THE CHEMISTRY OF COKE:

BEING THE

"GRUNDLAGEN DER KOKS-CHEMIE"

OF O. SIMMERSBACH.

TRANSLATED AND ENLARGED

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PREFACE.

Coke-making is at the present day so important an industry as to demand that it should be conducted under all circumstances on sound scientific principles. Yet it is doubtful whether, in the past, any extensive manufacture has been less scientific. With the recovery of bye-products, a branch that is only now beginning to be developed on a considerable scale, the well-known treatise of Lunge deals exhaustively; but very little literature is to be found which treats of the composition and properties of that which is, after all, the main product of the industry—namely, the coke itself. This circumstance had suggested to me some time ago the desirability of summing up in a small handbook the more important facts and views on the subject, when there came into my hands the "Grundlagen der Koks-Chemie," by Herr Oscar Simmersbach, manager of the blast furnace department of the Upper Silesia Iron and Coal Company. The book seemed so much akin to that which I had projected, that I was prompted to translate it, with only such alterations as seemed necessary to adapt it to the requirements of those engaged in coke-making in this country. With the consent of the author I have appended to the translation a chapter on methods for the examination and analysis of coal and coke, which I have myself found convenient in ordinary practice, and which, I trust, will prove useful to the works chemist who is called upon to make such determinations.

I shall be satisfied if the work contributes even a little towards placing the industry on a more scientific basis.

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THE CHEMISTRY OF COKE

INTRODUCTION.

WITH the vast increase of the coal and iron industry of Germany since the establishment of the Empire, the chemistry of fuels, and especially the scientific chemical investigation of coal, has come to be regarded in that country as every day demanding a larger amount of attention.

And certainly this view is not without justification, for the annual production of coal in the kingdom of Prussia rose from 23,316,237 (metrical) tons in the year 1870, to 42,172,944 tons in the year 1880, and 64,373,816 tons in the year 1890. During this period of twenty years, therefore, the output of coal has been almost trebled.

In 1896 the total output of the German collieries amounted to 85,690,000 tons (of 2240 lbs.). Nor has the extraordinary development of this fundamental industry been confined to Germany alone. An interesting paper issued by the Board of Trade in April of the current year gives the following figures which, as they include every country that produces coal with the exception of Chili, Tonking, China, and the Transvaal, may be taken to represent the world's output in 1896:—

Coal output of	Tons.	Average Cost.
United Kingdom, - -	195,361,000	5/10¼
Russian Empire, - -	9,229,000	...
Sweden, - - -	226,000	7/11½
German Empire, - -	85,690,000	6/11
Belgium, - - -	21,252,000	7/7¼
France, - - -	28,750,000	8/8¼
Spain, - - - -	1,853,000	6/0¾
Austria, - - -	9,900,000	5/11¼
Hungary, - - -	1,133,000	8/7¼
Japan (1895), - -	4,849,000	5/0¼
United States, - -	171,416,000	4/9¼
British India, - -	3,848,000	3/8¼
Canada, - - -	3,743,234	8/9
New South Wales, -	3,909,517	5/9
Victoria, - - -	226,562	10/
Queensland, - - -	371,390	8/4
Tasmania, - - -	43,549	8/
New Zealand, - -	792,851	10/
Cape Colony, - -	105,365	...
Natal, - - - -	216,106	10/

Last year the output in the United Kingdom exceeded 200,000,000 tons, and in the United States 190,000,000 tons.

Even more remarkable is the increase in the manufacture of coke, which forms the subject of the present work.

In the district of Dortmund alone, which is the most important coal and coke area in Germany, the production of coke increased from 341,000 tons in the year 1870 to 2,280,000 tons in 1880, 4,187,780 tons in 1890, and 6,263,338 tons in 1896; so that in that locality it has been multiplied during the period of twenty-six years more than eighteen times.

No statistics are available to indicate the total amount of coke produced annually in the United Kingdom. The following figures show the quantities shipped to places at home and abroad during the last four years:—

Shipments of Coke from Ports in the United Kingdom.

	1894.		1895.		1896.		1897.	
	Foreign.	Coastwise.	Foreign.	Coastwise.	Foreign.	Coastwise.	Foreign.	Coastwise.
	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.	Tons.
N.E. Coast of England,	402,941	8,453	471,597	7,143	427,209	11,593	648,409	16,785
Liverpool, - - -	18,448	2,945	25,058	929	18,810	175	19,175	1,460
South Wales Ports, -	109,219	4,714	97,975	1,019	77,250	7,609	101,519	3,531
West of Scotland Ports,	6,349	129	9,466	215	8,560	65	10,708	236
East of Scotland Ports,	1,400	35	3,724	..	4,798	10	5,493	75
	538,357	16,276	607,820	9,306	536,627	19,452	785,304	22,087

The literature relating to the chemistry of coal and kindred subjects which has been published since 1870 shows a corresponding development. The works of a succession of men of high scientific attainments have thrown light on the chemical composition of fuels, and their properties and reactions under different conditions and at different temperatures. New inquiries and researches have followed, and new scientific methods have been elaborated and critically examined.

Moreover, every advance thus made in the chemistry of coal itself naturally causes attention to be similarly paid to the products derived from it. The scientific investigations connected with the recovery and subsequent working up of the volatile constituents of coal (bye-products of carbonising) afford abundant evidence of the forward movement in this special department. A voluminous and excellent technical literature in this branch of the chemistry of coal is the outcome of scarcely thirty years' work.

In the case of coke, which is the fixed residue of coal distillation, scientific investigation has not been so successful; for, although in the literature a great number of scattered memoirs and notices regarding the technical investigation of the residue of coal are to be met with, a beginning has scarcely been made in the direction of systematic investigation from the purely chemical standpoint.

To give a complete account of the chemistry of a substance which forms so valuable a fuel for the smelter is therefore a task which still remains to be discharged.

The knowledge of this fact led to a desire on the part of the author to make a beginning of enunciating the principles underlying the chemistry of coke. The present work, which is the outcome of that desire, contains an exposition of many matters connected with coke manufacture, the chemical phenomena of coking, and the chemical and physical properties of the product which have been dealt with separately in professional journals and in special treatises, and, in addition, indicates very briefly the historical development of the chemistry of coke, and the position it occupies at the present time.

The literature dealing with the subject, some of which has been made use of in the present volume while the rest has been consulted for the sake of completeness, is set forth in detail in the succeeding pages.

History of the Chemistry of Coke.

While the manufacture of coke from coal was known and practised as early as last century, the chemical investigation of the substance dates back no further than the sixth decade of the present one. Only then did scientific chemists begin to direct their attention to these problems.

Several points in the general field of "coke chemistry" had indeed already been made clear from practical working, but the results of these researches, which were naturally confined within very narrow limits, were known at first only to a small circle, because no special interest was evinced in a discussion and critical examination of the practical results from a scientific point of view.

Constituting our earliest possessions in the literature of coke, there are extant certain monographs on coal and a limited number of published papers on that subject in professional journals.

In W. Stein's work, "Chemical and Technical Investigations on the Coals of Saxony" (Chemische und Chemisch-technische Untersuchungen der Steinkohlen Sachsens), published in 1857, the remark was made for the first time that from the percentage composition of the coals no certain conclusions could be drawn regarding their coking power and *vice versâ.*

Stein's assistant for the time being, who subsequently became Professor Dr. Hugo Fleck, soon afterwards pointed out that the hydrogen atoms in the coal are partly united directly to the carbon and in part through the medium of oxygen; and on the basis of this view of "free" and "combined hydrogen" Fleck came to the conclusion that the source of the caking and sintering of coals is to be looked for in the hydrogen which they contain, to wit, that part which is "free."

In the year 1870 E. Richters sharply criticised the systematic hydrogen classification of Fleck in his preliminary researches on coal ("Zeitsch. für Berg, Hütten u. Salinenwesen in Preussischen Staat" and "Dingler's Polytechnisches Journal," 1 vol., pp. 119, 193, 195). Dr. F. Muck took up the same position in his "Chemischen Aphorismen über Steinkohle," 1873, and showed by experiments with the three isomeric carbohydrates, cellulose, starch, and gum, that in carbon itself instances of isomerism may be met with, as is well known to be frequently the case in chemical compounds. These researches of Muck were the beginning of a further elucidation of the problem.

The researches of Richters gave a fillip to the investigation of coal and coke. He established the fact that, in general, the yield of coke is smaller the larger the quantity of oxygen, and especially the larger the quantity of hydrogen, contained in the coal; and in his valuable "Investigations on the changes which coals undergo from lying in the air" (Untersuchungen über die Veräuderungen welche die Steinkohlen beim Lagern au der Luft Erleiden) he advanced direct proof of the predominating influence exerted by the hydrogen. At the same time he showed that, by lying in the open air and also on gentle heating, coal undergoes an appreciable change as regards its property of caking.

Richters, after thirty years' study, unfortunately abandoned the investigation of coke, which was at the time his special department, and in his stead Dr. Muck took the lead in this field of research. He also pointed out, as Richters had done, that the results of Fleck's investigations were erroneous, and, at the same time, by conclusive experiments which he had been led to make in the exercise of his office as director of the Laboratory of Practical Mining and teacher of chemistry in the Westphalian School of Mines at Bochum confirmed the aforementioned conclusions of Richters. In his "Development of the Chemistry of Coal in the last fifteen or twenty years, and the present position of Coal research in general" (Entwickelung der Steinkolen Chemie in den letzten fünfzehn bis zwanzig Jahren, und die dermaligen Ziele der Steinkohlenforschung überhaupt), published as a handbook in 1886, Muck commended the researches of Richters as hitherto the best monographs connected with the investigation of coal and coke.

