trade names. The list below are those which were produced by the Cerro de Pasco Copper Corporation (New York) for making moulds, castings, fillers for tube bending, etc. They can be easily melted and poured into a sloping mould of angle iron to give a handy stick of solder.

Wood's metal—50% Bi, 25% Pb, 12.5% Sn, and 12.5% Cd melts from 65° to 70°C.

Cerrobend—a eutectic alloy of 50% Bi, 26.7% Pb, 13.3% Sn, and 10% Cd melts at 70 °C. It can be conveniently used as a substitute for Wood's metal and expands slightly on casting.

Cerrobase—a eutectic alloy of 55.5% Bi and 44.5% Pb melts at 124 °C, contracts slightly on casting.

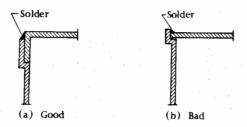


Fig. 10.3

Cerrotru—a eutectic alloy of 58% Bi and 42% Sn melts at 138°C. This alloy expands slightly on casting but then shows very little further growth or shrinkage, unlike most of these alloys which continue to grow or shrink slightly for some hours after casting.

Cerrolow 117—a eutectic alloy of 44·7% Bi, 22·6% Pb, 8·3% Sn, 5·3% Cd, and 19·1% In melts at 47°C.

Cerrolow 136—a eutectic alloy of 49% Bi, 18% Pb, 12% Sn, and 21% In melts at 58°C and like Cerrolow 117 expands slightly on casting and later shows a slight shrinkage for some hours.

Cerroseal 35—containing approximately equal amounts of Sn and In, this is a special glass-wetting alloy which melts from 116–126 °C.

Special solders

Listed below are some less common solders of interest in low-temperature research:

Zinc-cadmium solder—a eutectic alloy of 82.5% Cd and 17.5% Zn melting at 265 °C is often used for attaching electrical potential leads to metal specimens as it is not superconducting in the liquid-helium range of temperatures, unlike Wood's metal and most other soft solders which are superconducting below 7 or 8 K. This Zn-Cd solder flows quite freely on many metal surfaces when molten and is used in a similar manner to a tin-lead soft solder.

Bismuth—this is a non-superconducting solder with melting point at 271 °C which forms a rather mechanically weak joint as it does not 'wet' a metal surface very thoroughly.

Bismuth-cadmium solder—a eutectic alloy of 60% Bi and 40% Cd melting at 140°C which does not become superconducting above 0.8 K (Cochran *et al.* 1956).

Indium—melting at 155 °C, it bonds well to many metals and is sometimes preferred to alloy solders at low temperatures. It will bond to aluminium with a suitable fluoride flux and has been used for soldering to thin metal films or glass (Belser 1954); indium is highly ductile.

Gallium—melting at 29.5 °C, has also been recommended for use at liquid helium temperatures when good heat conduction is needed (Reynolds and Anderson 1976).

Thermal-free solder—a solder containing 70·44% Cd, 29·56% Sn, which gives a low thermo-electric force with respect to copper, is commercially produced by the Leeds and Northrup Company. Philadelphia.

4. Vacuum seals and cements

Most of the books listed at the beginning of this chapter describe various ways of making vacuum seals including welding, brazing, soldering, elastomers, cements, etc. Perhaps the most comprehensive is *Vacuum sealing techniques* by A. Roth (1966, Pergamon Press, Oxford). In the present book we are concerned chiefly with those seals which withstand repeated cooling to low temperature without leaking.

Metal-glass seals

Copper-glass seals of the Housekeeper type appear to be generally reliable and have been used, for example, in the 'tail' of small Linde helium liquefiers for long periods without any cracking. They have been used in sizes at least up to 2 cm diameter and remain vacuum-tight in the presence of liquid helium-II, the 'super-fluid component' of which has a vanishingly small viscosity and therefore magnifies the effect of any small leak that is present.

Seals made with platinum wire or platinum tubing to soft glass also seem to be quite satisfactory in maintaining complete vacuum tightness at liquid-helium temperatures. If adequately annealed they can withstand repeated cycling between room temperature and the lowest temperatures.

Seals to hard glass can be made with metals having suitable expansion characteristics, the linear expansion coefficient usually being between 4 and $5\times 10^{-6}~\rm K^{-1}$ at room temperature. Fernico and Kovar are two such alloys, containing 54% Fe, 28–29% Ni, 17–18% Co ($\alpha\approx 4\cdot 6\times 10^{-6}~\rm K^{-1}$ at room temperature), which seal to some of the borosilicate glasses that are made by Chance or Corning.

Many commercial firms make metal-to-glass and ceramic-to-metal seals but not all are satisfactory after repeated cooling. For example, some years ago varied experiences were reported with the Kovar seals made by Stupakoff Ceramic and Manufacturing Company, Pennsylvania. Some experimenters (e.g. Lane 1949)

found them satisfactory in liquid helium while others (e.g. Corak and Wexler 1953) found small leaks. We have found seals from Wesley Coe Ltd. of Cambridge, UK, to be satisfactory. However in many cryostats there is not enough space available for metalglass seals which can carry a large number of electrical leads so that epoxy seals are more common (see Fig. 10.4 and text).

Sealing cements and compounds

Apiezon Products Ltd. supply many hydrocarbons for high-vacuum work in addition to the diffusion pump oils. These include a viscous low-vapour pressure oil Apiezon J, a very viscous oil Apiezon K, greases L, M, and N for use in conical ground joints and taps, and a tap grease T with a low temperature coefficient of viscosity useful for joints which may be raised above room temperature; also a sealing compound and waxes. Silicone tap greases are also widely used.

The Apiezon sealing compound Q is a graphite-grease mixture with the consistency of plasticine which is very useful for temporary vacuum seals. Apiezon W, W100, and W40 are black waxes of low vapour pressure which flow easily onto a solid surface when molten and melt respectively at about 100°, 80°, and 45 °C. Other common waxes which can be used for making vacuumtight joints are shellac, beeswax-rosin mixture (m.p. 57 °C), de Khotinsky cement (shellac and wood tar mixture, m.p. 140 °C), and Picein (black wax, melting at 80-100 °C depending on the variety used). Of these waxes, the Apiezon W series are very easy to use but are somewhat brittle and dissolve readily in a number of organic solvents. De Khotinsky wax is available in hard, medium, and soft grades (e.g. from Central Scientific Company) and is a little more difficult to apply than the W waxes but is less brittle and is not affected by many common organic liquids, including butyl phthalate.

These sealing compounds are not of much use in cementing materials which are to be cooled to low temperature, as they become brittle and tend to flake. For securing or thermally anchoring electrical wires to solid surfaces, some liquid cements—particularly those which can be cured by baking—provide a method of attachment which withstands repeated cooling quite well; bakelite varnish, Formel varnish, GE7031, and glyptal lacquer may all be dried and hardened at a temperature of

120-140 °C and used for this purpose. Nail polish is also a useful cement for anchoring wires providing they are not subject to appreciable mechanical stress; it withstands low temperatures quite well.

The most satisfactory materials for making seals between metals (apart from solder) or between metal and non-metals which can be cooled down to the lowest temperatures are the epoxy resins. These are made in various forms by CIBA (Araldite), Shell Chemical Company (Epikote and Epon), and Dow Chemical Company. They are also distributed by many other firms (see Appendix), often with the addition of fillers to reduce the expansion coefficient; examples are Stycast (Emerson and Cuming Inc.), Scotchcast (3M Company), Torr Seal (Varian Associates), and Epibond (Furane Plastics). These epoxy resins may be available (i) in solid or liquid form which cures when heated to 180-200 °C for a specified time (~1 h for Araldite Type I), or (ii) as liquid to which a hardener is added before use, after which the resin cures and hardens at room temperature in a few hours; in some cases the hardening is accelerated and the strength is improved by heating to ~100 °C for an hour or so.

These resins will not provide strong vacuum-tight seals between solids at low temperatures if the resin has a very much larger expansion coefficient than the solid and the bond between resin and solid is poor. As mentioned, fillers such as powdered alumina may be added to reduce the expansion coefficient; also the bond can be improved by cleaning and suitably treating the surface.

In the writer's experience many epoxy resins bond strongly to aluminium and stainless steel but bond less strongly to copper and brass. Mylar, nylon, and polythene have all been bonded with epoxy resin but surface treatment is important; rubbing the surface of Mylar with a fine abrasive helps and nylon can be cleaned with a 50 per cent nitric-acid solution. Hickman *et al.* (1959) Mehr and McLaughlin (1963), and Collins, Mayer, and Travis (1967) have each described bonding of Mylar with epoxy resin.

Balain and Bergeron (1959) have reported the use of epoxy resin for sealing of electrical leads through $\frac{1}{8}$ -in copper tubes using a Stycast epoxy which has an expansion coefficient similar to copper at room temperature. This seal was leak-tight at helium temperatures.

Wheatley (1964) has described a nylon-epoxy-copper junction in which Epibond 100A provides an intermediate tubular junction-piece between a nylon tube and a copper tube, both the latter tubes being 'feathered' (like a Housekeeper seal) where they join to the epoxy. The excess epoxy is machined away after curing and the join is reported to be leak-tight in liquid helium II.

Anderson (1968) has also described a stycast-copper electrical leadthrough which has a high success rate as far as vacuum tightness is concerned (see also Lounasmaa 1974, p. 9, for a similar design). He separates the electrical leads and feathers and cleans the copper tube carefully. A rather similar seal is used by the writer and his colleagues (see Fig. 10.4) and is now made in a demountable form. The upper or 'seal' section can be removed from the cryostat by means of the indium O-ring joint. The other important features in ensuring 100 per cent vacuum-tightness seem to be in having individual holes for the leads so that they do not bunch together and a thin copper wall, well cleaned with nitric acid and water. When casting the epoxy resin around the copper and the leads, a split Teflon mould is used as a 'former'. During curing, the seal is warmed slightly by an electric lamp as this helps the epoxy to flow more easily among the wires before setting.

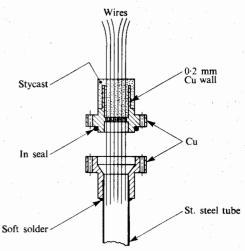


Fig. 10.4. Stycast epoxy-copper electrical leadthrough, showing indium seal for demounting, and individual holes in the copper for leads (after C. Andrikidis, private communication).

Demountable vacuum seals

For many years the most common vacuum seal used by the low-temperature physicist was Wood's metal or a similar low-melting alloy. These are still useful, particularly where space is limited, but they require acid flux and this produces corrosion problems. Now joints sealed with a gasket of ductile metal (or sometimes a plastic) have become widely used, just as they have at moderately high temperatures for bakable vacuum systems. Wexler, Corak, and Cunningham (1950) first described a seal made between metal surfaces with a gold O-ring of 0·05-cm diam. wire; their tests showed that the seal remained vacuum-tight at temperatures down to and below the λ -point of liquid helium.

Since then many other metals have been used, including copper, silver, aluminium, tin, lead, and indium. Of these indium has proved most popular as less pressure is required to make it flow and seal, and the O-ring can be welded very easily from wire by simply pressing the two ends of a piece together. Wire 1-mm diam. is frequently used and can be placed as in Fig. 10.5a (after Seki 1959) or in a shallow groove (Fig. 10.5b) (after Fraser 1962), or simply between two surfaces which have been ground to fit well together; Fig. 10.5c illustrates this latter construction

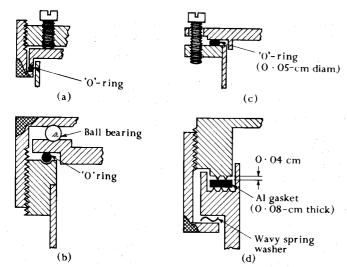


Fig. 10.5

used by the writer and his colleagues. In all these cases sufficient tension, compression or spring-loading on the screws is needed to ensure a residual compression on the indium after cooling.

A typical cryostat with this indium seal was illustrated in Fig. 7.7 (p. 184). This had eight Allen screws spaced around the 70 mm diam. flange to provide sealing pressure. In one such cryostat brass was used for both the 'mating' surfaces, i.e. for the plate and flange; this could be cooled quickly in liquid nitrogen without showing a vacuum leak. Another cryostat has dissimilar metals, namely a brass plate above a stainless steel flange. If the combination is cooled carefully, by slowly raising a dewar of liquid nitrogen over a period of 30 minutes, the indium seal always remains vacuum-tight but if cooled suddenly it always leaks due to differential contraction affecting the seal.

Most of the harder metals require more local pressure than exists in (c) in order to effect a good seal, although we have found tin wire of «0·1-cm diam. will seal quite well in this arrangement. Aluminium gaskets can be sealed with the tooth-like arrangement shown in (d) (after Atoji 1966).

Seals between smooth flat surfaces can also be made with a thin layer of Loctite AV, a thread sealant which remains soft (at room temperature) so the seal can be easily broken when necessary. Reeber (1961) and Ashworth and Steeple (1965) have described these. Thorough degreasing or ultrasonic cleaning of the metal surface helps to give a more reliable seal; the seal should be left for an hour or two to harden a little after the initial tightening of the screws and then retightened before cooling. Thin polythene gaskets ($\leq 0.1 \text{ mm}$ thick) lightly greased with silicone grease can also be used in joints like that in Fig. 10.5c; sometimes they are thoroughly leak-tight in liquid helium but on other occasions they may show a small leak.

We have tried thin Teflon sheet in these seals but with only partial success. Edwards, Budge, and Hauptli (1977) describe the use of a thin-film polymide gasket for the whole range from 1 to 550 K, and Gylling et al. (1977) have successfully used an 'expanded' form of Teflon in a ring seal, designed so that contraction on cooling did not disturb the vacuum joint. With sufficient ingenuity differential contraction can be made to help the sealing process and not destroy it. A good example is the 'Schumacher' seal in which small metal tubes in a cryostat are joined by a

plastic (PVC) sleeve which contracts onto the metal on cooling (G. Schumacher private communication).

Other commercial preparations which remain pliable after evaporation of their solvent and are often useful for low-temperature seals include RTV-102 silicone rubber (General Electric Company, New York), Loctite (American Sealant Company, Conn.), and Goo (W. K. Walters, Wisc.).

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CHAPTER XI

PHYSICAL PROPERTIES OF SOLIDS

1. Heat capacity of solids

Introduction

The specific heat at constant volume of most solids may be represented tolerably well by the Debye function

$$C_{v} = 9Nk(T/\theta)^{3} \int_{0}^{\theta/T} \frac{x^{4}}{(e^{x} - 1)(1 - e^{-x})} dx$$
$$= 9R(T/\theta)^{3} J_{4}(\theta/T).$$

The derivation of such a formula is based on the elastic continuum model of a solid for which the number of modes of vibration in a frequency interval ν , $\nu + d\nu$ is given by

$$f(\nu) d\nu = bV\nu^2 d\nu = 4\pi \left(\frac{1}{v_1^3} + \frac{2}{v_2^3}\right)V\nu^2 d\nu;$$

V is the volume of the solid and v_1 , v_t are the wave propagation velocities for longitudinal and transverse waves respectively. The maximum frequency ν_m is given by the normalizing condition that in a volume V containing N atoms, there are only 3N modes:

$$3N = \int_0^{\nu_{\rm m}} f(\nu) \, d\nu = \frac{1}{3} b V \nu_{\rm m}^3$$

and the Debye characteristic temperature

$$\theta_{\rm D} = h \nu_{\rm m}/k,$$

In Table D (in the Appendix) are given values of $C_{\rm v}$ computed from Debye's expression for various values of θ/T .† Note that for $T > \theta_{\rm D}$, $C_{\rm v} \to 3R = 24.94$ J/mol K, and for $T \le \theta_{\rm D}/20$, $C_{\rm v} = 1943.8 (T/\theta_{\rm D})^3$ J/mol K.

[†] These values are taken from the Landolt-Bornstein physical tables. A more complete tabulation of the Debye J_4 integral and J_3 , J_5 , etc., integrals is given by Rogers and Powell (1958).

As might be expected, experimental values for C_v often depart quite considerably from those given by the Debye model, a large part of the discrepancy arising from the fact that the real frequency spectrum in the atomic lattice is very different from the $f(\nu) \propto \nu^2$ spectrum assumed by Debye (see for example Rosenberg 1963 and Gopal 1966).

What is perhaps surprising is that the discrepancies in most solids are so small. Usually they are represented by deriving an appropriate value of $\theta_{\rm D}$ from each experimental value of $C_{\rm v}$ (using the tabulated Debye function) and drawing a graph of $\theta_{\rm D}$ versus T; in such a graph the Debye theory would demand complete constancy of $\theta_{\rm D}$ from $T=0~{\rm K}$ upwards. Figure 11.1 shows experimental $\theta_{\rm D}$ plots for a number of solids.

At high temperatures, that is at temperatures comparable with $\theta_{\rm D}$, the value of $\theta_{\rm D}$ calculated from experimental data appears to be fairly constant for any particular solid, and the major variations occur at temperatures below about $\theta_{\rm D}/5$. For purposes of cryogenic design it is usually sufficient to assume the validity of the Debye approximation and calculate for any solid in question the specific heat on the basis of the values of $\theta_{\rm D}$ listed in Table E (in the Appendix) and the tabulated Debye function in Table D. The values of $\theta_{\rm D}$ shown for the various elements are calculated from specific heat data obtained in the region between $\theta_{\rm D}/2$ and $\theta_{\rm D}$. They are not the limiting values obtained from low-temperature specific heats; the latter are usually signified by $\theta_{\rm 0}$ and may be found in Gopal (1966) and compilations listed below (p. 278).

The value of heat capacity at constant volume, C_v , is related to the quantity which is usually measured, namely the heat capacity at constant pressure, C_p , by the thermodynamic relation

$$C_{\rm p} - C_{\rm v} = VT\beta^2/\chi$$
;

here β is the volume expansion coefficient and χ is the compressibility. It follows to a first approximation that

$$C_{\rm p} - C_{\rm v} = AC_{\rm v}^2 T,$$

where the constant A may be calculated at one temperature. The difference $C_p - C_v$ is negligible at low temperatures but usually becomes of the order of 1 per cent at temperatures in the vicinity of $\frac{1}{2}\theta_D$.

In metals the free electrons contribute to the specific heat, their contribution being proportional to the absolute temperature. The electronic specific heat is usually expressed as

$$C_{\rm e} = \gamma T$$

where γ varies from c. $0.6\,\mathrm{mJ/mol}~\mathrm{K^2}$ for Cu, Ag, and Au to nearly $10\,\mathrm{mJ/mol}~\mathrm{K^2}$ for some transition metals. C_e becomes important at very low temperatures, being comparable with the lattice specific heat at $\sim 5\,\mathrm{K}$ for many metals; it should also

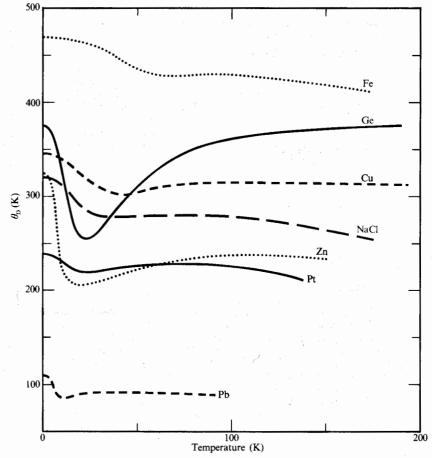


Fig. 11.1. Variation of θ_D with temperature for some solids.

become important again at very high temperatures, e.g. $T = 1000 \, \text{K}$ or more. However, for cryogenic design the electronic heat capacity is not usually of major importance.

Data

Useful compilations of data on heat capacity are Corruccini and Gniewek (1960), *The thermophysical properties of matter* (1970, Vols. 4, 5, and 6, Plenum Press, New York), and Landolt-Börnstein (1961, Vol. II, Part 4, Springer-Verlag, Berlin).

Among technical materials whose heat capacity is important in calorimetry, the following are included in the tables compiled by Corruccini and Gniewek (1–300 K):

- (i) common metallic elements;
- (ii) alloys such as constantan, monel, Wood's metal;
- (iii) supporting materials like graphite, Pyrex, silica glass, Teflon; and
- (iv) cements including Glyptal, Araldite type I, Bakelite varnish.

Subsequently further data have been published for a number of materials including:

(a) Silica and sodium silicate glasses:

Flubacher et al. (1959), 2-20 K;

Krüger (1972), 2-100 K;

White, Birch, and Manghnani (1977), 1-20 K;

Stephens (1973), 0.05-1 K (also a borosilicate glass).

From 1 to 4 K, $C \approx (1.5 \pm 0.5)T + (2.5 \pm 0.5)T^3 \mu J/g$ K.

(b) Nylon:

Brewer et al. (1966), 1-4 K;

Reese and Tucker (1965), 1-4 K (also measured Teflon and polyethylene).

From 1 to 4 K, $C \approx (20 \pm 2) T^3 \mu J/g K$.

(c) Araldite (epoxy) resin: Brewer et al. (1966), 1–4 K. $C \approx 18 T^3 \mu \text{J/g K}$.

(d) Eccobond 56C epoxy (contains 85 wt.% Ag): Berton et al. (1977), 1.3-300 K. Below 4 K, $C \approx 8T^3 \mu J/g$ K. (e) GE7031 Cement: Phillips (1959), 1.5-4 K; Cude and Finegold (1971), 4-18 K; Stephens (1975), 0.2-1 K. From 1-4 K, $C \approx (35\pm 10)T^3 \mu J/g$ K.

(f) Apiezon 'N':

Wun and Phillips (1975), 0·4–20 K; Bevolo (1974), 1–50 K; Bunting, Ashworth, and Steeple (1969), 80–320 K. From 1–4 K, $C = (29 \pm 3)T^3 \mu J/g$ K.

(g) Apiezon 'T':

Westrum et al. (1967), 1-300 K. From 1-4 K, $C \approx 30T^3 \mu J/g$ K.

(h) Soft solders (Pb–Sn alloys containing 40–60 per cent Pb):
 de Nobel and du Chatenier (1963), 1–20 K;
 Zeigler and Mullins (1964), 20–300 K.
 Approximate values at 2 and 4 K respectively are 60 μJ/g K and 500 μJ/g K.

(i) Stainless steel (17.5% Cr, 10.1% Ni, 0.86% Mn): du Chatenier, Boerstoel, and de Nobel (1965), 1–30 K and 60–90 K. Below 10 K, $C \approx 460T + 0.38T^3 \mu J/g$ K.

(j) Constantan and manganin:

Ho, O'Neal, and Phillips (1962), 0·2-4 K, observed a large hyperfine contribution proportional to T^{-2} which predominates below 0·5 K.

 $C \approx 2.8 \, T^{-2} + 205 \, T^3 \, \mu \text{J/g K}$ (constantan below $0.3 \, \text{K}$) $C \approx 11.5 \, T^{-2} + 60 \, T + 2.9 \, T^3 \, \mu \text{J/g K}$ (manganin below $2 \, \text{K}$).

(k) Nichrome:

Stephens (1975), 0.05-0.2 K, found T^{-2} term similar in magnitude to constantan and pointed out that Pt+9% W alloy (Baker Platinum Division) is a more appropriate resistance wire for use below 1 K in calorimetry. Pt+10% Rh should also be useful and is commercially available.

(l) Machineable-glass ceramic (Corning): Roth and Anderson (1976), $0\cdot06-2$ K; Lawless (1975), 2-20 K. Near 4 K, $C\approx3T^3$ μ J/g K but C decreases less rapidly than T^3 below 2 K.

(m) Allen-Bradley carbon resistors:

Alterovitz and Gershenon (1974), 0·3-4 K, measured a 116 Ω bare carbon resistor and concluded that its heat capacity was similar to graphite in this range, viz. $C \sim 1 \cdot 1 T + 2 \cdot 3 T^3 \, \mu \text{J/g K}$.

Other measurements on Allen-Bradley resistors (Keesom and Seidel 1959; see also Stephens 1973) have given values of *C* an order of magnitude higher than this.

It is important to realize that the heat capacities per gram of the resins, cements, and plastics mentioned above are far greater than that of copper at low temperatures. For example, at 2 K, $C \approx 28 \,\mu\text{J/g}$ K for copper compared with a 300 μ J/g K for GE7031. Thus cements used in the assembly of a calorimeter should be of minimum quantity and carefully weighed. Also the large hyperfine contribution below 1 K in manganin, nichrome, and constantan resistance wires should be recognized.

Frequently in cryogenic design we also need to know the 'integrated' heat capacity or enthalpy of a component in order to calculate the quantity of refrigerant needed to cool it. The enthalpy is given by

$$H(T) = U + PV = \int_0^T C_p dT.$$

Since $C_p - C_v$ is not a unique function of T/θ but depends on the expansion coefficient and compressibility, no general table of H as a function of T/θ can be compiled. However at temperatures below θ , C_v is a fair approximation to C_p and therefore $U = \int C_v \, \mathrm{d}T$ will approximate the heat content for most practical purposes. In Table 11.1 are given values of $(U-U_0)/T$ as a function of θ/T based on the Debye function and taken from Landolt-Börnstein tables. Apart from inadequacies of the Debye model, errors will also occur if there are significant contributions to C from magnetic or other interactions.