In his "Chemischen Aphorismen" Dr. Muck discusses "the unequal yield of coke from coals of the same or similar percentage composition and the importance of coke estimation," and further, "the relation between chemical composition and yield of coke." Two years later, in 1875, there appeared on the same subject A. Schondorff's important research, "The Yield of Coke and Caking Power of the Saar Coals" (Koksausbeute und Backfahigkeit der Saarkohlen, "Preuss. Zeitsch.," 23, 135).

On "Coking Experiments" and "The influence of the quantity of ash upon the Yield of Coke," Muck enlarges further in his "Steinkohlen-Chemie," 1881, pp. 6-15.

The chief service that Muck has rendered to the chemistry of coke is undoubtedly to be found in his discovery of new points of view in coal and coke research. He established the connection that exists between the coking power as recognised in the form, colour, and other properties of the coke residue on the one hand, and—

(1) The chemical composition,
(2) Yield of coke,
(3) Quantity of Ash, and
(4) Temperature of coking,

on the other.

These relations are partly set forth in the "Chemischen Aphorismen uber Steinkohle" and the "Chemischen Beitragen Zur Kenntniss der Steinkohle," 1876, and are recapitulated and amplified in his "Steinkohlen Chemie," 1881, pp. 18-31.

The chemical composition of coke and the influence of individual constituents on its quality was Muck's first subject of investigation.

Hydrogen.—For thirty years coke was viewed as the ultimate product of complete carbonisation. Percy was the first to take note of the fact that an elementary analysis of the substance shows a constant loss of carbon, resulting from the presence of gaseous substances (oxygen and nitrogen).

In 1872 John Parry, chemist at the Ebbw Vale Ironworks in Wales, investigated the gaseous part of coke, and his researches proved that it contains not only oxygen and nitrogen but hydrogen as well ("Chem. News," 25, 98; "Dingler's Poly. Jour.," 204, 470).

The view of Parry that the gases are occluded in the coke was assailed in 1881 by Dr. Muck in his "Steinkohlen Chemie," with the fundamental objection that the gases were retained in the form of solid carbon compounds which were stable on heating.

More recent investigations, however, especially those of Dr. Thörner (1886), support the conclusion of Parry, so that to-day both views have their value (see this work, chapter IV.).

Nitrogen.—The first to occupy himself with the retention of the nitrogen in the gasification of coal was Dr. Knublauch, chemist of the gasworks at Cologne on the Rhine. The chief results of his investigations in this connection are contained in the

"Jr. für Gasbeleuch," 1883, p. 440. (See also "Jr. Soc. of Chem. Ind.," 1896, pp. 106, 107.)

The estimation of nitrogen was, until ten years ago, a matter of minor importance until the development of coal distillation rendered it necessary to have an accurate and easily worked method for the purpose. Of the general methods, that of Dumas was very tedious and difficult to work, and the evolution method devised by Varrentrapp and Will did not yield sufficiently accurate results; it was therefore of no use for valuation purposes. In consequence of this, Sigismund Schmitz (a former assistant of Muck) employed in a modified form the method which Kjeldahl had published in 1883 for the estimation of nitrogen in fixed organic bodies ("Stahl und Eisen," 1885, p. 47, and "Jr. Soc. Chem. Ind.," 1886, pp. 506, 507). The method of Schmitz has found very general employment.

Sulphur.—With reference to the sulphur contained in coal and coke, Crace-Calvert was the first ("Chem. News," 1886, p. 201) to show, by certain investigations which he made, that the sulphur in coal is present not only as pyrites (bisulphide of iron) but also in the form of sulphate.

In 1886 Dr. Muck also undertook an investigation of the sulphur in coal, and to him is due the credit of having completely cleared away the widespread error that the quantity of sulphur in the coal depends entirely upon the quantity of metallic sulphides (FeS_2, ZnS, PbS) present. In his valuable paper "On the Combination of Sulphur in Coal and Coke, and the production of Coke low in Sulphur" ("Stahl und Eisen," 1886, p. 7), Muck drew the conclusion that an important part of the sulphur is present also in the form of organic compounds. Besides the statements of Muck, other observations which have been published, particularly those of L. Blum ("Zeitsch. für Anal. Chemie," 1888, p. 445), have directed attention to the organic sulphur. The conclusions to which he was led were in substance the same as those of Muck.

The method employed till about twenty years ago for estimating the sulphur was that of deflagrating with potassium nitrate and sodium carbonate. This method was, however, tedious and inaccurate, and was subsequently replaced by that of Sauer. More recently the latter, too, has had to give way before the exceedingly useful oxidation method of Eschka.

Rothe, a chemist in the laboratory of the Mining School at Berlin, has proposed a very useful modification of the Eschka method (Rothe, "Mittheilungen," 1881, p. 107; Wedding, "Eisenprobirkunst," p. 266).

Iron.—Dr. Muck, in the above-mentioned research, "Uber die Bindung des Schwefels, &c.," was the first to draw attention to the importance that attaches to the quantity of iron present in coals, especially with reference to the production of a coke low in sulphur. Muck arrived at the important result that it is impossible even by careful preparation to diminish appreciably the quantity of sulphur contained in the coke in cases where the ash of the coal contains large quantities of iron, calcium, and magnesium compounds, especially of oxide of iron.

With this research of Muck the state of matters previously existing in the manufacture of coke was completely altered. For the production of a coke low in sulphur, the method of desulphurisation was henceforth abandoned and a means sought in another direction, namely, in selection of the raw material used, *i.e.*, the coal itself.

Phosphorus.—The presence of phosphorus in coal was first pointed out by Creath, who found considerable quantities in some varieties from the Pittsburg basin. The paper referring to this point is to be found in "Iron," 1889, No. 333. Subsequently to Creath, Le Chatelier and M. Carnot (Compt. rend., 99, 154) occupied themselves with the question of phosphorus in coal, and Carnot, in particular, endeavoured to elucidate its origin.

Copper.—Percy mentions in his "Metallurgy" (1862) that the anthracite of Wales contains copper. F. Stolba was the first to detect its presence in coke (Kerpely, "Fortschritte der Eisenhüttentechnik," 1879-80). At first copper was credited with much too great an influence upon the production of pig-iron, until the illusion was destroyed by B. Platz ("Stahl und Eisen," 1887).

Silica.—Until quite recently importance had been attached to the silica contained in the ash of coke, only in so far as it influences the formation of slags in the blast furnace. In chapter IV. of the present work reference is made to the close connection between the quantity of silica and the strength of the coke, namely, that with increase of silica the hardness of the coke diminishes, and *vice versâ*.

Upon the physical properties of coke, experiments were carried out first of all by Americans. In 1875 John Fulton, then manager of the Cambria Ironworks Company at Johnstown, Pa., discussed the variable action in the blast furnace of fuels containing the same quantity of carbon. This variability he ascribed to difference in their physical condition; anthracite, coke, and wood charcoal being, as he showed, characteristically unlike in structure ("Iron," 1884, No. 602; "Berg und Hüttenmannische Zeitung," 1884, p. 526).

During the following years the investigation of coke remained dormant until the publication of a paper by Dewey, in the Transactions of the American Institute of Mining Engineers for 1883, on measurements with reference to the porosity and specific gravity of coke. In the same year Fulton again came forward with a contribution on the physical condition of coke. The results of his investigations went to prove that the value of blast-furnace coke was determined by the hardness of the coke substance, coupled with well-developed cell-structure, purity, and uniformity (Proc. of meeting, Instit. Amer. Min. Engineers, Troy, 1883; "Iron," 1884, No. 602).

More important are the highly interesting researches of Dr. Thörner, carried out in 1886, in his "Analytisch microscopischen und Chemisch-technischen Institut" at Osnabrück.

Dr. Thörner investigated particularly the form and size of the pores in coke and wood charcoal, and drew clear distinctions between the structural condition of different kinds of coke. As the result of his microscopical investigations, Thörner came to the conclusion that the action of coke in the blast furnace, and in reduction processes generally, becomes more favourable, the more the physical structure of the coke approaches that of wood charcoal. The results of Dr. Thörner's experiments are published in "Stahl und Eisen," 1886, p. 71, *et seq.*, and, in the same place, photographs are given showing the characteristic difference in structure of various kinds of coke and of wood charcoal.

Very ingenious, too, is Thörner's method of determining directly the specific gravity of the coke substance and the pore space in the cokes. His method might well be less roundabout than the plan recommended by C. Reinhardt for the same purpose ("Stahl und Eisen," 1884, pp. 594, 706; 1884, p. 521; and 1885, p. 501 *).

To determine the strength, John Fulton used a cube of coke, of one-inch side. Dr. Thörner, who was the second to occupy himself with this subject, endeavoured to determine the hardness of the coke indirectly ("Stahl und Eisen," 1886, No. 2). Fulton's method Dr. Thörner regarded as "thoroughly uncertain," because experiments "conducted with one and the same kind of coke did not yield concordant results, but gave differences amounting sometimes to as much as 40 per cent."

This condemnation of Thörner's is, however, much too sweeping; for in every mass of coke considerable

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* Cp. W. Carrick Anderson, "Jr. Soc. of Chem. Ind.," 1896, p. 20.

differences exist, since the strength of coke diminishes from the sides to the middle, or from the top to the bottom of the oven, according as the coking proceeds from the sides to the centre, or from the top downwards.