As an example consider cooling from 90 to 4 K one mole of copper (63.6 g) for which $\theta_D \approx 310 \text{ K}$.

At 90 K,

$$\theta/T = 3.44$$

therefore

$$U - U_0 = 90 \times 5.5 = 495 \text{ J/mol}.$$

Values of $\frac{U-U_0}{T} = \frac{1}{T} \int_0^T C_v dT$ in J/mol K, from the Debye model

θ/Τ	$\frac{U-U_0}{T}$	θ/T	$\frac{U-U_0}{T}$	θ/Τ	$\frac{U-U_0}{T}$
0.2	23.10	2.2	10.08	6.0	1.93
0.4	21.38	2.4	9.23	6.5	1.59
0.6	19.76	2.6	8.44	7.0	1.31
0.8	18.24	2.8	7.73	7.5	1.09
1.0	16.81	3.0	7.07	8.0	0.912
1.2	15.47	3.5	5.66	9.0	0.653
1.4	14.23	4.0	4.53	10.0	0.481
1.6	13.07	4.5	3.64	11.0	0.364
1.8	11.99	5.0	2.93	12.0	0.281
2.0	11.00	5.5	2.37	15.0	0.144

At 4 K,

$$\theta/T = 78$$
.

therefore

$$U-U_0\approx 0.$$

Hence

$$U_{90} - U_4 = 495 \text{ J/mol}.$$

About 190 ml of liquid helium would be needed to cool 63.6 g of copper from 90 to 4 K, using only the latent heat of vaporization.

2. Thermal expansion

Introduction

For most solids the volume coefficient of thermal expansion $\beta=3\alpha$ varies with temperature in much the same way as does the heat capacity. At temperatures $T \ge \theta_D$, β is fairly constant and as $T \to 0$, $\beta \to 0$ with similar temperature dependence to C_v . The thermal vibrations usually contribute the major part of β (and C_v) at all but the lowest temperatures.

Grüneisen first observed that β/C_v was essentially constant at

temperatures $T > \theta/5$ and expressed the ratio in the form

$$\frac{\beta}{C_{\rm v}} = \gamma \frac{\chi_{\rm T}}{V},$$

where γ is a dimensionless parameter, known as the Grüneisen or anharmonicity parameter. Alternatively we may write

$$\frac{\beta}{C_{p}} = \gamma \frac{\chi_{s}}{V}.$$

 $\chi_{\rm T}$ and $\chi_{\rm s}$ are respectively the isothermal and adiabatic values of the compressibility, usually determined from the elastic constant; V is the molar volume. Assuming that lattice vibrations are the major source of energy in a solid, then γ can be shown to be the weighted mean of the volume dependences of the individual modes of vibration of frequency $\nu_{\rm i}$, i.e. of

$$\gamma_i = -\frac{V}{\nu_i} \frac{\mathrm{d}\nu_i}{\mathrm{d}V} \,.$$

This is $\gamma = \sum \gamma_i C_i / \sum C_i$ where the weighting factor C_i is the contribution of the *i*th mode to the heat capacity.

Being an average over the whole spectrum of excited modes, γ will not necessarily have the same value at low temperatures (when only low frequencies are excited) as at high temperatures (when all modes are excited). At the lowest temperatures, $\gamma(T)$ has a value γ_0 related to the limiting value of $\theta_D(T)$ by

$$\gamma_0 = -\frac{V}{\theta_0} \frac{\mathrm{d}\theta_0}{\mathrm{d}V}.$$

Fuller discussions of this are given by Barron (1957), the review of Collins and White (1964), and by Yates (1972).

Some knowledge of the thermal expansion or contraction is necessary in cryogenic design, whether it be for large-scale storage tanks, transfer tubes, vacuum seals, or for the components of a dilution refrigerator. The change in length with temperature between 300 K and 4 K amounts to nearly 4 mm per metre for a brass tube and is between 10 and 20 mm per metre for most plastics and resins. Clearly these changes can cause serious stresses and mechanical failure if not taken into account. This is very evident in vacuum seals involving metals and plastics or with

coaxial tubes which are of different materials or are at different temperatures.

Data

Data on the linear coefficient of expansion at low temperature and on the integrated length change on cooling from 293 K are given in the NBS compilation by Corruccini and Gniewek (1961) and in Volumes 12 and 13 of *Thermophysical properties of matter* (1976–7, Plenum Press, New York). Some other useful sources are as follows.

- (i) Hamilton, Greene and, Davidson (1968): epoxy resins including Stycast (Emerson and Cuming Inc., Mass.), Epon (Shell Chemical Company) with various amounts of silica filling. $\Delta l/l$ (300–4 K) ranges from 4 to 12×10^{-3} with some filled epoxies matching quite well to 18/8 stainless steel, brass and aluminium.
- (ii) Seligman and Sarwinski (1972): $\Delta l/l$ from 295 to 4 K for epoxies including Epibond 100A (Furane Plastics Inc.) for which $\Delta l/l = 9.6 \times 10^{-3}$, solders including 60 Pb-40 Sn (5.6×10^{-3}) , and AGOT graphite (0.6×10^{-3}) .
- (iii) Mackowski *et al.* (1976): epoxy resins including Stycast, Scotchcast (3M Company, Minn.) and Torr Seal (Varian Associates, Calif.) with $\Delta l/l$ ranging from 4.5 to 15× 10^{-3} .
- (iv) White (1976) and White, Birch, and Manghnani (1977): $\alpha(T)$ for machineable glass-ceramic (Corning), ultra-low expansion ceramic-glasses, vitreous silica and sodium-silicate glasses from 2–30 K and 55–90 K.
- (v) Clark (1968): Al-, Ni-, Cu-, and Fe-based alloys from 20 to 293 K; representative values of $\Delta l/l$ are 4.2×10^{-3} for Al 5083 (Al+4.75% Mg, 0.6% Mn), 2.4×10^{-3} for Hastelloy X, 2.8 and 1.9×10^{-3} respectively for annealed and precipitation hardened AISI 633 (Fe+16% Cr, 4.5% Ni, 2.8% Mo) and 0.4×10^{-3} for Invar.
- (vi) Kroeger and Swenson (1977) for pure Cu and Al and Lyon *et al.* (1977) for Si give $\alpha(T)$ from 5 to 320 K with uncertainty of <0.2 per cent (or $\sim 0.2 \times 10^{-8}$ /K) over much of this range; these constitute useful reference standards.

Table E in the Appendix gives values of α at 295 K for most of the solid elements. Some, such as bismuth, titanium, zinc, etc., are anisotropic in elastic and expansion properties. For those which have axial symmetry (hexagonal, tetragonal, or rhombohedral) there are two principal coefficients, α_{\parallel} parallel to the symmetry axis and α_{\perp} , normal to the axis. The value of α listed in the Table is the average given by $\beta/3 = (2\alpha_{\perp} + \alpha_{\parallel})/3$. The observed α for a polycrystalline sample without preferred orientation should approximate to this average.

Table F lists experimental values of the integrated contraction per unit length in cooling from 293 K to a temperature T = 200, 150, 100 K, etc., for commonly used materials.

When experimental values are not readily available at low temperatures, an estimate can be made by assuming that the Grüneisen γ or the ratio α/C is constant and using the temperature dependence of the heat capacity as a guide to $\alpha(T)$. It is clear from Table F that most of the contraction on cooling occurs above 50 or 60 K, i.e. in the region above $\theta_D/5$ in which γ and θ_D are fairly constant so that the Debye function can give a realiable guide to $C_v(T)$ and to $\alpha(T)$.

As an example, for copper, $\alpha = 16.7 \times 10^{-6} / \text{K}$ and $C_v \approx 24 \text{ J/mol K}$ at 295 K.

To find α at 60 K, assume

$$\frac{\alpha(60)}{16.7\times10^{-6}} = \frac{C_{v}(60)}{24}.$$

Using $\theta_D = 310 \text{ K}$, $\theta/T = 5.2 \text{ at } 60 \text{ K}$, Debye function in Table D gives $C_v = 8.6 \text{ J/mol K}$

$$\alpha = 6.0 \times 10^{-6} / \text{K}$$

cf. experimental value is 5.5×10^{-6} /K.

3. Electrical resistivity

Introduction

In an element which is a metallic conductor, some electrons are free or quasi-free so that they can be accelerated by the action of an applied electric field. The conductivity remains finite due to the influence of various electron scattering processes, chiefly thermal vibrations of the metallic ions in the crystal lattice and the chemical or physical impurities present in the lattice. If these processes are such as to produce a finite mean free time τ or mean free path l for the electrons, we should expect that the electrical conductivity

$$\sigma = \frac{Ne^2\tau}{m} = \frac{Ne^2l}{mv},$$

where N is the number of conduction electrons per unit volume, e the electronic charge, m the electronic mass, and v is the average velocity of the electrons at the top of the band, i.e. near the Fermi surface. The electrons involved are only those within a region of the order of the thermal energy kT from the Fermi surface; their energy at the surface is 1-7 eV (equivalent to thermal energy at ≥ 20000 K), therefore the velocity v at ordinary temperatures is practically temperature independent; also N, e, and m are constants. Calculation of the electron-free path is difficult although the temperature dependence can be estimated at high temperatures $(T > \theta)$ or at low temperatures $(T \ll \theta)$. When $T > \theta$, the wave number **k** of the electron and wave number **q** of the lattice wave or phonon with which it interacts are comparable in magnitude. Therefore the change in direction or momentum of an electron at a collision with a vibrating ion is considerable and l is simply the average distance an electron travels between collisions. When $T \ll \theta$, **q** is very small and collisions with phonons become rare and less important since static imperfections (chemical impurity atom, dislocation, grain boundary) are still present and cause elastic scattering.

So that:

(i) For $T > \theta$, resistivity is due chiefly to scattering by phonons, which is denoted by ρ_i .

Now $\rho_i \propto l^{-1}$.

 \propto mean square amplitude of vibration or ions $\propto T/Mk\theta^2$ (M = atomic weight).

(ii) For $T \ll \theta$, impurities dominate and

$$\rho_i \rightarrow 0$$

and

$$ho \simeq
ho_{\rm r}$$

therefore $\rho \simeq \text{constant}$, since l = constant.

In practice we may expect that at moderately high temperatures the electrical resistance of a fairly pure metallic element is due to thermal vibrations and that the resistivity ρ_i should be proportional to T. For elements in a non-magnetic state this holds to a first approximation. Change in the Fermi surface with temperature and thermal expansion do affect the linearity of $\rho_i(T)$, but for many cryogenic calculations it is sufficient to assume $\rho_i \propto T$ over a range from $T \sim \frac{1}{2}\theta$ up to a temperature approaching a phase change or the melting temperature. At temperatures sufficiently low that $\rho_r \gg \rho_i$, the resistance becomes sensibly constant unless a superconducting transition occurs; in this context the phrase 'sufficiently low' depends on the purity of the element. Elements such as Mg, Sn, and In may be readily obtained with a chemical purity exceeding 99.999 per cent and elements may have a residual resistivity ρ_r , 100 000 times smaller than their resistivity at room temperature; in such instances ρ . only becomes dominant for $t < \frac{1}{50}\theta$.

We have not discussed the behaviour of ρ_i at temperatures below the region $(T \ge \theta)$ where scattering is elastic. The direction of motion and the energy of an electron before and after a collision with a phonon are governed by the conservation laws:

 $\mathbf{k'} = \mathbf{k} + \mathbf{q}$ (conservation of wave number)

and $E' = E \pm h\nu$ (conservation of energy).

As $h\nu \sim kT$ and $E' \simeq E$ is the Fermi energy, the change in energy at a collision is small. However, at temperatures $T \sim \theta_D$, $|\mathbf{q}| \sim |\mathbf{k}|$ and the change in direction or momentum is large. As the temperature decreases, the wave number \mathbf{q} of the dominant lattice waves decreases, unlike the electron wave number \mathbf{k} which is sensibly constant. Since $h\nu \sim kT$, therefore $\mathbf{q} \propto T$ and it follows that to a first approximation the angle of deflexion of an electron by interaction with a lattice wave is given by

$$\phi \sim |\mathbf{q}|/|\mathbf{k}| \sim T/\theta$$
.

At temperatures low in comparison with θ_D , the density of phonons effective in scattering varies at T^2 (Dugdale 1977). The electron-phonon scattering matrix varies as T so that the probability of scattering of an electron should be proportional to T^3 but the angle ϕ may be so small as to make a single scattering a

very inefficient resistive process. If, indeed, a series of scatterings of an electron is required to deflect it from its 'conduction path' then the probability of its being scattered through a large angle in a series of random scattering processes will vary as $(T/\theta)^2$.