In chapter IV. of the present work an apparatus for determining the strength of coke is described, which for the last two years has been used in the laboratory of the "Westfälische Kokssyndikat," and which gives sufficiently good results, notwithstanding its simplicity. The apparatus, which is made by H. Flottmann of Bochum, might therefore with advantage find general application.

With reference to the chemical behaviour of coke on heating, it was first pointed out by I. Lowthian Bell, in a paper published in the Journal of the Iron and Steel Institute, 1872, I., p. 74, and repeated in his "Principles of the Manufacture of Iron and Steel," London, 1884, p. 287, that the surface of the coke acts on the carbonic acid present with formation of carbonic oxide gas.

Bell's investigations were resumed, and in a manner completed, by Dr. Thörner, who completely elucidated the behaviour of coke and wood charcoal towards carbonic acid. Omitting the details of Thörner's paper, published in "Stahl und Eisen," 1886, p. 77, the following conclusion at which he arrived may be stated. "The fuels so highly valued for blast-furnace work, namely, wood charcoal and meiler coke, possess a markedly greater chemical activity at high temperatures than ordinary coke."

Thus, during the last twenty years, the results of investigation into the chemistry of coke have gone on accumulating. The whole subject has been placed on a firmer basis, and several matters have been made clear, even to the smallest detail. For this result, no little gratitude is due to the journal of the German ironmasters, "Stahl und Eisen."

During the same period, corresponding with the advances in the technology of blast-furnace work, a lively interchange of opinions has taken place with reference to fuels in general, and to coke in particular, in which scientific discussions have borne fruit in practical work.

CHAPTER I.

Purpose of Coking, and Uses of Coke.

Purpose of Coking.—In consequence of the increasing use of wood charcoal in metallurgical operations, the supply of wood was unable to keep pace with the demand; hence arose the necessity of providing a substitute for the wood charcoal, which, first of all in England, where wood is comparatively scarce, led to the coking of coal.

About the year 1860 coke had completely displaced wood charcoal throughout Europe, except in Sweden, Russia, and Austria, where want of coal, abundance of wood, or the existence of certain special methods of manufacture, justified the retention of the former practice. In the United States of America, indeed, half a million tons of wood charcoal were still used in furnaces, but there too the employment of coke went on apace. Whereas in the year 1872, 500,000 tons of wood charcoal were used in iron smelting, with 947,000 tons of coke and 1,407,000 tons of anthracite (and anthracite + coke), in 1892 the proportion stood as follows:—537,000 tons of wood charcoal, 7,154,000 tons of coke, and 1,798,000 tons of anthracite (and anthracite + coke).

Just as wood charcoal was produced from wood for the sake of obtaining a fuel rich in carbon, so coke was manufactured from coal at first with the same intention. The desire was to obtain a fuel that—

(1) Possessed a high calorific value.
(2) Was smokeless.
(3) Was infusible.

The first of these advantages is obtained partly through concentration of the carbon—and this is promoted by increasing the density — partly by expulsion of the volatile, although partly combustible, constituents. In this process, however, a not inconsiderable loss of fuel takes place, since the volatilisation renders latent a large quantity of heat. As regards the second point, raw coals have the property to a greater or less extent of evolving disagreeably smelling gases and smoke, which give rise to trouble in smelting operations. Coke, on the other hand, burns without producing smoke and soot, because the volatile constituents which give rise to these in the case of coal are expelled by the coking. For these reasons coke is more suitable for metallurgical and for all heating processes than the coking coal from which it is manufactured. Thirdly, the raw coal—except anthracite—becomes soft in the heat and swells up, in consequence of which the employment of it in the blast furnace in the raw condition is attended with difficulty, since by this property of caking the uniform sinking of the materials is interfered with. Coke, on the other hand, is infusible, and moreover by its porosity increases the permeability of the charge in a considerable degree. Not less important is the fact that raw coals, especially those which are rich in oxygen, absorb heat when carbonised in the blast furnace, which, in the case of previous coking, is saved to the furnace.

A further, at first altogether unintentional, result of coking is the expulsion of the sulphur contained in the coal. The expulsion of sulphur depends principally upon the property possessed by the pyrites, which is contained in the coal, of being decomposed by simple heating, whereby a part of the sulphur is evolved. Some more of the sulphur is likewise expelled on quenching the newly-drawn coke, in consequence of the contact of the water with red-hot sulphides.

In many metallurgical processes it is impossible to use coal slack, and likewise the small produced by the washing of "fat coals." But in the coke oven this small coal is converted from its previously loose, finely divided condition into a strong, massive block. The advantage which is thus obtained is specially obvious in such a locality as Westphalia, where the proportion of "slack" at mines producing bituminous coals usually amounts to from 40-50 per cent. of the output. Consequently, the development of the mining industry there is dependent upon the manufacture of coke.

In earlier days, the volatile products of coking, to wit, tar and ammonia, were generally neglected, and were lost. Only in recent times, since 1880, has a beginning been made of condensing these valuable bye-products, and of leading the incondensable gases back to the ovens for the purpose of heating the latter. The view formerly held, that the production of good coke was not compatible with the saving of ammonia and tar, has been proved to be nothing more than a prejudice. The manufacture of coke without recovery of bye-products is to-day frequently regarded as scarcely any longer a payable industry.

Uses of Coke.—Oven or metallurgical coke is used for the production of high temperatures, such as are needed for the extraction of metals from their ores, and in the conversion of them into articles of commerce. This is effected by reduction of the ores—that is, the removal of oxygen by the coke. In the case of simple melting and heating processes, for example in the cupola furnace, coke serves only for the production of heat; in blast-furnace operations, on the other hand, the coke serves not only for the production of heat but for the formation of carbonic oxide. Hence a distinction is made between foundry coke and blast-furnace coke. The differences in chemical composition and physical properties between these two kinds of coke will be more fully considered in chapters IV. and V.

In the Ruhr district the total quantity of foundry coke produced in 1892 was 470,994 tons (metrical); blast-furnace coke amounted to 3,064,817 tons = 78·72 per cent. The ironworks, for the most part, produce the coke they require by utilising the escaping gases in the coke ovens themselves.

In the year 1891 the ironworks consumed the following quantities of coke:—

Gutehoffungshütte, -	230,000	tons.
Rheinische Stahlwerke, -	120,000	,,
Union, - - - -	120,000	,,
Phœnix, - - -	100,000	,,
Krupp, - - - -	60,000	,,
Georgs-Marienhütte, -	60,000	,,
Hörder Verein, - -	50,000	,,
Ilsede, - - - -	50,000	,,
Bochumer Verein, - -	50,000	,,
Carl von Born, - -	40,000	,,
Niederrheinische Hütte, -	40,000	,,
Schalke, - - -	40,000	,,
Aplerbeckerhütte, - -	35,000	,,
Köln Müsen, - - -	25,000	,,
Friedrich Wilhelmshütte,	20,000	,,
Urbach, - - -	20,000	,,
Vulkan, - - -	20,000	,,
Grevenbrück, - -	10,000	,,
Troisdorf, - - -	—	none for the time being.
Hochdahl, - - -	—	,,
Mathildenhütte, - -	—	,,
Sundry, - - -	10,000	tons.
Total, - - -	1,100,000	,, (metrical).

Coke is also used in the manufacture of soda for the reduction of sulphate and for generating heat; likewise in sugar manufacture for the production of lime and of carbonic acid, &c. Small coke is used for heating rooms, drying chambers and evaporators, and generally in cases where combustion is being carried on without special draught.

On the advent of railways, the firing of locomotives also afforded a very important outlet for coke. In the year 1850, according to reports, 90 per cent. of the coke produced in the Dortmund district — about 7300 tons — was used in locomotives. The local railway companies consequently constructed coking works for themselves in the Ruhr district.*

The Düsseldorf and Elberfeld Railway, for example, in the year 1840 already owned a coke work at the Sälzer mine. The Cologne and Minden Railway followed in 1847 with two coking establishments at Dortmund and Herne, the Taunus Railway had one in Altenessen. By the beginning of the year 1860, the coke produced in the Ruhr district fell far short of what was needed to satisfy the growing requirements of the railways. The latter then resorted to the use of coal, which they found to be cheaper than coke, for which there was at the time a brisk demand.

The inducement to have recourse to coal for firing locomotive engines is now completely removed by the enormous development of the coke industry, a development so great that there would be no serious difficulty in supplying the demands of the German railway system for locomotive coke in every connection.

The extent to which the manufacture of coke in the Rhenish-Westphalian coal district has increased since 1868 may be gathered from the fact that, while in that year the production amounted to 240,455 tons, in 1893 4,780,489 tons were manufactured, an increase

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* F. M. Simmersbach, "Die Koksfabrikation im Oberbergamtsbezirk Dortmund," Berlin, 1887.

of 1888 per cent. The production of coke in all the districts of Germany together—excluding that from ovens in connection with blast furnaces—was, in 1892, 6,843,330 tons. Belgium produced in 1890 2,177,000 tons, the North of France in 1891 about 1,000,000 tons, and Mährisch-Ostrau 200,000 tons. An idea of the coke production of Germany, in the last seven years for which statistics are available, may be had from the table p. 24.

While nowadays the allegation of a scarcity of locomotive coke can no longer be made, on the other hand, firing by means of coke offers, as compared with heating by coal, a series of advantages that must not be under estimated. In respect of cohesion, coke stands naturally at the head of the list of fuels with 96 per cent. according to official tests; that of coals being on an average of 45·5 per cent. Moreover, coke can neither catch fire spontaneously, nor be decomposed by air, nor deteriorate on lying, as happens in the case of all coals. The railways might therefore, with greater advantage, form their permanent stores of fuel of coke. Coke of good quality does not attack the grate, nor does it "clinker" in the latter. When burned in properly constructed fireboxes its heating power is not surpassed by any kind of coal. With reference to the quantity of ash contained in coke, this is about 40 per cent. more than is present in coal. In this connection, however, it must be remembered that the quantity of carbon contained in dry coke amounts to 92 to 93 per cent.; in the case of bituminous coal it is about 10 per cent. less. This difference must be taken into account in

District.	1890. Tons (Met.)	1891. Tons.	1892 Tons.	1893. Tons.	1894. Tons.	1895. Tons.	1896. Tons.
1. Westphalia, Ruhr Mines,	4,187,780	4,388,010	4,560,984	4,780,489	5,398,612	5,562,503	6,265,338
2. Upper Silesia, - -	1,065,335	1,072,955	1,003,629	1,060,235	1,121,587	1,113,706	1,268,722
3. Lower Silesia, - -	254,178	293,372	325,015	366,110	415,963	427,409	443,361
4. Aachen, - - - -	246,923	265,954	258,613	218,551	207,098	286,878	310,161
5. Obernkirchen, - -	23,888	25,487	25,518	26,923	24,486	27,152	27,292
6. Saar, - - - -	557,353	584,128	587,315	573,581	695,045	713,047	743,639
7. Kingdom of Saxony, -	76,063	82,184	82,256	73,329	78,600	70,449	77,086
Total, - - -	6,411,520	6,712,090	6,843,330	7,099,218	7,941,391	8,201,144	9,135,599
	Increase.	4·4 %	2 %	3·6 %	11·8 %	3·3 %	11·4 %

comparing weights. Thus 1 ton of coke contains 2240 × ·93 = 2083 lbs. of carbon; 1 ton of coal contains 2240 × ·82 = 1837 lbs. 1 ton of coke (sp. gr. 1·0) occupies 35·8 cubic feet; 1 ton of coal (sp. gr. 1·3) occupies 27·5 cubic feet. Carbon in coke per cubic foot, 58·2 lbs.; carbon in coal per cubic foot, 66·8 lbs. Further, a consideration of the cost price of the pure carbon in coke and coal gives the following result as the cost of the carbon per ton, assuming in each case a price at the pithead of ten shillings per ton:—

In the case of coal (82 per cent. C.), 12·19 shillings.
,, coke (93 ,, 10·75 ,,
A difference of $13\frac{1}{3}$ per cent in favour of coke.

With reference to the practical advantages of firing by means of coke, emphasis must in the first place be laid on the fact that the latter, by reason of its greater porosity, is more readily penetrated by the air required for combustion than is coal; moreover, especially where bituminous coal is used, excessive caking takes place on the surface of the fire and frequent breaking up of the crust of coal is necessary. In the case of firing with coke, therefore, the door of the firebox does not need to be open so often, nor for the same length of time, as when the firing is done by coal, so that the loss of fuel which is thus occasioned is less. A coke fire, regularly attended to at stated intervals, goes on burning quietly and maintains a constant high temperature, so that the evaporation remains completely uniform and the steam pressure is always the same. The possibility of a train being left lying on the line by reason of shortness of steam—as sometimes happens under the present system of heating by coal—is absolutely precluded by using coke!

In addition to these economic and technical advantages, firing by means of coke must be granted to possess a great superiority in its entire freedom from smoke and sparks.* In long tunnels especially, the suffocating smoke emitted by the engine is most objectionable. This fact is recognised by the railway authorities, since, at least in the Gothard and some other tunnels, the locomotives are heated by means of coke. Coke firing is likewise practised on the Berlin City Railroad, and on a number of street railways. But the same reasons which have induced the management to return to the method of heating by means of coke on the Berlin City Railroad should have been equally valid in the case of the other roads—indeed, even more so, since, in addition to the already mentioned injuries to health and the danger arising from firing by coal, the evil effects of coal smoke are noticeable in rural districts as well. The districts traversed by railway trains are injuriously affected by the soot and smoke which they produce; the gases in the smoke contain sulphuric, hydrochloric, and sulphurous acids which destroy the vineyards, orchards, meadows, woodlands, and so forth. Particularly is this the case with pines, which are destroyed in a very short time by the smoke.

From the foregoing statements it is obvious that,

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* Cp. Professor E. Dietrich in "Deutschen Bauzeitung" for 1892 and "Glückauf," 1892, p. 917.

alike from the point of view of agriculture, and particularly from considerations of health as well as on economic grounds, coke must be regarded as in every way superior to coal for the firing of locomotive engines. And what is said here with reference to locomotives applies with equal force to steamships, where firing by means of coke would bring with it the same advantages.

CHAPTER II.

The coking power of coal in relation to fusibility, preparation, yield of coke, temperature of coking, and type of oven. Remarks on theoretical and practical coke yield.

NOT every coal can be coked; several conditions must be fulfilled before a useful coke can be manufactured from it. The usefulness of a coal for coking depends pre-eminently on its fusibility, that is to say, its capacity for caking more or less in the heat, and of giving a sufficiently coherent residue.

In earlier days it was conjectured that the fusibility or non-fusibility of a coal stands in a definite relation to the percentage composition, and a number of instances appear to support this view. The cause of the non-fusibility or fusibility and the degree of the latter is usually to be sought in the chemical composition of the coal, but no simple relation can be shown to exist between them.

The view that the resinous constituents of the coal condition the fusibility has been proved to be erroneous.* In every case the quantity of hydrogen

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* Siepmann, "Zeitsch. Berg, Hutten u. Salinenwesen," 1891, p. 27; also W. Carrick Anderson, "Trans. Glasgow Phil. Soc.," 1897-98.

and oxygen contained in the coal plays a far more important part than the carbon. Coals very rich in hydrogen and in oxygen no longer melt, neither do those very poor in hydrogen and oxygen. Thus anthracite and those kinds of coal which approach in composition the brown coals do not cake together; in the former this property is lacking because the quantity of hydrogen and oxygen is too small, in the latter because it is too large. The constituents of coal thus fall within definite limits above and below. The following table exhibits the series of solid fuels, arranged with reference to their chemical composition and yield of coke.

SERIES OF FUELS.

KIND.	C.	H.	O.	Free H.	Coke Yield.	Sp. Gr.	Time of Formation.
Wood, - - -	44	6	50	...	15	0·35	Present Day.
Peat, - - -	60	6	34	2	20	·6	
Brown Coal, - -	65	7	28	3	40	1·00	Tertiary and Chalk.
Coal, (*a*) Flaming,	75	6	19	4	50	1·25	Carboniferous Period.
,, (*b*) Gas, -	80	6	14	4	60	1·3	
,, (*c*) Coking, -	85	5	10	4	70-80	1·35	
,, (*d*) Lean Coal,	90	4	6	3	90	1·40	
,, (*e*) Anthracite	95	2	3	1½	95	1·50	
(and Coke),						(1·90)	
Graphite, - -	100	...	...	...	100	2·	Silurian.

It is evident from this series that the caking property is in some measure bounded by the following limits:—Hydrogen, 5-6 per cent.; oxygen, 10 per cent.; free hydrogen, 4; and sp. gr. 1·35.

Such a statement cannot, however, by any means be regarded as a rule of general application, especially seeing that among coals cases of isomerism occur, in which, of two coals identical in composition, the one cakes and the other does not. The coking property must therefore be determined by the presence of certain compounds of carbon, hydrogen, and oxygen, regarding which no further knowledge has been gained up to the present time. Apparently they are tarry bodies, which, at a higher temperature, are decomposed into volatile constituents and fixed carbon, the latter of which by its stiffness serves as a cement. In opposition to these conclusions is the view of Wedding, which is accepted as correct by numerous chemists. The latter expresses himself in his lectures at the Royal Mining School at Berlin to the effect that of a "fusibility" of carbon it is altogether impossible to speak. Hydrocarbons may, indeed, be partly fusible bodies, but at the high temperature of the coking oven, even with these it can only be a question of an intermediate fluid condition. The occurrence of caking, as well as the formation of stalactites and "hairs," may rather be explained in this way, namely, that the hydrocarbons at a higher temperature separate off carbon. For example, the heavy hydrocarbon C_2H_4, which is evolved in consequence of the lowering of the temperature within the coal, on reaching the hotter parts of the oven loses carbon ($C_2H_4 = C + CH_4$), which deposits in exceedingly fine tubes. These carbon tubes then ramify in such a way that several separate pieces grow together. While caking coal shows this property in the highest degree, in the case of the sinter coals only the adjacent parts of one and the same piece unite together, and in the case of the sand coals, rich in gas, as in the case of anthracite, which is poor in gas, even this does not take place any longer, but the coals crack up and give coke powder. The fact that in the apparently fused coke hairs, which are, however, in reality as in the case of soot formed only of fine carbon, one can often recognise hydrogen, and oxygen is, according to this view, to be ascribed simply to the incomplete nature of the decomposition as carried out in practice.

A third view regarding the coking property in coals has recently been propounded by Ed. Donath.*

Donath starts from the view of W. Lugi,† to wit, that carbon can appear in numerous modifications, and that the cause of allotropy in the element is not to be sought merely in a different arrangement of the molecules (that is in a physical difference only), but lies deeper, namely, in the different size and structure of the molecule itself, to which, moreover, rather than to anything else, is to be ascribed the extraordinary difficulty, or rather in the majority of cases the absolute impossibility, of converting the modifications of carbon into one another.