Hence

$$\rho_{\rm i} \propto T^3 (T/\theta)^2$$
$$\propto T^5.$$

A more general expression for the resistivity due to thermal scattering, which reduces to the T^5 -relation at low temperatures and to a T-dependence at normal temperatures, is that of Bloch and Grüneisen:

$$\rho \propto \frac{T^5}{\theta^6} \int_0^{\theta/T} \frac{x^5 dx}{(e^x - 1)(1 - e^{-x})}.$$

This should be valid for a simple free-electron model of a Debye solid in the absence of Umklapp processes. With suitable choice of characteristic temperature θ it can express the resistance-temperature relation tolerably well for some elements, without specifying the magnitude. Generally, however, θ (or θ_R) must be allowed to vary at least 20 or 30 per cent at lower temperatures to achieve agreement. This is not unlike the specific heat wherein departures from the Debye model may be represented by variations in θ_D of 10 to 30 per cent. Note that θ_R and θ_D are not necessarily the same: they represent different averages over the frequency spectrum, though naturally they are similar in magnitude.

Detailed accounts of the theroetical background may be found in Ziman (1960, 1964) or Dugdale (1977), Rosenberg (1963) etc.

Data on metallic elements

It is interesting to compare experimental values of the reduced resistivity ρ_i/ρ_θ at different reduced temperatures T/θ_D with the predictions of the Grüneisen-Bloch equation. Curve A in Fig. 11.2 is calculated from

$$\frac{\rho_{i}}{\rho_{\theta}} = \left(\frac{T}{\theta}\right)^{5} \int_{0}^{\theta/T} \frac{x^{5} dx}{(e^{x} - 1)(1 - e^{-x})} / \int_{0}^{1} \frac{x^{5} dx}{(e^{x} - 1)(1 - e^{-x})}$$

$$= \left(\frac{T}{\theta}\right)^{5} J_{5}(\theta/T) / J_{5}(1)$$

$$= 4 \cdot 226(T/\theta)^{5} J_{5}(\theta/T).$$

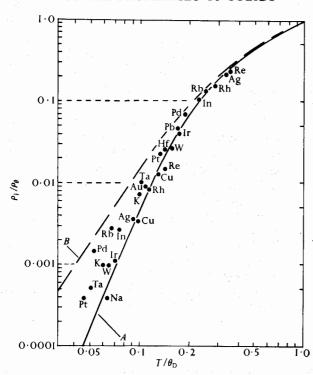


Fig. 11.2. Reduced electrical resistivity (o_i/ρ_0) as a function of reduced temperature (T/θ_D) .

The second theoretical curve (B in Fig. 11.2) is based on a $J_3(\theta/T)$ function and is the type of functional relation between electrical resistance and temperature which Wilson (1938) has suggested might be valid for some transition elements, at least over a restricted temperature range. Wilson deduced a resistive contribution due to s-d scattering to be given by

$$\rho_{sd} = b(T/\theta)^3 \int_{\theta_E/T}^{\theta/T} \frac{x^3 dx}{(e^x - 1)(1 - e^{-x})}.$$

We may derive a relation $\rho_i/\rho_\theta = f(\theta/T)$ based on the dubious assumptions that

$$\rho_i \simeq \rho_{sd}$$

and

$$\rho_{sd} = b (T/\theta)^3 \int_0^{\theta/T} \frac{x^3 dx}{(e^x - 1)(1 - e^{-x})}.$$

Hence

$$\frac{\rho_i}{\rho_{\theta}} = (T/\theta)^3 J_3(\theta/T)/J_3(1)$$
$$= 2 \cdot 084 \left(\frac{T}{\theta}\right)^3 J_3(\theta/T).$$

The experimental values of ρ_i/ρ_θ mostly lie in the region between curves A and B (Fig. 11.2) and at the lowest temperatures have temperature dependences between $T^3(B)$ and $T^5(A)$. In some transition elements such as Pt there is strong evidence for a T^2 term at helium temperatures which is usually identified with electron–electron interactions.

The points in Fig. 11.2 have been plotted with values of $\theta = \theta_D$ taken from Table E and resistivities given in the review by Gerritsen (1956), White and Woods (1959), Meaden (1965) and Landolt-Börnstein, Vol. 2, Part 6 (1959, Springer-Verlag). The values given in Table G for ρ_i of Ag, Al, Au, etc., are from the same sources. Numerical tabulations of the J_3 and J_5 integrals may be found in Rogers and Powell (1958) and in abbreviated form in Table D of the Appendix.

Tables D and G give a guide to how ρ_i varies with T and therefore can be used to make an estimate of the electrical resistance of a rod or wire of uncertain purity and resistivity. The procedure is to measure the electrical resistance R at room temperature and when dipped in a dewar of liquid helium. Then knowing R_{295} and $R_4 = R_r$ we can obtain R_i at room temperature (= $R_{295} - R_r$), by assuming Matthiessen's rule. If desired the shape factor $l/A = R/\rho$ can be calculated using a value of $\rho(295 \text{ K})$ from Table E. Then at any other intermediate temperature, T,

$$\rho_{\rm i} = \rho_{\rm i}(T) + \rho_{\rm r}$$

290 or

$$R = R_{i}(T) + R_{r},$$

where $R_i(T)$ or $\rho_i(T)$ is estimated using $\theta = \theta_D$ (Table E) from the Grüneisen-Bloch equation or from values of ρ_i in Table G.

Example

Given a rod of copper, it is found that

$$R_{295} = 0.016 \Omega$$
, $R_4 = 0.000 27 \Omega$,

and it is required to know R at 110 K. First,

$$R_i(295) = 0.0160_0 - 0.00027 = 0.0157_3 \Omega.$$

Assuming

$$\rho_{\rm i}/\rho_{\theta} = (T/\theta)^5 J_5(\theta/T) \div J_5(1)$$

we have

$$\frac{\rho_{i}(110)}{\rho_{i}(295)} = \frac{\rho_{i}(110)}{\rho_{i}(\theta)} \frac{\rho_{i}(\theta)}{\rho_{i}(295)}.$$

For $T/\theta = 110/310$ Table D gives $\rho_i(110)/\rho_i(\theta) = 0.249$ and for $T/\theta = 295/310$ gives $\rho_i(295)/\rho_i(310) = 0.945$; hence

$$\frac{\rho_{\rm i}(110)}{\rho_{\rm i}(295)} = 0.263$$

and

$$R_i(110) = 0.263 \times 0.016 = 0.00414 \Omega$$
.

Now

$$R = R_i(110) + R_4$$

\$\sim 0.0044 \Omega\$ at 100 K.

Metallic alloys

For a disordered solid-solution of an impurity element in a solvent metal, the impurity resistance produced by a concentration c of solute atoms is described by Nordheim's rule (e.g. Gerritsen 1956, Meaden 1965)

$$\rho_{\rm r} = ac(1-c).$$

In most alloys, excepting those very dilute alloys which may be regarded as slightly impure metallic elements, the residual or impurity resistance is relatively high. In many important alloys such as the stainless steels, monel, cupro-nickel, etc., ρ_r is much greater than the resistivity due to thermal vibrations and hence $\rho \simeq \rho_r$ is practically independent of temperature. As we mentioned earlier (§ 4.7) some alloys (manganin and constantan) show an anomalous decrease in resistance as the temperature falls below 100 K, but the total change in resistance in cooling from 300 to 4 K is still less than 20 per cent of the total.

Table H (Appendix) gives values of electrical resistivity at 295 K, 90 or 77 K, and 4 K for some of the alloys used in cryogenic equipment. More extensive tables and original references are in Meaden (1965, p. 119) and Landolt-Börnstein, Vol. 2, Part 6 (1959, Springer-Verlag). Clark, Childs, and Wallace (1970) give values at 4, 20, 76, 192, and 273 K for about 80 engineering alloys based on aluminium, nickel, copper, titanium, and iron.

4. Thermal conductivity

Electronic conduction

In the metallic elements such as Cu, Al, Mg which are good electrical conductors, the electronic thermal conductivity λ_e is much larger than the lattice conductivity λ_g at all temperatures. The same scattering processes limit λ_e as limit the electrical conductivity. We may adopt a simple kinetic model for which

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 $\lambda_e = C_e v l/3$, where the electronic specific heat C_e is proportional to T and v is practically constant.

Then at temperatures for which the mean free path l is the same for electrical or thermal transport we expect theoretically that

$$\rho \lambda_{e} = \frac{\lambda_{e}}{\sigma} = \frac{\pi^{2}}{3} \left(\frac{k}{e}\right)^{2} T = LT.$$

The Lorenz constant L has the value $2.45 \times 10^{-8} \text{ V}^2/\text{K}^2$.

At high temperatures $(T \ge \theta_D)$, large angle elastic scattering of the electrons by thermal vibrations occurs, and we expect the effective mean free path l to vary as T^{-1} and to have the same magnitude for thermal or electrical transport; hence just as we expect $\rho \propto T$, so should λ_e be constant and

$$\frac{\rho \lambda_{\rm e}}{T} = L \qquad (T \geqslant \theta_{\rm D}).$$

Experimental data on good conductors at temperatures $T \ge \theta_D$ show that this Wiedemann-Franz law is obeyed within a few per cent (see for example Laubitz 1969).

At sufficiently low temperatures where impurity scattering is dominant, the mean free path should be constant so that $\rho \simeq$ constant, and $\lambda \propto T$. Measurement at liquid-helium temperatures on a large number of metallic elements have confirmed that

$$\frac{\rho_{\rm r}\lambda_{\rm r}}{T} = \frac{\rho_{\rm r}}{W_{\rm r}T} = 2.45 \times 10^{-8} \text{ V}^2/\text{K}^2.$$

within the limits of experimental accuracy which are about ± 1 per cent; here λ_r and $W_r (=1/\lambda_r)$ are respectively the electronic thermal conductivity and electronic thermal resistivity limited by static impurities.

At all temperatures we expect the thermal resistivity due to impurities W_r , and that due to thermal vibrations W_i , to be additive, at least to a first approximation; that is, the thermal equivalent of Matthiessen's rule should be approximately correct:

$$1/\lambda = W = W_{\rm r} + W_{\rm i},$$

where

$$W_r = A/T$$
 (A is a constant)

$$W_i = W_i(T)$$

= W_{∞} , a constant, for $T \ge \theta_D$.

The theoretical solutions of the transport equations for $W_i(T)$ and $\rho_i(T)$ in real metals are difficult as the energy spectra for both the phonons and for the electrons are complex and so is the scattering probability. Discussions by Ziman (1960), Klemens (1956, 1969), Berman (1976), etc., show that agreement between experiment and the soluble theoretical models is not generally good. Fortunately one quasi-empirical equation seems to fit the data for $W_i(T)/W_{\infty}$ tolerably well as shown in Fig. 11.3. This

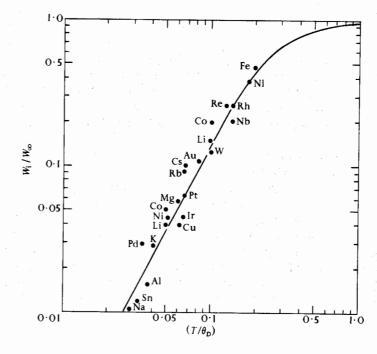


Fig. 11.3. Reduced thermal resistivity $(W_i W_\infty)$ as a function of reduced temperature (T/θ_D)

$$W_i/W_{\infty} = 2(T/\theta)^2 \int_0^{\theta/T} \frac{x^3 dx}{(e^x - 1)(1 - e^{-x})}.$$

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equation

$$W_i/W_\infty = 2(T/\theta)^2 \int_0^{\theta/T} \frac{x^3 dx}{(e^x - 1)(1 - e^{-x})}$$

was shown to fit experimental data on the alkali metals by MacDonald, White, and Woods (1956) and has proved useful in representing W_i for a number of metallic elements (see also White and Woods 1959). The experimental points in Fig. 11.3 are taken from Powell and Blanpied (1954), White and Woods (1959), etc. As mentioned in §3, the J_3 function for this equation is tabulated by Rogers and Powell (1958) and abbreviated in Table D of the Appendix.

This suggests that with a knowledge of the thermal resistivity of a metallic element at room temperature and at liquid-helium temperatures, both $W_i(T)$ and $W_r = A/T$ can be calculated approximately at any intermediate temperature; hence the electronic thermal conductivity, $\lambda_e = (W_i + W_r)^{-1}$, can be obtained. More simply, the Wiedemann–Franz law allows us to calculate an approximate value for W_∞ and a good value for $A = W_r T$ directly from electrical resistance measurements made at room temperature and at the temperature of liquid helium.