Taking his stand upon this dictum of Lugi, Donath regards the difference in behaviour of the varieties of coal when subjected to dry distillation as founded on the great difference in structure of the carbon substance. In the matter of which the true coals are

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* E. Donath. Ueber neuere Forschungen der chemischen Forschung in ihrer Beziehung zur Metallurgie, in der "Oesterreichischen Zeitschrift für Berg und Hüttenwesen"; also "Zeitsch. des Oberschlesischen Berg und Hüttenmännischen Vereins," October, 1894.

† W. Lugi. Ber. der deutsch Chem. Gesellsch. in Berlin, 1891, 4085; 1892, 1378.

composed the arrangement and concatenation of the carbon atoms in the molecule may even be different from that which exists, for example, in brown coal, and this may also show itself by their behaviour on heating and in the condition of the residue.

Donath considers that the different varieties of carbon which can be prepared pure by chemical treatment, for example, from coal coke, the residue of brown coal, wood charcoal, and soot are, chemically speaking, quite distinct, and reserves it to himself to adduce experimental proof of this if possible. "Indeed, the properties of coke which are known to us," he proceeds, "the greater difficulty of burning it as compared with wood charcoal, and the greater resistance it offers to liquid oxidising agents, enable us to conclude that the carbon molecule in it is differently constructed from that of wood carbon. Perhaps the carbon of coke exhibits a transition between the ordinary (soot) carbon and amorphous graphite. The foregoing would, moreover, afford an explanation of the fact that the brown coals, &c., do not coke, because in them the molecule has not that structure which conditions the property of yielding coke."

Interesting as the conclusions of Donath are, they will only be deemed satisfactory, if, besides, in the case of coals with similar chemical composition—but of which the one is a coking and the other a non-coking coal—a different structure of the carbon substance can be shown.

The caking power of coal shows a variation in degree in different coal basins. According to the percentage of bitumen (gasifiable constituents) they contain, coals are divided, as is well known,* into classes—corresponding at the same time to their geological age—as follows:—

(1)	5-10	per cent. volatile constituents—	Lean anthracitic coal (geologically the oldest).
(2)	10-15·5	,,	Sinter coal (old) poor in gas.
(3)	15·5-33·3	,,	Caking coal (old) poor in gas.
(4)	33·3-40	,,	Caking coal (recent) rich in gas.
(5)	40-44·4	,,	Sinter coal (recent) rich in gas.
(6)	44·4-50	,,	Sand coal (recent) rich in gas (geologically the youngest).

Among those coals which are geologically the most recent as well as among the earliest formed, the caking power increases uniformly, and reaches a maximum in the case of those which lie in the middle (3 and 4), but variation in the overlying strata exercises considerable influence upon the properties of the seams. With increased thickness in the overlying mountain masses, coals that are geologically older become better adapted for coking, while those which are more recent develop the coking property in proportion as the thickness of the superincumbent strata diminishes. As regards the relation of the

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* Wedding, "Grundriss der Eisenhüttenkunde," p. 46.

coking power of the coal to the geological period in the Ruhr basin, the property of caking increases, on the one hand, throughout the whole formation, from the bottom upwards, and, on the other hand, in zones from west to east. The table on p. 35 shows the coking power of the coals from the different formations of the Saar district.*

The property of caking is in the case of certain coals a somewhat unstable one. Many kinds of coal lose the caking power very quickly after extraction. The cause of this is to be found in the more or less rapid weathering of the coal. By contact with air the coking power of the coal is diminished, and this is accompanied by a decrease in the quantity of hydrogen, especially of free hydrogen, and by an increase in the oxygen contained in the substance. This decrease takes place more rapidly the greater the surface exposed to the oxygen of the air, and consequently more rapidly in powdered coal than when the latter is in the form of lumps.

The fusibility of the coal can be easily judged from the degree of intumescence with which it is closely connected. The swelling up may be appropriately compared with the action of yeast. A dough that is too thin does not rise because the gas bubbles soon burst and the dough falls down again. A dough that is not so thin, and therefore tougher, offers more resistance to the ascending bubbles of gas and larger cavities result, the tougher walls of which do not collapse when the bubble finally bursts (Jüptner,

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* Remy, "Kohlenaufbereitung und Verkokung in Saargebiet." 1890.

Kind of Coal.	Content of Carbon.	Content of Free H.	Ash content.	Yield of Gas from 100 kilos. air-dried Coal at 10° and normal press.		Yield of Coke from Ash-free Coal.		Quality of the Coke.	Caking power of the Coal.
	In Ash-free Coal dried at 90 .					Dried at 90°.	Air-dried.		
	Per cent.	Per cent.	Per cent.	Cbm.	Illum. Power.	Per Cent.	Per Cent.		
Saar district—Upper division of formation, - -	75·33-76·92	2·29-2·38	7·94	23,063	4·80	63·11	62·37	Sand.	No Caking Coal.
Middle division of formation. Upper division of flaming Coal, -	74·34-82·14	1·34-3·29	7·14	24,411	10·22	64·07	64·40	Sand, and to a small extent Sinter.	
Middle division of formation. Lower division of flaming Coal, -	73·64-84·34	1·83-3·65	6·77	25,908	11·77	63·41	63·14	Sand, to a large extent Sinter, even to some extent Caking.	Caking Sinter Coal.
Fat Coal division—Lower division of formation - -	75·46-85·64	2·39-4·65	5·28	27,453	13·12	67·25	66·51	Only exceptionally Sand, often Sinter, particularly Caking.	

"Heizstoffe"). Coals which do not melt, or which do so only partially, do not swell up. On the other hand, coals which melt easily form a thin fluid mass and consequently become stiff only after a long time; hence, on coking, they show less tendency to swell up than coals which are difficultly fusible, maintain a viscous condition, and more quickly become stiff. This is also the reason why many coals swell up to the same extent even although the temperature be different, while in other cases the degree of intumescence varies. As regards the influence of temperature on the amount of intumescence, cokes are more strongly swollen up the more moderate the heat to which they have been exposed, and *vice versâ*.

In Westphalia, according to Muck,* the coals which swell up strongly on heating and differ only slightly in respect of free hydrogen are characterised generally by the following features:—

(1) The total hydrogen is low.
(2) The combined hydrogen is low.
(3) The yield of coke is high.

These rules hold, however, only for the coals of the Ruhr district. Relations between the degree of swelling and the percentage composition of the coals have not hitherto been established authoritatively. In all probability, however, in the case of caking coals the higher yield of coke everywhere runs parallel with the more powerful intumescence.

A. Schondorff † divides coals into five classes based upon the swelling up.

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* Muck, "Steinkohlen Chemie," p. 34.

† "Preuss. Zeitsch.," vol. 23, p. 135, *et seq.*, "Koksausbeute und Backfähigkeit der Saarkohlen."

The free surface of the coke made in the platinum crucible appears—

Rough,	Loose all over or at least up to near the rim,	(i.) Sand coal.
Like fine sand,	Sintered hard, loose only in the middle,	(ii.) Sintered sand coal.
Black,	Sintered hard all over,	(iii.) Sinter coal.
Grey and hard, breaking off in the form of buds,		(iv.) Caking sinter coal.
Smooth, with metallic lustre and hard,		(v.) Caking coal.

The caking coals are best adapted for the preparation of a coke of good quality. In consequence of the caking property which they possess it is possible even from caking coals which are high in ash to manufacture a coke relatively low in ash by pulverising and subjecting them to treatment before coking. The process of treatment may be either a dry or a wet one, and effects the separation of shale, pyrites, &c. According to the specific gravity, the pyrites (sp. gr. 5·1) will settle down first, then the shale (2·4), and last of all the coal (1·35), in sharply divided layers.

Preparation of the coal is necessary in the generality of cases, because, with increase in the quantity of ash, the caking power of the coal diminishes. Stein, however (*loc. cit.*), found a coal containing over 21 per cent. of ash which still caked.

The ash contained in coal comes partly from the organic substance of which the coal is composed, and partly from fireclay and other incombustible matter which has been enclosed in the coal when it was laid down, and also to some extent from included rocks and stones introduced in the winning of the coal, the number of which depends upon the care exercised therein as well as upon the method of working. The latter part of the ash is easily and completely separated by washing, the former, however, cannot be removed. The shale is frequently so intimately mixed with the substance of the coal that the latter is removed along with it in the mechanical treatment.

The individual constituents of the ash affect the caking power of coals in so far as excessive quantities of silica, clay, and iron hinder the caking by reason of their high melting point. If the ash, on the other hand, contains an excess of lime its melting point is lowered, a circumstance which promotes the caking, since thereby coal particles that only cake with difficulty become baked together through the fusion of the ash, and form a dense coke of good appearance.

The dictum, "the purer the coal, the purer the coke," holds generally. In Pennsylvania,* however, there is a noteworthy exception. The Connelsville coal there contains a very small quantity of ash, and is so soft that it goes directly to the coking process without any further preparation.

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* "Die Bedingungen des Koksbrennens," reprinted from the mining weekly, "Der Bergbau" (Carl Bertenburg Gelsenkirchen). The author of this paper is not Dr. Muck as stated in Schnabel's "Lehrbuch der Allegm. Hüttenkunde," but F. M. Simmersbach of Bochum.

The composition of this coal is—

Carbon, - - - - -	59·616	per cent.
Volatile constituents, - -	30·107	,,
Sulphur, - - - - -	·784	,,
Ash, - - - - -	8·233	,,
Water, - - - - -	1·260	,,

A still less quantity of ash is found in the coke region of West Virginia. The coal — according to Wedding—has the following average composition—

Water, - - - - -	1·01	per cent.
Volatile constituents, - -	18·81	,,
Fixed carbon, - - - -	74·26	,,
Sulphur, - - - - -	·73	,,
Ash, - - - - -	5·19	,,

The coke has an average composition—

Water, - - - - -	·35	per cent.
Volatile constituents, - -	·76	,,
Fixed carbon, - - - -	92·55	,,
Sulphur, - - - - -	·60	,,
Ash, - - - - -	5·75	,,

The quantity of ash often varies considerably in individual instances, but always remains exceptionally low, so that scarcely any ground exists for washing the coal, since sometimes the cokes manufactured from unwashed coals contain less than 2 per cent. of ash (Wedding, "Stahl und Eisen," 1893, p. 21).

In many works in America even raw coal, with its contained shaly matter and sulphur, is filled directly into the ovens without having to undergo anything in the way of separation, washing, or pulverising. Many works have indeed tried washing, but have soon relinquished it, for the coke from washed coal brought no better price as fuel than that from unwashed. So great a loss in coal dust took place on washing, and the physical structure was so much deteriorated, that it was found more advantageous to retain the ash at the cost of an increase in the quantity of fuel used than to diminish it by washing.

It follows, therefore, that washing is not necessary or advantageous in the case of all coals. Obviously, however, coal which is too impure and contains too much ash and pyrites to be coked in the unwashed and merely sifted condition is benefited by being subjected to a process of washing.

A distinction is made between "washed" and "unwashed" coking coal, and coke is also spoken of as "washed" and "unwashed." Washed coking coal should contain at the most 6 per cent. of ash and 7 per cent. of water. By careful treatment, and by the use of coal of proper quality, the ash may be reduced to 4 per cent., so that a coke with about 5·5 per cent. is obtained. With regard to the moisture, it is advisable that it should not exceed 7 per cent. When in this state of humidity, the coking coal still packs together, does not enclose too much air, and settles together sufficiently fast in the oven, which of itself has an influence upon the structure of the coke.

The grain of the coking coal should not, as a rule, exceed 4 mms. ($\frac{1}{6}$ inch). If the size of the grains is greater than 4 mms. and is not uniform, then undoubtedly an increased burning off of carbon in the oven is the result. The finer the grain of the coal is, the denser is the coke, and the smaller the loss of combustible matter through burning. Finely ground coal, and indeed coal mud, even that high in ash, gives a very dense coke, which, however, it may be said, is useless for metallurgical purposes. The nearer the pieces lie to one another, and the smaller and more compressed they are, the more easily do they cake together. At the same time, coarse-grained coal can also yield good coke, as the American round-oven coke proves.

According to R. de Soldenhoff's* view, as good a coke is produced when coarse bituminous coal, the grains of which do not exceed 9·5 mm., is employed as with completely pulverised coal. Soldenhoff refers to the well-known fact that in using completely dry pulverised coal considerable losses take place owing to coal being carried away with the evolved gases.†

Corresponding to this there naturally results a diminished yield of coke, and the coal thus carried over may, by choking up the passages, cause interruptions of the process.

In Staffordshire coke is manufactured from very few bituminous coals, in some places only by the use of coarse coal. The larger the pieces of coal that are used, the more massive are the pieces of coke which result; by the employment of finely powdered coal either no coke is obtained at all or only one of inferior quality.

It is therefore by no means necessary to reduce the coal to powder to produce a good metallurgical coke;

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* R. de Soldenhoff. Proc. of the So. Wales Instit. of Engineers, "Stahl und Eisen," 15th May, 1891.

† See among others Hüssner, "Stahl und Eisen," 1892, p. 194.

it depends rather on the kind of the coal, whether a coarse or a fine grain is to be preferred.

The coking property appears in coals of from 70-80 per cent. yield of coke at most. Coals which have a very high (82-90 per cent.) or a very low yield of coke no longer cake. The yield of coke diminishes in Westphalia, as a rule, from the lower to the upper strata. For Saar coals A. Schondorff (*loc. cit.*) found the following minimum and maximum values:—

	Yield of Coke.
Caking Coal, - - - -	60·93–71·80
Caking Sinter Coals, - - -	60·35–70·66
Sinter Coals, - - - - -	56·44–74·76
Sintered Sand Coals, - - -	59·89–71·02
Sand Coals, - - - - -	59·34–81·95

Ruhr coals give a considerably larger yield, about 70-87 per cent.

The coals which are rich in carbon and poor in gas (short flaming caking coals) give a higher yield of coke than those which are much superior in respect of caking but give off more gas, and are generally long flaming. Thus the coking process is more profitable, so far as yield is concerned, the nearer the caking coals stand in their properties to the anthracitic.

In consequence of this the practice has recently been resorted to of mixing coals which are of inferior quality as regards caking, but are rich in carbon, with coals which cake well but yield a large amount of gas, in order thereby to obtain a material suitable for coking. The intimate mixture of different kinds of coal is naturally facilitated in the case of prepared coals by these being already in a finely divided condition.

Coals which cake readily and give off a large quantity of gas give, in consequence of their strong swelling up, porous cakes of low specific gravity, with weak cell-walls which are easily broken down. Those caking coals which yield little gas give dense cokes of higher specific gravity.

For this reason also it is an advantage, under certain conditions, to mix the coals. If it is desired to obtain a relatively dense coke from coals rich in gas which cake readily, the decomposition must not terminate too hastily, and while it is going on, the coals must be submitted to a heavy pressure under which the volume of the gases being evolved is correspondingly reduced.

In the Semet-Solvay ovens, which, without employment of a special regenerator or air heater, go to a very high temperature and evolve gas quickly, in consequence of which they are specially suited to the coking of lean coals, mixtures of 75 per cent. fat coal and 25 per cent. lean coal are converted into very good coke. At the Phoenix the mixture of coals used consists of 73-77 per cent. of fat coal, giving 25-26 per cent. of gas, with 23-27 per cent. of lean coal, giving 7-8 per cent. of gas, so that it contains only 20-21 per cent. of gas. At the Georgs-Marienhütte at Osnabrück there is added to the caking coal 25 per cent. by weight of Piesberg anthracite.

So-called anthracite coke is manufactured in South Wales, according to L. N. Lukens,* by mixing 60 per

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* "Eng. and Min. Jr.," 40, p. 239; and "Jahresber. über die Leist. der Chem. Technologie," 1886.

cent. of anthracite dust, 35 per cent. bituminous coal, and 5 per cent. of pitch. The coke obtained has the following typical composition:—

Carbon, - - - - -	94·63	per cent.
Hydrogen, - - - -	·30	,,
Oxygen and nitrogen, - -	1·48	,,
Sulphur, - - - - -	·23	,,
Ash, - - - - - -	3·36	,,

The Landore Works in Pennsylvania also obtain a coke fit for use in the blast furnace from a mixture of 50 per cent. anthracite dust and 50 per cent. bituminous coal.

A more careful examination of the influence exerted by individual constituents of the coal upon the yield of coke reveals the fact that a relation exists between the latter and

(1) The quantity of hydrogen and oxygen.
(2) The quantity of hygroscopic water.
(3) The amount of ash in the coal.

The yield of coke depends mainly upon the quantity of free hydrogen in the coal, and upon the particular compounds of carbon that are produced in the coking process.

The quantities of hydrogen and oxygen contained in the coal regulate the proportion of fixed and gaseous bodies formed in the distillation, in so far as in the coking process oxygen and hydrogen, except a small residue remaining in the coke, are completely expelled, the oxygen being driven off with the corresponding part of the hydrogen as water, or with carbon as carbonic acid (or carbonic oxide); while the surplus free hydrogen is evolved in the form of condensable or non-condensable hydrocarbons, and is likewise contained, though only to a small extent, in the oxygenated acids and bases of the tar. But to convert one atom (=12 parts by weight) of carbon into CO_2 requires two atoms (=32 parts by weight) of oxygen; while, on the other hand, only four atoms (=4 parts of weight) of hydrogen are needed to convert one atom of carbon into CH_4. Consequently, the free hydrogen is capable of vaporising a quantity of carbon eight times as great as oxygen can. Since even in methane or marsh gas (CH_4), the hydrocarbon poorest in carbon, the carbon amounts to 75 per cent., the free hydrogen has an exceedingly unfavourable effect upon the yield of coke, and, on the contrary, a favourable effect upon the yield of gas.

The case may easily occur where a coal containing a larger quantity of carbon and less hydrogen and oxygen gives a smaller yield of coke than one which has less carbon but more oxygen. This happens, according to Dr. Muck,* at the Hannover Mine at Bochum, seam 11.

The Mattkohle ("dull coal"), with a composition,

C,	84·740	per cent.
H,	5·261	,,
O,	9·999	,,

yields 63·80 per cent. of coke.

The Glanzkohle ("bright coal"), with a composition,

C,	82·988	per cent.
H,	5·301	,,
O,	11·701	,,

yields 68·05 per cent. of coke.

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* "Steinkohlen Chemie," p. 21.

But for 1000 parts of carbon there is contained in the "Mattkohle," 47·33 parts of free and 14·75 parts combined hydrogen; in the "Glanzkohle," 46·23 parts free and 17·64 parts combined hydrogen. Consequently, the small difference of 1·10 parts of free hydrogen and 2·89 combined hydrogen, for 1000 parts of carbon, determines the important difference of almost 5 per cent. in the yield of coke.

Sometimes the yield of coke is determined by the amount of free, sometimes by the combined hydrogen (or oxygen). According to Muck (*loc. cit.*), in cases where the total hydrogens are nearly the same, the yield of coke is diminished with

(1) Increase of combined hydrogen (or oxygen).