Lattice thermal conductivity

In insulators all the heat current is carried by lattice waves; in semiconductors and in semi-metals like bismuth, graphite, or antimony, lattice conductivity is usually dominant at low temperatures; while in many disordered alloys the lattice heat conductivity may be at least comparable with the electronic heat conductivity at low temperature so that $\lambda = \lambda_e + \lambda_g$. The temperature dependence of the lattice conductivity is more complex and therefore less predictable than that of the electronic conductivity; this arises from the variation in frequency or wavelength of the dominant lattice waves with temperature which results in a very different temperature dependence for scattering by the different classes of lattice imperfections.

At high temperatures the lattice conductivity λ_g , is chiefly limited by thermal vibrations, i.e. interaction between the waves (or phonons) themselves due to the anharmonic nature of the coupling between the vibrating atoms. If we denote this thermal

resistance by W_u , then it is dominant at temperatures $T \ge \theta_D$ except in highly disordered solids.

The effect of physical and chemical impurities on lattice waves is complicated because the important frequencies are temperature sensitive. As we should expect from physical intuition it is found that at very low temperatures, where only long waves are excited in the solid, planar irregularities scatter the waves much more effectively than do small point defects. As discussed by Ziman (1960), Klemens (1956, 1969), and Berman (1976), grain boundaries (resistivity $W_{\rm B}$), dislocations ($W_{\rm D}$), and impurity atoms or vacancies ($W_{\rm P}$) provide three distinct scattering processes in addition to the anharmonic interaction between lattice waves ($W_{\rm U}$).

At low temperatures, the heat capacity C varies approximately as T^3 therefore the T-dependence of these resistivities follows from dependence of mean-free path l upon frequency ν , assuming $\lambda \approx \frac{1}{3}$ (Cvl).

(i) grain boundaries: l_B is frequency independent

 $\therefore \lambda_{\mathbf{B}} = W_{\mathbf{B}}^{-1} \propto T^3.$

(ii) dislocations: $l_D \propto \nu^{-1} \propto T^{-1}$

 $\therefore \lambda_{D} = W_{D}^{-1} \propto T^{2}$

(iii) point defects: $l_P \propto \nu^{-4} \propto T^{-4}$ (Rayleigh scattering)

 $\therefore \lambda_P = W_P^{-1} \propto T^{-1}.$

In the case of boundary scattering, a reasonable estimate of the magnitude of $l_{\rm B}$ and $\lambda_{\rm B}$ can be made using the treatment of Casimir (1938). He deduced that in an extended crystalline solid

$$\lambda_{\rm B} = 2.3 \times 10^3 RA^{2/3} pT^3 \text{ W/m K}$$

where R is the radius of the crystal, assumed to be of circular cross-section, p is approximately a constant which depends on the ratio of sound velocities in different directions, the usual value being $p \approx 1.4$. A is the constant in $C_{\nu} = AT^3 \text{ J/m}^3 \text{ K}$.

The contribution from phonon-phonon interaction, $W_{\rm u}$, dominates at higher temperatures $(T \ge \theta_{\rm D})$ where it varies approximately as T^{-1} . Leibfried and Schlömann (1954, see also Berman, Ziman, Klemens, etc.) calculated the magnitude on a simplified model of a cubic crystal, from which

$$\lambda_{\rm u} \approx 3.6 \times 10^{-5} aA\theta_{\rm D}^3/\gamma^2 T \text{ W/m K}.$$

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Here a is the lattice constant (in nanometres), A is the atomic weight, and γ is the Grüneisen parameter.

Agreement with experiment is clearly sensitive to the choice of θ_D and γ which are not necessarily the same averages over the phonon spectrum as are important in the heat capacity and thermal expansion. However if we use θ_D determined from room-temperature heat-capacity data and take $\gamma \sim 2$, agreement is generally within a factor of two.

In metals a most important source of scattering of lattice waves is the free electrons. Makinson (1938) first showed that this thermal resistance ($W_{\rm E}$) is proportional to T^{-2} at low temperatures and (see also Klemens 1956) is related to the electron-phonon coupling which is responsible for $\rho_{\rm i}$ and $W_{\rm i}$ in the respective electron transport processes.

An earlier figure (Fig. 5.1, p. 132) illustrates the differing temperature dependences of the total thermal conductivity in a pure metallic element, a crystaline dielectric solid, an alloy, and a glass.

More detailed discussions of heat conduction in solids are given in reviews by Klemens (1956, 1969), Ziman (1960), and Berman (1976).

Data on metallic elements

A practical example of the folly of assuming particular values of thermal conductivity for a material merely because it is labelled by the name of a certain element is illustrated by Fig. 11.4. These curves are experimental values for various samples of copper and show the tremendous variation of conductivity, particularly from 10 to 30 K, that arises with slight change in chemical or physical purity.

Data for a large number of metallic elements, as well as alloys, non-metals, glasses, etc., are given in the following compendia:

- (i) NBS Circular 556, Thermal conductivity of metals and alloys at low temperatures, by Powell and Blanpied (1954, US Govt. Printing Office, Washington, DC).
- (ii) NBS Monograph 131, Thermal conductivity of solids, by Childs, Ericks, and Powell (1973, US Govt. Printing Office).
- (iii) NSRDS-NBS 8 and NSRDS-NBS 16, Thermal conductivity of selected materials, Pt 1 (1966) and Pt 2 (1968) (US Govt. Printing Office).

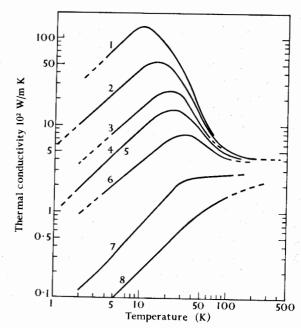


Fig. 11.4. Thermal conductivity of copper samples. 1, pure (99·999%, annealed, American Smelting and Refining); 2, pure (99·999%, annealed, Johnson Matthey); 3, coalesced (99·98%, oxygen-free annealed, Phelps Dodge); 4, pure (99·999%, cold worked, Johnson Matthey); 5, electrolytic tough pitch (99·9 +%, representing some tubes, much sheet and plate); 6, free-cutting tellurium (99% + 0.6% Te, representing machining rods and bar); 7, pure Cu+0.056% Fe (annealed); 8, phosphorus deoxidized (99·8% + 0.1% P, representing some tubes, pipe, sheet, and plate). Curves 1, 3, 5, 6, and 8 from Powell, Rogers, and Roder (1957); curves 2 and 4 from White (1953), and curve 7 from White and Woods (1955).

- (iv) Landolt-Börnstein, Vol. 2, Part 5b (1968, Springer-Verlag).
- (v) Thermophysical properties of matter, Vol. 1 (1970, Plenum Press, New York).

Bearing in mind that the data for pure materials at low temperatures $(T < \theta/10)$ are only representative of the actual samples used, these compendia are a very useful guide to the behaviour pattern of many solids. These are particularly useful for alloys, glasses, and plastics whose conductivity is not too sensitive to composition even at low temperatures; also for elements or dielectric crystals at temperatures greater than $\theta/5$ or $\theta/10$, where defects are less important.

At higher temperatures $\lambda \simeq \lambda_{\infty}$ is relatively insensitive to purity or temperature; the values of λ_{295} which are listed in Table E are intended to represent the best experimental estimates of the conductivity of the metallic elements in states of high purity and at a temperature sufficiently high that $\lambda \to \lambda_{\infty}$.

When the practical problem arises of calculating approximate values of $\lambda(T)$ for a particular sample of a metallic element the suggested procedure is:

- (i) Measure its electrical resistance at room temperature and in liquid helium to obtain R_{295} and R_4 ; by comparing $R_{295}-R_4$ with ρ_i at 295 K given in Table E, the shape factor l/A may be calculated.
- (ii) Then calculate $W_{\infty} = \rho_{\rm i}(295~{\rm K})/2\cdot45\times10^{-8}$. 295 m K/W or obtain W_{∞} direct from Table E, assuming $W_{\infty} = 1/\lambda_{295}$. Also obtain $W_0T = \rho_4/2\cdot45\times10^{-8}~{\rm mK}^2/{\rm W}$.
- (iii) At each temperature T calculate $W_0 = \rho_4/2.45 \times 10^{-8} T$; and using Table D or Fig. 11.3 calculate

$$W_i = 2W_{\infty}(T/\theta_D)^2$$
. $J_3(\theta_D/T)$.

(iv) Then at each temperature $W \simeq W_0 + W_i$.

Metallic alloys

As we discussed above for pure metallic elements, a relatively easy measurement, that of $\rho_4 = \rho_r$, allows a rough estimate of the electronic thermal conductivity λ_e , to be made. In cases where the impurity scattering is not excessive, for example wherever $\rho_r/\rho_{295} < 0.5$, it may be assumed that electronic conductivity λ_e , is the dominant mechanism, i.e.

$$\lambda = \lambda_e + \lambda_g$$

$$\simeq \lambda_g.$$

It is in the technically important alloys such as monel, stainless steel, and cupro-nickel that the residual resistance is very high and λ_e is reduced to become comparable with λ_g . Estimation of λ_g from other physical data is difficult. At high temperatures, anharmonic interactions dominate and W_u can be estimated roughly from the Leibfried-Schlömann expression discussed above.

At low temperatures, scattering of phonons is chiefly by electrons and/or by dislocations, each of which cause an approximate T^2 dependence for λ_g . By making assumptions about the process of phonon-electron interaction, a relation between W_E (or λ_E) and W_i can be deduced. This can also lead to a crude estimate of W_E (or λ_E) in terms of $\rho_i(295)$ (see for example Klemens 1956, 1969, and White and Woods 1957):

$$\lambda_{\rm E} \simeq 2 \times 10^{-2} (T/\theta)^2 / \rho_{\rm i}(295) \,{\rm W/m} \,{\rm K},$$

e.g. for nickel

$$\rho_i \approx 7 \cdot 1 \times 10^{-8} \Omega \text{m}, \ \theta \approx 390 \text{ K}$$

$$\lambda_E \approx 0 \cdot 02 \ T^2 \text{ W/m K.}$$

Fortunately there are measured values of the total thermal conductivity for most of the alloys commonly used in cryogenics. These are in Table I and are taken from more complete compilations listed above, i.e. NBS Circular 556, NBS Monograph 131, and *Thermophysical properties of matter*, Vol. 1.

Dielectric crystals

These are not of great interest in cryogenic design with the exception of paramagnetic crystals used in cooling (see § 9.5) and some ceramics used for heat-sinks. The latter are generally buttons of alumina (or sapphire) and beryllia which are metallized on each side so that an electrical lead can be thermally anchored with solder to one side and the other side soldered to a brass or metal surface in the cryostat.

The conductivity of some dielectric crystals is illustrated in Fig. 5.1. As discussed above, the conductivity is limited by phonon-phonon interactions at higher temperatures and by grain boundaries at the lowest temperatures. At intermediate temperatures dislocations, point defects, etc., reduce the conductivity. Therefore particular data in a table may be considered to be representative at higher temperatures $(T > \theta/5)$; but at low temperatures the conductivity may differ markedly from sample to sample.

Pure crystals of beryllia and alumina both have conductivities which can reach 1000 W/m K or more. At temperatures below 10 K, the conductivity is controlled by the grain size and by the Casimir equation discussed in § 3.

Glasses, nylon, Teflon, etc.

Glass is a highly disordered substance, and the conductivity, which is due to lattice waves, might be expected to be given by

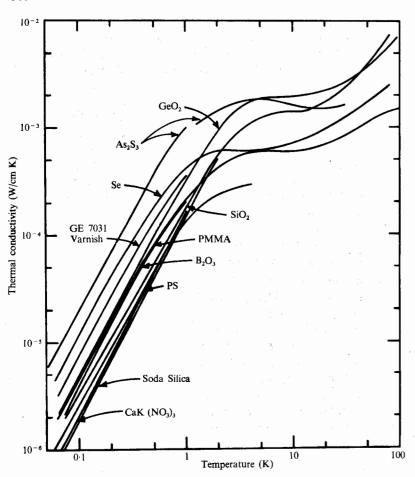


FIG. 11.5. Thermal conductivity of some amorphous solids, including vitreous silica, germania, and selenium, GE cement, polymethylmethacrylate (PMMA), and polystyrene (after Stephens 1973).

the product Cvl/3 where the mean free path l is of the order of the interatomic distance. This seems to be true above 30 or 40 K but below this $\lambda(T)$ behaves in a more complicated fashion for all non-crystalline solids, as illustrated by Fig. 11.5 (from Stephens 1973). There is a plateau or 'knee' in $\lambda(T)$ near 10 K and below 1 or 2 K, λ varies as T^2 (see Stephens and also Berman 1976, Ch. 9).