(2) Decrease of free hydrogen.

In cases where the free hydrogens are nearly equal, it diminishes almost proportionally with the increase of total hydrogen; and where the combined hydrogens are approximately the same, it diminishes with increase of free hydrogen.

A large percentage of oxygen in the coal also diminishes the yield of coke, inasmuch as it gives rise to many difficulties in the working of the process. Thus, in consequence of the presence of oxygen, a very brisk and violent evolution of gas and smoke takes place at the beginning, which, if the flues are small, renders it necessary to open the lids in the ovens in order to provide a way of escape.

When weathering of the coal takes place, hydrogen and oxygen exercise a further influence upon the yield of coke. The weathering is the result of an absorption of oxygen, which oxidises a part of the carbon and hydrogen of the coal into carbonic acid and water, while another part of it enters directly into the composition of the coal.

If, now, the hydrogen does not diminish simultaneously with the increase of oxygen, as is generally the case when the oxidation takes place at a little over 100°, weathering causes a decrease in the yield of coke: if, on the other hand, the loss of hydrogen exceeds the proportional gain of oxygen, there results an increase of the coke yield, especially if the oxidation takes place at a much higher temperature than 100°. As a rule, however, the yield of coke is diminished by weathering.

The quantity of hygroscopic water contained in coal naturally causes a decrease in the yield of coke. The formation of steam in the oven absorbs very considerable quantities of heat, so that the carbonisation is thereby retarded, although a certain quantity of water promotes the closer packing of the oven charge, and secures a uniform melting of the coal particles. The latter result can also be obtained, however, with dry coals, as is proved by the hard coke manufactured at the Rheinpreussen Mine at Homburg on the Rhine.

As regards the influence of the ash on the yield of coke, the latter rises with increase in the quantity of ash, because the ash-substance, being a bad conductor of heat, causes a lowering of the temperature of coking.

If the coking capacity of a coal depends preeminently on its quality, yet the contrivances for coking are none the less to be taken into account.

Certain South Staffordshire* coals for example which, when treated under ordinary conditions, give a brittle fritted coke, yield a hard product when the heat is raised quickly to bright redness.

According to Dr. Muck (*loc. cit.*), such coals as by gentle heating in the crucible yield either an imperfectly melted product or show a tendency to excessive swelling absolutely require a hot working of the oven, otherwise a frothy friable coke is obtained, with more of a sooty black than a metallic appearance. On the other hand, in the case of coals which swell up only slightly, whether they be heated gently or strongly, hot working is not an absolutely necessary condition, although it always has a favourable effect.

If caking coals be heated gradually instead of quickly they no longer melt regularly, and the result is a very ill-formed and strongly swollen coke residue. The fusible substance of the coal is destroyed by partial distillation.

The same thing happens even when the coking takes place with sufficient rapidity, if the entrance of air be not sufficiently guarded against, since under these conditions partial decomposition takes place through oxidation.†

If caking coals be heated gently for a lengthened period of time in the open air to about 300°, there results from the originally readily fusible substance a new carbon compound or a mixture of such, which has the property of melting in a much less degree or indeed not at all.

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* Muspratt's "Chemistry," 3rd edition, 1876.

† Cp. W. Carrick Anderson, Trans. Glasgow Phil. Soc., 1897-98.

The more difficult the coal is to cake, the higher must the temperature be, and the more quickly must the coking process be carried on to yield useful coke. The speed of the coking process is consequently in every case determined by the percentage composition of the coking coal.

Coals, as has been already stated, do not always coke equally well at different temperatures, and the same is true of different types of oven. In the Lürmann oven, for example, fat coals seem to be unable to coke without some admixture of gas or lean coal.*

With respect to fat coals as such, one can distinguish, as in the case of all classes of coal, different degrees, high, *i.e.*, fat, half-fat, and normal coking coal with about 18 per cent. of volatile constituents. "High-fat coal," with a content of volatile constituents of 25-30 per cent. and upwards (much oxygen), cokes with strong swelling up on account of the violent evolution of gas and smoke, and cannot therefore be treated in the horizontal ovens of the Coppee, Otto, and similar types like ordinary coking coal.

At some coke works the rapid evolution of gas in these ovens is checked by the presence of much water in the coals, 12-18 per cent., certainly to the detriment of the ovens and with great waste of carbon. It would be more rational when "high-fat coal" is being employed in the Coppee ovens to allow the process to begin slowly by the action of the heated gases, in order to moderate the rapid evolution of gas at the start.

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* Cp. "Stahl und Eisen," 1887, vii.

The ovens best suited for such coals are the beehive ovens (round ovens), because in these which have a small store of heat the coal itself must supply the heat required to effect the carbonisation, and this proceeds downwards from the top so that the coking process is thereby rendered slow at first (duration up to seventy-two hours). The Americans have not erred very far in retaining the use of round ovens for their "high-fat coals."

The "forest-clay coal" of Obernkirche produces a very large quantity of gas, so that there the method of coking in open "Meiler ovens" has been retained, in which, likewise, the coal itself is the source of heat. In South Wales the horizontal type of oven is employed; in Durham, on the contrary, the beehive type, because in the latter district the coking coal is much more bituminous than in the first-named basin.

In this way the kind of coal determines the use of one type of oven or another.

The suitability of a coal for coking is ascertained in the laboratory by determining the caking power and the yield of coke. For the various methods, Post's "Chemisch-technische Analyse," Kerl's "Probirkunst," Wedding's "Eisenprobirkunst," and others may be referred to.

It is evident that a determination of the coke yield by experiment in the laboratory cannot be a completely satisfactory test, since the theoretical yield of coke is generally higher than the practical yield with high temperature ovens and normal working. In every case, however, the crucible coking test gives a certain figure from which the coke yield may be inferred. The best and most reliable results, however, are got from experiments in the coke oven itself.

The causes of the divergence between the theoretical and practical yield of coke may be of many different kinds. In the first place, it is very difficult to obtain an average sample. Further, the laboratory method of heating is one quite different from that employed on the large scale. In the small crucible the coal quickly reaches a high temperature, the melting takes place fairly quickly and uniformly throughout the whole mass; the gases can escape quickly, and the coke that is finally got appears swollen to an extent which is never realised in actual practice. In the latter case, the distillation takes place against the resistance of a molten crust of ever-increasing thickness, and under the pressure of the oven gases. If, further, towards the end of the coking, the last portion of coal in the middle of the oven is decomposed, while the coal particles next the walls have been already for some time coked, the gas and steam rising from the middle pass over the already formed glowing coke and thereby become combined with as much as 2 per cent. of carbon.

The principal cause of the difference, however, is to be found in the destruction of carbon by burning, through air being admitted during the continuance of the coking process, and this is dependent upon three factors, viz., the mode of charging, imperfect closing of the oven doors, and the method of coking employed.

The more carefully the charge of coal is levelled in the oven so as to get rid of the elevations on the surface, the less frequently will a subsequent coking be necessary (which may often last several hours); this in itself has an effect on the yield of coke.

When the ovens are being charged a large quantity of cold air streams in at once, and the same takes place on opening the oven doors. In this way, not only is a part of the carbon lost, and smoke—which is in many ways troublesome and injurious to health—produced, but the temperature of the flame is lowered, and in consequence the transmission of heat to the coal particles to be heated is lessened. Under these conditions the fumes contain not only soot, *i.e.*, unburnt coal, but also carbon monoxide, which, if a larger quantity of heat were developed, would be able to burn.

The method of coking exercises an influence upon the amount of loss by burning. Where the walls of a newly charged oven become at once heated to a very high temperature, the first gases which do not need a great heat for their production will come off somewhat violently, and towards the end of the coking process, when they are absolutely necessary for the production of the very high temperature that is required to complete the process, they fail. The consequence of this is that the coke burner must permit air to enter through the sight holes, in order that, by the burning of a part of the carbon, he may make compensation for the failing supply of heat, and this naturally at the expense of the yield.

It appears to be advisable, therefore, to allow the gasification to proceed slowly at first, and afterwards at a continually increasing temperature in order to lessen the surface burning of the charge. A further reduction of this burning is made if the air for combustion meets with the gases from the coking at their exit from the oven space, and the combustion takes place not in the oven space but in the lateral flues. The last protection from burning is to be found in the quickest possible cooling of the coke mass on its withdrawal from the ovens.

In the case of beehive ovens it is impossible to avoid the burning of a part of the carbon, since a quantity of air must be admitted into the oven to allow the process to go on. Thus Connelsville coal (U.S.A.) containing 59·62 per cent. of fixed carbon produces in beehive ovens 54·25 per cent. of coke carbon = 91 per cent. of the total fixed carbon; Miller coal (U.S.A.) containing 68·50 per cent. C, a coke with only 50·35 per cent. C = 73½ per cent. (Weeks' "Report on the Manufacture of Coke").

This experience has been met with, however, not only where the coking has been conducted in open ovens, but also where other systems have been in use. The Miller coal, already mentioned, with 68·5 per cent. of C, yielded in Belgian ovens coke carbon to the extent of 61·25 per cent. = 89·4 per cent. of the total.