The T^2 -dependence below 1 K is also illustrated above in Chapter IX (Fig. 9.8, p. 239) for 'pyrex', nylon, and Teflon. Table I in the Appendix gives some values from $0.1~\rm K$ to $300~\rm K$ for λ and Table 5.1 (p. 133) gives some mean values for temperature intervals 77–4 K, 4–1 K, etc.

More extensive data are in the NBS Circular 556, NBS Monograph 131, and in the papers below:

- (i) McTaggart and Slack (1969): 1-300 K, GE7031;
- (ii) Kreitman and Callahan (1970): 1-4 K, Apiezon N;
- (iii) Schmidt (1975): 1·5-20 K, Ciba epoxy and copper powder;
- (iv) Hust (1975): 14-100 K, epoxy and fibre composite;
- (v) Locatelli, Arnaud, and Routin (1976): <1 K, epoxies, nylon;
- (vi) Ashworth, Loomer, and Kreitman (1973): 1-360 K, nylons and Apiezon greases;
- (vii) Stephens (1973): 0.05-2 K, glasses, GE7031, PMMA, etc.

Powder insulators

The importance of some powdered materials in providing thermal insulation for liquid-air vessels has already been mentioned (§ 2.1).

The effective thermal conductivities of many powder insulators and cellular glass or cellular plastic insulators are very similar at room temperature in the presence of an atmosphere of air. Due partly to the effect of radiation as a mode of heat transfer, some experimental values suggest that the thermal conductivity may not be uniquely defined in such materials but depends slightly on thickness or temperature difference. However, to a first approximation, the apparent thermal conductivities of a broad group of insulators such as Zerolite, rock-wool, corkboard, cellular glass blocks, Styrofoam, Santocel (silica aerogel), and fibre-glass wool all lie in the range of 30-50 mW/m K. If the mean temperature is reduced, the conductivity decreases in an almost linear fashion which is consistent with the fact that a large part of the conductivity is apparently due to the air or gas present in the porous medium, and a lesser fraction is due to radiation. A very marked decrease in thermal conductivity occurs if the gas pressure can be reduced to $\sim 10^{-3}$ Torr. As Fig. 11.6 shows, further reduction in

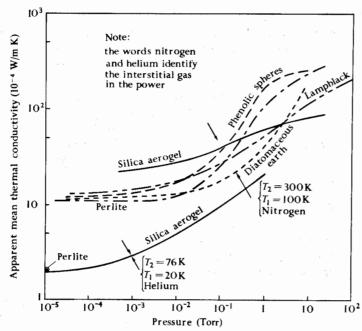


Fig. 11.6. Apparent mean thermal conductivity of some power insulators as a function of gas pressure (after Fulk, Devereux, and Schrodt 1957).

pressure is less effective, presumably because radiation becomes predominant. Fulk *et al.* (1957) showed that the apparent heat conductivity of silica aerogel could be reduced by a further factor of 3 to 4 when finely divided aluminium was added as a radiation trap.

Fulk (1959) has written an interesting review of the role of powder insulation in low-temperature equipment.

Of the cellular or foamed plastic insulators, perhaps the most commonly used in recent years has been Styrofoam, an exploded polystyrene which has a conductivity of about $43 \, \text{mW/m} \, \text{K}$ at room temperature. From data given for Styrofoam by Waite (1955) we may obtain: λ is 43 at a mean temperature of 300 K, 29 at 227 K, 22 at 173 K, and 16 at 116 K. Such figures indicate that Styrofoam insulation is comparable with Santocel insulation when air at or near atmospheric pressure is present in the Santocel. If, however, the interstitial air is removed from the Santocel its conductivity becomes much lower.

Insulation can be made even more effective if it consists of multilayer sandwiches of reflecting sheets with insulating layers between. These are so-called 'superinsulations', which normally use aluminium foil or aluminized Mylar for the reflecting layers and fibreglass mat or nylon net between them. When evacuated and at liquid-air temperatures, the effective thermal conductivity is at least an order of magnitude less than evacuated powder insulation. It may be as low at 10^{-5} W/m K. Naturally such insulation has become widely used in storage dewars for liquid air, hydrogen, or helium. It has made it possible for large liquid-air containers to have evaporation rates of a few tenths of a per cent in 24 hours; also liquid-helium storage dewars can be made with superinsulation instead of a liquid-air shield and still preserve a satisfactory evaporation rate of 2–3 per cent per 24 hours.

Details of the first use of superinsulation may be found in the Proceedings of the 1959 Crogenic Engineering Conference (Advances in cryogenic engineering, Vol. 8, 1960, Plenum Press, New York). More recently, Scurlock and Saull (1976) have shown that interleaving superinsulation with a carbon-loaded paper to act as getter can reduce the effective conductivity below the $10~\mu\,\mathrm{W/M}~\mathrm{K}$ level.

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APPENDIX

TABLES

TABLE A

Vapour pressure—temperature

(See Chapter IV, § 5, for references and comments)

p	³He ⁴He		Equilibrium —H ₂	Normal —H ₂	N_2	O_2		
					Armstrong			
			33711	XX711	(1964)	Muijlwijk,		
YY.			Woolley,	Woolley,	(T > 63.2 K)	Moussa,		
mm Hg at 0°C,	1962	1958	Scott, and Brickwedde	Scott, and Brickwedde	Keesom and Bijl (1937)	and Van Dijk		
,			(1948)	(1948)	(T < 63.2 K)			
standard	scale	scale	` /	(1948) (K)		(1966) (K)		
gravity	(K)	(K)	(K)	(K)	(K)	(K)		
800	3.2395	4.2700	20.44	20.56	_	90.671		
780	3.2152	4.2427	20.37	20.48	77.58	90-427		
760	3.1905	4.2150	20.27_{3}	20.39_{0}	77·36 ₄	90.178		
740	3·1653	4.1868	20.18	20.30	77.14	89-924		
720	3.1396 4.1580		20.09	20.21	76.91	89.664		
700	3.1134	4.1287	20.00	20.11	76.67	89.399		
680	3.0866	4.0989	19.90	20.02	76.43	89-128		
660	3·05 9 4	4.0684	19.80	19.92	76.18	88.851		
640	3.0315	4.0373	19.70	19·82 ₅	75.93	88.567		
620	3.0030	4.0056	19.60	19.72	75.68	88.276		
600	2.9739	3.9731	19.50	19.62	75.41	87.978		
580	2.9441	3.9399	19.40	19.52	75.13	87-671		
560	2.9136	3.9059	19.30	19.41	74.85	87-357		
540	2.8824	3.8711	19·18 ₅	19.30	74.56	87.034		
520	2.8504	3.8354	19·06 ₅	19·18 ₅	74.27	86.701		
500	2.8175	3.7987	18.94	19.06	73.97	86.358		
480	2.7838	3.7611	18.82	18·94 ₅	73.66	86.004		
460	2.7491	3.7224	18.69	18.82	73.34	85.639		
440	2.7133	3.6825	18.57	18.69	73.00	85.260		
420	2.6765	3.6414	18·43 ₅	18.55	72.66	84.869		
400	2.6285	3.5990	18.29	18·40 ₅	72.30	84.462		
380	2.5992	3.5551	18.15	18.26	71.92	84.038		
360	2.5586	3.5097	18.00	18.11	71.54	83.597		
340	2.5164	3.4625	17·83 ₅	17.96	$71 \cdot 13$	83.136		
320	2.4726	3.4134	17.67	17.79	70.70	82.653		
300	2.4269	3.3622	17.50	17.62	70.25	82.146		

TABLE A (cont.)

р	³He	⁴He	Equilibrium —H ₂	Normal —H ₂	N ₂	O ₂
mm Hg at 0 °C, standard gravity	1962 scale (K)	1958 scale (K)	Woolley, Scott, and Brickwedde (1948) (K)	Woolley, Scott, and Brickwedde (1948) (K)	Armstrong (1964) (T>63·2 K) Keesom and Bijl (1937) (T<63·2 K) (K)	Muijlwijk, Moussa, and Van Dijk (1966) (K)
- Gravity	(14)	(11)	(IX)	(11)	(11)	(IX)
290	2.4033	3.3357	17·41 ₅	17.53	70.01	81.882
280	2.3792	3.3086	17·32 ₅	17·43 ₅	69.77	81.611
270	2.3545	3.2808	17.22	17.34	69.53	81.332
260	2.3292	3.2524	17.13	17-25	69.28	81.045
250	2.3033	3.2231	17.03	17.15	69.02	80.749
240	2.2767	3.1931	16.93	17.05	68.75	80.443
230	2.2493	3.1622	16·82 ₅	16.94	68.48	80.127
220	2.2212	3.1304	16·71 ₅	16·83 ₅	68.18	79.800
210	2.1922	3.0976	16.61	16·71 ₅	67.88	79.460
200	2.1623	3.0637	16.49	16.60	67.57	79.108
190	2.1314	3.0287	16.36	16·48 ₅	67.25	78.740
180	2.0994	2.9924	16·23 ₅	16·36 ₅	66.91	78.358
170	2.0663	2.9546	16.10	16.23	66.56	77.957
160	2.0318	2.9153	15.97	16.10	66.20	77.537
150	1.9959	2.8744	15.83	15.95	65.81	77.096
140	1.9585	2.8315	15.68	15.80	65.42	76.630
130	1.9192	2.7865	15.52	15.64	64.98	76.137
120	1.8779	2.7390	15.35	15.47	64.52	75.611
110	1.8343	2.6888	15.18	15.29	64.03	75.069
100	1.7881	2.6354	15.00	15.10	63.50†	74.444
90	1.7387	2.5781	14.77	14.89	62.94	73.787
80	1.6856	2.5163	14.56	14.68	62.39	73.068
70	1.6279	2.4489	14.30	14.42	61.77	72.270
60	1.5646	2.3745	14.04	14.15	61.06	71.373
50	1.4939	2.2911	13.73‡	13.83§	60.24	70.344
45	1.4550	2.2450	13·57 ₅	13.67	_	69.763
40	1.4131	2.1952	13.40	13.51	59.28	69.127
35	1.3676	2.1413	13.21	13.30	_	68.420
30	1.3176	2.0827	12.99	13.09	58.08	67.624
25	1.2617	2.0174	12.74	12.85		66.709
20	1.1978	1.9427	12.46	12.57	56.48	65.624

[†] Triple point at 63·15 K (94·0 mm Hg) from Keesom and Bijl (1937). ‡ Triple point at 13·81 K (52·8 mm Hg). § Triple point at $13\cdot95_7$ K (54·0 mm Hg). $\parallel \lambda$ -point at $2\cdot1720$ K (37·80 mm Hg).

TABLE A (cont.)

р	³ He	⁴He	Equilibrium —H ₂	Normal —H ₂	N ₂	O_2
					Armstrong (1964)	Muijlwijk
			Woolley,	Woolley,	(T > 63.2 K)	Moussa,
mm Hg			Scott, and	Scott, and	Keesom and	and
at 0°C,	1962	1958	Brickwedde	Brickwedde	Bijl (1937)	Van Dijk
tandard	scale	scale	(1948)	(1948)	(T < 63.2 K)	(1966)
gravity	(K)	(K)	(K)	(K)	(K)	(K)
18	1.1692	1.9092	12.32	12.43		65.125
16	1.1384	1.8729	12·17 ₅	12.28	55.65	64.577
14	1.1049	1.8333	12.02	12.115	_ .	63.968
12	1.0679	1.7893	11.83	11.92		63.281
10	1.0266	1.7396	11.62	11.72		62.488
9	1.0038	1.7120	11.50	11.59		62.040
8	0.9791	1.6820	11.36	11.47	- ·	61.547
7	0.9523	1.6490	11.23	11.34		60.998
6	0.9227	1.6123	11.08	11.17	_	60.378
5	0.8894	1.5707	10.88	10.98	- ,	59.662
4	0.8512	1.5221	10.65	10.76	_	58.810
3.5	0.8295	1.4943	10.53	10.64	_	58.313
3.0	0.8055	1.4632	10.38	10.50		57.750
2.5	0.7785	1.4277	10.23	10.32	_	57.100
2.0	0.7474	1.3863	10.02	10.12	 .	56.325
1.5	0.7101	1.3359	_		_	55·359¶
1.0	0.6624	1.2699				
0.9	0.6508	1.2536				
0.8	0.6383	1.2359				
0.7	0.6246	1.2162				
0.6	0.6093	1.1942				
0.5	0.5920	1.1691				
0.4	0.5720	1.1395				
0.3	0.5477	1.1032				
0.2	0.5163	1.0554				
0.1	0.4693	0.9814				
0.08	0.4556	0.9595				
0.06	0.4391	0.9325				
0.04	0.4174	0.8967				
0.02	0.3844	0.8407				
0.01	0.3557	0.7907				
0.005	0.3305					
0.001	0.2829					

[¶] Triple point at 54.36 K (1.14 mm Hg).

TABLE B

Mean values of $Z = (R_T - R_4)/(R_{273} - R_4)$ and $\Delta Z/\Delta T$ for 50 high-quality platinum thermometers (after Besley and Kemp (1978) discussed in Chapter IV, § 6); deviations are shown in Fig. 4.10. The bracketed values are only approximate

T(K)	10°Z	$10^6 \Delta Z/\Delta T$
(11	356)	· _
(11.5	422)	-
(12	496)	_
(12.5	581)	_
(13	677)	
(13.5	785)	_
14.0	908.7	256
14.5	1043.5	284
15.0	1192.9	314
15.5	1358-2	347
16.0	1540-4	382
16.5	1740-3	418
17.0	1958· 9	457
17.5	2197-2	497
18.0	2456.2	5 39
18.5	2736.7	583
19.0	3039.7	62 9
19.5	3366.1	677
20.0	3716.7	726
21.0	4493· 6	82 9
22.0	5376.0	937
23.0	6368-3	10 49
24.0	7474-2	1164
25.0	8696.8	1282
26.0	10 038	1401
27.0	11 500	1522
28.0	13 083	1644
29.0	14 788	1766
30.0	16 615	1887
31.0	18 562	2007
32.0	20 628	2126
33.0	22 812	2242
34.0	25 111	2356
35.0	27 523	2468
36.0	30 045	2576

TABLE B (cont.)

T(K)	$10^{6} Z$	$10^6 \Delta Z/\Delta T$
37	32 674	2681
38	35 406	2783
39	38 238	2880
40	41 166	2974
42	47 293	3151
44	53 758	3311
46	60 528	3456
48	67 572	3586
50	74 862	3701
52	82 368	3803
54	90 065	3892
56	97 929	3970
58	105 937	4037
. 60	114 071	4095
65	134 839	4205
70	156 050	4274
75	177 535	4316
80	199 174	4337
	220 881	
85		4344
90	242 600	4342
95	264 293	4334
100	285 935	4322
105	307 511	4308
110	329 014	4293
115	350 439	4277
120	371 787	4262
125	393 058	4247
130	414 253	4232
135	435 376	4218
140	456 431	4204
145	477 420	4191
150	498 346	4179
155	519 213	4169
160	540 025	4157
165	560 783	4147
170	581 490	4138
175	602 150	4127
180	622 765	4118
185	643 335	4110
190	663 864	4102
195	684 352	4094
200	704 802	4086
205	725 213	4079

TABLE B (cont.)

T(K)	10 ⁶ Z	$10^6 \Delta Z/\Delta T$
210	745 588	4071
215	765 927	4064
220	786 230	4057
225	806 499	4050
230	826 733	4043
235	846 933	4037
240	867 099	4030
245	887 232	4023
250	907 333	4017
255	927 401	4011
260	947 43 9	4005
265	967 447	3999
270	987 427	3993
273.15	1 000 000	3990

TABLE C

Thermoelectric potential difference E with respect to 0 K and thermopower S = dE/dT (after Sparks and Powell 1972; Sparks et al. 1968 in Ch. 4)

)2% Fe		7% Fe romel	Constantan v. Cu					
T(K)	$\frac{E}{(\mu V)}$	S (μV/K)	$\frac{E}{(\mu V)}$	S (μV/K)	$\frac{E}{(\mu V)}$	S (μV/K)				
1	8.3	9.23	7.9	8.67	-	_				
2	18.3	10.86	17.3	10.13						
3	29.9	12.20	28.0	11.38	1.1	0.99				
4	42.7	13.29	40.0	12.44	2.2	1.35				
5	56.4	14.16	52.9	13.34	3.8	1.69				
6	70.9	14.83	66.6	14.10	5.6	2.01				
7	86.0	15.35	81.0	14.74	7.8	2.30				
8	101.6	15.72	96.0	15.27	10.2	2.59				
9	117-4	15.97	111.5	15.70	12.9	2.86				
10	133.5	16.12	127.4	16.05	15.9	3.12				
12	165.8	16.19	160.0	16.54	22.7	3.63				
14	198.0	16.02	193.4	16.83	30.4	4.12				
16	229.8	15.70	227.2	16.96	39.2	4.61				
18	260.8	15.31	261.2	17.00	48.9	5.09				
20	291.0	14.87	295.2	16.97	59.5	5.58				
22	320.3	14.44	329.0	16.90	71.2	6.06				

TABLE C (cont.)

		02% Fe romel		07% Fe romel		tantan Cu
	$oldsymbol{E}$	S	\boldsymbol{E}	S	\boldsymbol{E}	S
T(K)	(μV)	$(\mu V/K)$	(μV)	$(\mu V/K)$	(μV)	$(\mu V/K)$
24	348.8	14.03	362.8	16.81	83.8	6.55
26	376.4	13.66	396.3	16.72	97.4	7.03
28	403.4	13.32	429.6	16.64	111.9	7.52
30	429.8	13.06	462.8	16.57	127.4	7.99
32	455.7	12·8 3	495.9	16.51	143.9	8.46
34	481.2	12·6 6	528.9	16.47	161.2	8.92
36	50 6 ·4	12·5 3	561.8	16.46	179.5	9.37
38	531.3	12.45	594.7	16.46	198.7	9.81
40	556.2	12.40	627.7	16.47	218.8	10.23
45	618.1	12.42	710.2	16.57	272.5	11.24
50	680.5	12.56	793.5	16.73	331.0	12.17
55	743.9	12·7 9	877.6	16.93	394.1	13.03
60	808.5	13·0 5	962.7	17.14	461.2	13.82
65	874.5	13.34	1049.0	17.36	532-2	14.58
70	941.9	13·6 3	1136.3	17.58	606.9	15.30
75	1010.8	13.92	1224.7	17.79	685.2	16.01
80	1081.1	14.22	1314.2	18.00	767.0	16.70
85	1152.9	14.51	1404.8	18.21	852.2	17.38
90	1226.2	14.80	1496.3	18.42	940.7	18.05
100	1377.0	15·3 6	1682.5	18.81	1127.8	19.37
120	1694.4	16·3 6	2065-9	19.51	1541.0	21.93
140	2030.4	17.22	2462.2	20.09	2004.5	24.42
160	2382.7	18.00	2869.1	20.59	2517.4	26.85
180	2749.6	18.67	3285.4	21.02	3077.8	29.18
200	3128.7	19.24	3709.5	21.38	3683.9	31.42
250	4120.6	20.36	4796.6	22.02	5386.5	36.58
273.15	4596.4	20.71	5309.3	22.27	6258.9	38.72

TABLE D Some important physical functions (see Chapter XI)

	-	1 7	. ,	`	1	
Τ/θ	θ/Τ	C _v (J/mol K)	$ ho_i/ ho_{ heta} \ (lpha T^5 J_3)^{\dagger}$		$\rho_i/\rho_\theta \ (\alpha T^3 J_s)$ ‡	W_i/W_{∞} $(\alpha T^2 J_3)$ §
(∞)	0	24.94	∞		∞	1.00
(10)	(0.1)	24.93	10.55		10.42	1.00
(5)	0.2	24.89	5.268		5.201	0.998
(2.5)	0.4	24.74	2.617		2.588	0.993
(2.0)	0.5	24.63	2.083		2.062	0.990
(1.667)	0.6	24.50	1·72 5		1.711	0.985
(1.25)	0.8	24.16	1.274		1.268	0.974
(1.0)	1.0	23.74	1.000		1.000	0.960
(0.833)	1.2	23.23	0.813		0.8186	0.943
(0.714)	1.4	22.66	0.678		0.6873	0.923
(0.667)	1.5	22·3 5	0.623		0.6341	0.913
(0.625)	1.6	22.02	0.574		0.5873	0.902
(0.556)	1.8	21.33	0.493		0.5084	0.878
(0.500)	2.0	20.59	0.426		0.4444	0.853
(0.400)	2.5	18.60	0.3043		0.3273	0.785
(0.333)	3.0	16.53	0.2220	•	0.2478	0.713
(0.286)	3.5	14.48	0.1639		0.1910	0.642
(0.250)	4.0	12.55	0.1216	1	0.1491	0.572
(0.222)	4.5	10.78	0.0906		0.1176	0.508
(0.200)	5.0	9.195	0.0679		0.093 60	0.449
(0.1667)	6.0	6.625	0.03849		0.060 82	0.350
(0.143)	7.0	4.761	0.022 20		0.04084	0.274
(0.125)	8.0	3.447	0.01308		0.028 32	0.217
(0.111)	9.0	2.531	0.007 91		0.020 25	0.175
(0.100)	10.0	1.891	0.004 92		0.01490	0.143
(0.0833)	12	1.117	0.002 071		0.00868	0.100
(0.0769)	13	0.882	0.001 401		0.006 84	0.0853
(0.0714)	14	0.707	0.000 972		0.005 48	0.0736
(0.0625)	16	0.474	0.000 500		0.003 67	0.0563
(0.0556)	18	0.333	0.000278		0.002 58	0·044 5
(0.0500)	20	0.243	0·000 1 64		0.001 88	0.0360
(0.0400)	25	0.124	0.000 052 6		0.000 96	0.0231
(0.0333)	30	0.072	0.000 022 0		-	

Physical properties of some elements at room temperature (295 K). For anisotropic elements the values listed are generally appropriate to the polycrystalline form

						1			
					Coefficient of			Superconducting	
					linear thermal	Electrical	Thermal	transition	
	Atomic		Density		expansion	resistivity	conductivity	temperature	
Element	weight	Structure	(g/ml)	$\theta_{_{\mathbf{D}}}(\mathrm{K})$	$(10^{-6}/\text{K})$	$(\mu\Omega cm)$	(W/m K)	(K)	
Aluminium	26.97	f.c.c.		380	22.91	2.76	235	1.1795	
Antimony	121.76	rhombohedral		210	10.9	41	25		
Arsenic	74-91	rhombohedral		290	14.5	29	37	}	Α
Barinm	137.36	b.c.c.		110	20.5	39		1	PF
Beryllium	9.013	h.c.p.		920	11.2	3.25	210	0.023	'Ε
Bismuth	209.0	rhombohedral		120	13-3	115	11	<u> </u>	ΝI
Boron	10.82	hexagonal (?)	2.53	≈ 1300	ν.	$\simeq 10^{12}$	30	ļ)[
Cadmium	112.41	h.c.p.		175	31	7.3	76	0.519	X
Calcium	40.08	f.c.c.		210	22.3	3.4	86	1	
Carbon:						$\sim \! 10^2)$		·	
(graphite)	12.01	hexagonal	2.22	~ 400	~3	$\sim 10^6$	$\sim\!200$	1	
(diamond)	١	diamond	3.52	≈2000	1.0	$>10^{12}$	$\sim \! 1000$	l	
Caesium	132-91	b.c.c.	1.87	45	26	20.0	~50	I	
Chromium	52.01	b.c.c.	7.2	480	5.1	12.9	06	1	
Cobalt	58.94	h.c.p.	8.92	380	13.7	5.80	100	. 1	
Copper	63.54	f.c.c.	8.96	310	16.66	1.68	400	1	
Gallium	69.72	orthorhombic	5.97	240	20	14.9		1.09	
Germanium	72.60	diamond	5.32	400	5.7	$\sim 5 \times 10^7$	09	: 1	
Gold	197.00	f.c.c.	19.3	185	14.2	2.21	317	1	315
)

TABLE E (contd.)

Superconducting 3.4146 7.1999 0.1051.700temperature 4·15 0·92 9·25 0·66 transition $\overline{\mathbf{x}}$ 30 (200 K) 135 90 52 86 conductivity $(Wm^{-1}K^{-1})$ Thermal 82 150 7-7 22 87 80 82 150 9/ 601 49 Electrical resistivity $(\mu\Omega cm)$ 30.6 8.8 5.05 6.804.30 21 5·33 7·05 10.55 10.42 4.78 21.0 14-4 7·2 18·7 9.3 9.1 40 linear thermal Coefficient of expansion $(10^{-6}K^{-1})$ 11.8 28.8 46 26 22 50 5·1 12·8 6.5 8.9 11.7 82 $\theta_{\rm D}$ (°K) 88 360 330 410 380 390 390 400 290 225 86 275 350 61 290 400 22.5 7.87 111.34 0.53 1.74 7.44 14·2 10·2 8·9 8·57 22·48 12·02 21.45 0.8512.44 1.53 13·3 7·31 21.0 Density (g/ml) cubic (complex) rhombohedral tetragonal f.c.c. h.c.p. b.c.c. h.c.p. b.c.c. f.c.c. b.c.c. f.c.c. b.c.c. f.c.c. f.c.c. b.c.c. h.c.p. b.c.c. f.c.c. Structure 95-95 58-69 24·32 54·93 195.09 39.10 85-48 14.76 55.85 6.94 200.61 92.91 186.31 102.91 207-21 190.2 106.4 92.2 Atomic weight Mercury (near Molybdenum Magnesium Manganese Rubidium Potassium Element 220°K) Palladium Niobium Rhenium Rhodium Hafnium Osmium Platinum Lithium Indiam **[ridium** Nickel Lead Fon Log

0.49	I		1	1	1	1	4.48	I	2.39	1.37	3.722		1	0.39	0.015	8.0	5.3	0.851	0.546
117	0.5	2	150	427	125		27	4	47	37				22	175	27	30	120	22
7.4	$>10^{12}$	$\sim 10^7$	$> 10^{10}$	1.64	4.75	21.5	13.0	$\sim 0.4 \times 10^{6}$	16.4	15.6	11.0		1	43.0	5.32	<25	20.0	5.95	42.4
9.9	20	4	2.57	19.0	69	22.6	6.5	18.0	30	11	22.0		1	9.8	4.5	14	7.7	30	5.7
450	ı	250	700	220	160	140	230	180	94	140	160		260	360	315	160	380	240	250
12.2_{5}	4.30	4.80	2.32	10.49	0.97	5.6	16.6	6.24	11.85	11.7	7.3		2.76	4.5	19.3	19.05	6.11	7.14	6.5
h.c.p.	vitreous	hexagonal	diamond	f.c.c.	b.c.c.	f.c.c.	b.c.c.	hexagonal	h.c.p.	f.c.c.	tetragonal	(diam. cubic)	(grey tin)	h.c.p.	b.c.c.	orthorhombic	b.c.c.	h.c.p.	h.c.p.
101.07	28.96	1	28.09	107.88	22.99	87-63	180.95	127.61	204.39	232-12	118.7			47.90	183.85	238.07	50.95	65.38	91.22
Ruthenium	Selenium		Silicon	Silver	Sodium	Strontium	Tantalum	Tellurium	Thallium	Thorium	Tin			Titanium	Tungsten	Uranium (α)	Vanadium	Zinc	Zirconium

(i) Atomic weights, structures, densities, thermal conductivities, and superconducting transition temperatures are from standard tables: American Institute of Physics handbook (3rd edn. McGraw-Hill, 1972). Thermophysical properties of matter (Ed. Touloukian et al., Plenum Press, 1970–77) and Landolt-Börnstein (Springer-Verlag, 1968, 1971 etc.).

(ii) Values of the Debye Temperature θ_D have been obtained from specific heat data in the range $\theta/2 - \theta$ which are given in reviews and compilations listed in Chapter XI; see also Gschneidner (1964). Solid St. Phys. 16, 275.
(iii) Values for electrical resistivity are from Meaden 1965 (see Ch. XI) and American Institute of Physics handbook (Note: 1 $\mu\Omega$ cm = 10^{-8} Dm).
(iv) Coefficients of linear expansion are generally taken from tables listed above in (i) supplemented by more recent data e.g. Swenson, White etc. on Cu, Al, Si mentioned in Chapter XI.

Linear thermal contractions, relative to 293 K. Units are $10^4 \times (L_{293} - L_T)/L_{293}$. Sources of data include Thermophysical properties of matter (1977), Corruccini and Gniewek (1961), and American Institute of Physics handbook (1972) (See § 11.2)

Substance	T(K)	0	20	40	09	80	100	150	200	250
Aluminium		41.4	41.4	41.2	40.5	39.0	36.9	29.4	20.1	9.6
Copper		32.6	32.6	32.3	31.6	30.2	28.3	22.1	14.9	7.1
Germanium		9.3	9.3	9.3	9.4	9.3	6.8	7.3	2.0	5.4
Iron		20.4	20.4	20.3	19.9	19.5	18.4	14.9	10.2	4.9
Lead		20.8	0.07	2.99	62.4	57.7	52.8	36.6	26.3	12.4
Nickel		23.1	23.0	22.9	22.6	21.8	20.8	16.5	11.4	5.4
Silicon		2.16	2.16	2.17	2.23	2.32	2.40	2.38	1.90	1.01
Silver		41.0	41.0	40.3	38.7	36.5	33.7	25.9	17.2	8.2
Titanium		15.1	15.1	15.0	14.8	14.2	13.4	10.7	7.3	3.5
Tungsten		9.8	9.8	8.5	8.4	8.1	9.2	6.5	4.0	1.9
Brass (65 Cu, 35	Zu)	38.4	38.3	38.0	36.8	35.0	32.6	25.3	16.9	8.0
Constantan		I	1	26.4	25.8	24.7	23.2	18.3	12.4	5.85
Invar*		4.5	4.6	4.8	4.9	4.8	4.5	3.0	2.0	1.0
304, 316 Stainles	ss steel	1	29.7	59.6	29.0	27.8	26.0	20.3	13.8	9.9
Pyrex		9.9	2.6	5.7	9.9	5.4	5.0	3.95	2.7	8.0
Silica (1000 °C)†		-0.1	-0.05	0.05	0.5	0.3	0.4	0.5	0.4	0.5
Silica (1400°C)‡		-0.7	-0.65	-0.5	-0.3	-0.2	-0.05	0.5	0.2	0.1
Araldite		106	105	102	86	94	88	71	20	25
Nylon		139	138	135	131	125	117	95	29	34
Polystyrene		155	152	147	139	131	121	93	63	30
Teflon		214	211	206	200	193	185	160	124	75

* The expansion of Invar or NiFe alloys containing c. 36 per cent Ni is very sensitive to composition and heat treatment. † These silicas were aged at 1000°C and 1400°C.

Table G Electrical resistivities of ideally pure elements in $\mu\Omega$ cm (see § 11.3) $(1~\mu\Omega~\text{cm}=10^{-8}~\Omega~\text{m})$

ΤK	Ag	Al	Au	Cu	Fe	Na	Ni	Pb	Pt	W
295	1.61	2.74	2.20	1.70	9.8	4.75	7.04	21.0	10-42	5.33
273	1.47	2.50	2.01	1.55	8.7	4.29	6.2	19.3	9.59	4-83
250	1.34	2.24	1.83	1.40	7.55	3.82	5.4	17.6	8.70	4.33
200	1.04	1.65	1.44	1.06	5.3	2.88	3.7	13.9	6.76	3.22
150	0.73	1.06	1.04	0.70_{5}	3.15	2.00	2.24	10.2	4.78	2.11
100	0.42	0.47	0.63	0.35	1.24	1.15	1.0_{0}	6.5	2.74	1.02
80	0.29	0.25	0.46	0.215	0.64	0.81	0.55	5.0	1.01	0.60
50	0.11	0.05	0.20	0.050	0.135	0.32	0.15	2.75	0.72	0.15
25	0.010	_	0.027	0.0025	0.012	0.039	0.017	1.0	0.084	0.011
15	0.0011	_	0.0037	0.00012	0.0034	0.005	0.004	0.25	0.0116	0.002

TABLE H

Electrical resistivity of alloys in $10^{-8} \Omega$ m (see § 11.3)

(note: $10^{-8} \Omega$ m = 1 $\mu\Omega$ cm = 10 $n\Omega$ m)

Alloy	Physical	295 K	90 K	77 K	4·2 K
Brass (70 Cu, 30 Zn)	strained	7.2	5.0	_	4.3
	annealed	6.6	4.2		3.6
Constantan					
(60 Cu, 40 Ni)	as received	52.5	45		44
Cupro-nickel					
(80 Cu, 20 Ni)	as received	26	_	24	23
Evanohm					
(75 Ni, 20 Cr, 2·5 Al,					
2.5 Cu)	as received	134	133	_	133
German silver					
(47 Cu, 41 Zn, 9 Ni, 2 Pb)	as received	30	27.5		26
Manganin					
(84 Cu, 12 Mn, 4 Ni)	as received	48	46	45	43
Monel	annealed	50	_	32	30
Niobium + 25 Zr	as received	40	28		25(11 K
Silicon bronze					
(96 Cu, 3 Si, 1 Zn)	as received	21.0		_	18.6
Platinum + 10 Rh	as received	18.2	,— ·	11.5	9.8

and plastics (see also Fig. technical alloys, glasses, in W/m K

	,	3 11.4 Joi 16	Jerences						
	0·1 K	0.4	-	4	10	40	80	150	300 K
Al 5083 (c. 4.5 Mg, 0.7 Mn)	!		0.7	3	∞	34	56	80	120
Al 6063 (c. 0·6 Mg, 0·4 Si)	I	1	%	35	87	270	230	200	200
Brass (70 Cu, 30 Zn)	90.0	0.2	0.7	3	10	37	65	85	120
Cu+30 Ni	900.0	0.03	0.1	0.5	2	~ 12	~ 20	\sim 25	30
Constantan	900-0	0.02	0.1	8.0	3	14	18	20	23
Inconel	1	1	0.05	0.4	1.5	7	10	12	14
Manganin	900-0	0.02	90.0	0.5	2	7	13	16	22
Silicon bronze (96 Cu, 3 Si, 1 Mn)	1	I	I	I	1.5	7	14	I	25
Soft solder (60 Sn, 40 Pb)	1	1	l	16	42	25	25	I	\sim 20
Stainless steels (18/8)	0.008	0.03	80.0	0.3	0.7	2	∞	11	15
Wood's metal	1	1	1	4.0	12	20	23	١	1
Nylon	1	9000-0	0.003	0.01	0.04	I	I	ļ	1
Polystyrene	ł	1	0.01	0.03	I	I	ļ	1	I
Pyrex	0.0003	0.003	0.01	I	I	1	0.5	8.0	1.1
Soft glass	I		0.015	0.1	0.5	0.3	0.5	I	I
Teflon	0.00002	0.0004	0.004	0.05	0.1	0.5	0.5	J	I
Vitreous silica	1		I	0.1	0.1	0.3	0.5	8.0	1.4
Epoxy	0.0000	0.0007	0.007	90.0	90.0	I	I	1	1

APPENDIX

Cryogenic equipment

The list of suppliers below is arranged under chapter headings so that, for example, firms manufacturing level indicators or transfer siphons for liquefied gases are listed under Chapter II: storage and transfer of liquefied gases. The list is not intended to be exhaustive but should include many of the major producers (in 1978) of *cryogenic* equipment in North America and Western Europe. Inevitably such a list soon becomes incomplete or in error as new firms arise and others are taken over by the larger concerns.

In Britain the Science Research Council and later the British Cryogenics Council has compiled a list of UK suppliers with some European and American firms included. This booklet is now called BCC Cryogenic Equipment Guide and new editions are issued periodically from the British Cryogenics Council, 15 Belgrave Square, London SW1X 8PT. Another valuable source of information is Cryogenic laboratory equipment by A. J. Croft Plenum Press, London). Finally Cryogenics (IPC Science and Technology Press, Surrey, UK) and the Cryogenic information report Technical Economics Associates, Estes Park, Colo., USA) list many new cryogenic items that are produced industrially.

Chapter I

Liquefiers and/or refrigerators

Airco Cryogenics, 1900 Main Street, Irvine, CA 92664, USA. Air Products and Chemicals Inc., PO Box 538, Allentown, Pa., USA. BOC Cryogenic Systems, Deer Park Rd., London, SW19 3UP, UK. CTI—Cryogenics, Kelvin Park, MA 02154, USA. Hymatic Engineering Company Rd., Redditch, Worcs., UK. L'Air Liquide, 75 Quai d'Orsay, Paris 7e, France. Linde A. G., 8023 Hoellriegelskreuth, near Munich, W. Germany. North American Philips, 100 E. 42nd St., New York, NY 10017, USA. N. V. Philips, Cryogenic Dept., Eindhoven, Netherlands. Sulzer Brothers Ltd., CH-8401, Winterthur, Switzerland.

Chapter II

Dewars, level indicators, level controllers

Advanced Kinetics Inc., 1231 Victoria Street, Costa Mesa, CA 92627, USA.

American Magnetics Inc., PO Box R, 461 Laboratory Road, Oak Ridge, TN 37830, USA.

Andonian Associates, 26 Farwell St., Newtonville, MA 02160, USA. BOC Cryoproducts, Manor Royal, Crawley, Sussex, UK.

Cryenco Engineering Co., 11051 Leroy Drive, Denver, CO 80233, USA.

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