In the case of Coppee ovens the difference is found to be still less, and in Westphalia amounts to 5-7 per cent. at most. In the case of ovens where tar and ammonia are recovered, the yield is several per cents. higher than in the ordinary coke ovens. This higher

TABLE I.*

SOURCE OF THE COAL.	Composition of the Ash-free Coal.			Hydrogen present per 1000 parts of Carbon.			Coke from Ash-free Coal.
	C	H	O + N	Free.	Combined.	Total.	
GERMANY.							
1. Average of 6 seams from the Carolus Magnus mine, - -	82·319	5·284	12·397	41·15	18·51	62·96	73·88
2. Coal with highest coke yield from the Carolus Magnus mine, - - - - - -	84·003	4·984	11·013	42·96	16·41	59·37	76·12
3. Coal with lowest coke yield from the Carolus Magnus mine, - - - - - -	79·887	5·404	14·708	44·61	23·01	67·62	71·74
4. Average of 11 seams from the President mine, - - -	88·124	5·264	6·612	50·36	9·37	59·73	77·70
5. Coal with highest coke yield from the President mine, -	88·807	5·185	6·008	49·93	8·45	58·38	79·80
6. Coal with lowest coke yield from the President mine, -	88·308	5·353	6·339	51·65	8·86	60·61	76·09
7. Average of 16 seams from the Courl mine, - - - -	86·201	5·145	8·654	47·07	12·55	59·62	78·24
8. Coal with highest coke yield from the Courl mine, - -	87·752	4·903	7·345	45·41	10·46	65·87	82·66
9. Coal with lowest coke yield from the Courl mine, - -	84·484	5·538	9·981	50·74	14·77	65·51	72·18
10. Coal from H. Beckstatt of the Roland mine,- - - -	88·128	5·241	6·631	50·05	9·41	59·46	81·63
11. Coal from the Sonnenschein seam of the Massen mine, -	87·097	3·941	8·962	32·38	12·84	45·22	83·65
LOWER SILESIA.							
12. Average of 9 seams from the Carl Georg Victor pit, - -	88·550	4·580	6·870	42·01	9·71	51·72	78·55
13. Coal with highest coke yield from the Carl Georg Victor pit, - - - - - - -	89·930	4·340	5·730	40·34	7·98	48·32	83·00
14. Coal with lowest coke yield from the Carl Georg Victor pit, - - - - - -	86·950	4·880	8·170	44·40	11·73	56·13	73·90
BELGIUM.							
15. Average of 6 seams from Mons, - - - - - -	88·660	4·880	6·460	46·00	9·12	55·12	77·80
16. Average of 7 seams from Centre. - - - - -	89·090	4·790	6·120	45·12	8·50	53·62	80·25
17. Average of 9 seams from Charleroi, - - - - -	89·290	4·800	5·910	45·16	8·28	53·74	81·00
FRANCE.							
18. Average of 5 seams from Denain near Valenciennes, -	86·790	5·540	7·670	51·72	11·06	62·78	67·2-65
19. Average of 9 seams of the Valenciennes basin, - -	87·750	5·190	7·060	49·09	11·05	59·14	73·1-67·7
20. Average of 3 seams—Lens, Hersin, and Bity-Montigny,	87·590	5·430	6·980	52·03	9·95	61·98	76·67
21. Coal from Rive de Gier, Henry pit, Bastard seam, - .	90·530	5·050	4·420	49·68	6·09	55·77	76·30
22. Coal from Rochebelle, near Alais, - - - - - -	90·550	4·920	4·530	48·08	6·25	54·33	77·70
23. Coal from Chaptal pit (Creuzot). - - - - -	88·480	4·410	7·110	39·77	10·06	49·83	80·40

* Muck, "Die Chemie der Steinkohle."

TABLE II.

		C	H	O	N	S	Ash.	Moisture.	Yield of Coke.
	AUSTRIA (1).								
1.	Ostrau district,	80·54	5·09	7·66	1·43	—	5·27	—	75·0
2.	,,	83·35	4·66	5·06	1·52	—	5·37	—	81·4
	HUNGARY (2).								
3.	,,	86·93	4·35	6·47		·86	·89	—	78·85
4.	,,	86·95	4·13	6·76		·99	2·85	—	83·14
5.	,,	80·67	4·38	6·30		2·83	5·82	—	82·82
6.	,,	69·59	4·12	9·35		5·53	11·41	—	77·81
7.	,,	79·63	4·46	4·68		·90	10·33	—	81·55
	RUSSIA (3).								
8.	,,	78·41	3·48	12·61		1·22	4·28	—	81·86
9.	,,	76·57	3·40	8·56		2·54	8·93	—	82·67
10.	,,	83·01	3·70	11·27		·62	2·02	—	87·13
11.	,	83·65	4·41	9·44		Trace	2·50	—	83·33
	ENGLAND (4).								
12.	Durham,	83·47	6·68	8·17	1·42	·60	·20	—	62·70
13.	South Wales,	83·78	4·79	4·15	·98	1·43	4·41	—	72·60
14.	Derbyshire,	79·69	4·94	10·28	1·41	1·01	2·65	—	59·32
15.	Lancashire,	77·90	5·32	9·43	1·30	1·44	4·88	—	60·22
16.	Northumberland,	78·65	4·6	13·66		—	2·49	—	—
17.	,,	82·42	4·82	11·11		—	·79	—	—
18.	,,	81·41	5·83	7·90	2·05	—	2·07	—	66·70
19.	,,	78·69	6·00	10·07	2·37	—	1·36	—	—
20.	Blaina, South Wales,	77·42	5·36	8·22	1·65	—	1·46	—	—
21.	,, ,,	—	5·71	5·93	1·66	—	2·45	—	—
22.	,, ,,	—	6·18	4·58	1·49	—	4·00	—	—
	NATAL (5).								
23.	Heet Dundee,	72·99	5·25	11·69	·80	4·02	7·32	1·95	77·54
24.	Smith Dundee II.,	75·32	4·73	7·25	1·01	2·28	10·03	1·66	78·52
25.	,, ,, I.,	76·65	4·68	7·62	1·78	2·80	7·35	1·92	74·66
26.	Meran Comp. VIII.,	75·37	4·43	5·90	·94	1·29	11·22	1·64	84·30
27.	,, ,, VI.,	75·07	4·29	6·08	·53	1·71	12·42	1·88	82·19
28.	Ramsey,	74·18	3·94	4·95	1·58	·42	14·18	1·17	84·03
29.	Elands-Saagte,	79·30	4·58	6·93	1·03	3·39	6·98	1·18	79·62
	NORTH AMERICA (6).		Volatile Constituents.						
30.	Connelsville,	59·616	30·107			·784	8·233	1·260	63·633
31.	Allegheny River,	55·545	35·520			·835	6·630	1·700	63·010
32.	,, ,,	88·360	1·106			1·076	9·228	·230	67·000
33.	Warrior Field,	71·640	28·240			·640	2·030	·120	73·670
34.	,, ,,	63·120	31·250			·890	5·630	—	68·750
35.	Cahaba Field,	59·590	34·370			·660	6·050	—	65·630
36.	,, ,,	60·530	34·60			·680	4·870	—	65·400

yield is the result of the complete exclusion of air, which is produced by the thick luting, with, at the same time, a slight excess pressure in the ovens. The smaller the entrance of air is, that is to say, the more rationally the coking is conducted on the large scale, the nearer will the practical yield of coke be to the theoretical.

The foregoing tables show the typical composition of coking coals from various countries, with the percentage of coke they yield.

NOTES TO TABLES.

1. W. Jicinsky, "Oesterr. Zeitsch. für Berg. u. Huttenwesen," No. 40, p. 528.

2. Weeks—"Manufacture of Coke."

3. P. Hagemans, "Stahl und Eisen," 1887, p. 261; and "Jahresbericht über die Leist. d. Chem. Techn.," 1887.

4. No. 12-15, Durre, "Neuere Koksofen," p. 24; No. 16-22, Weeks (*loc. cit.*).

5. R. Hefelmann and A. Jähn, "Chemiker Zeitung," 1889, p. 1190; and "Jahresber. über d. Leist. d. Chem. Techn.," 1889.

6. Weeks (*loc. cit.*).

CHAPTER III.

The Coking Process and its Influence on the form and appearance of the Coke.

THE manufacture of coke is conducted, as a rule, in air-tight ovens, which are heated from without by burning the combustible gases generated in the coking process itself, sometimes, as in the making of wood charcoal, by admission of air into the oven, which consumes a part of the carbon, and thus produces the temperature necessary for coking the remainder of the coal.

The chemical process of coking resembles that of carbonizing, and differs from it only in that it takes place at a more elevated temperature. In the process of carbonizing only the extra-radicle atoms or atomic groups, or, employing structural representations, only the side chains take part in the decomposition; in coking, on the other hand, the central part or radicle reacts as well.

The working of the coke oven is divided into the following stages:—

(1) Charging with coal.
(2) Heating the coal by means of the gases of the adjoining ovens.
(3) Coking.
(4) Drawing of the coke.

An attempt is here made to reduce the process of coking to a definite system, and to distinguish well-marked periods in its course. No great error will be committed, however, in looking askance at all such attempts, because in the conversion of the coal into coke continual changes are going on as it passes from the one condition into the other, without any sharp line of demarcation.

Such a succession of stages in the coking process ought rather to be made out for each individual particle of coal, seeing that every single particle changes gradually from the time of charging to the time of emptying, and, in fact, the course of the coking proceeds differently according as the particles of coal lie in the middle or in immediate contact with the hot walls. In consequence of this, different stages are simultaneously in progress in different parts of the coke oven.*

To effect the combustion a certain amount of air is requisite. This supply of air must be large enough to secure a combustion of gas adequate to produce the necessary temperature. The combustion will be more complete the more strongly the air is heated beforehand.

Coking naturally begins at those places where the air introduced from without acts with most effect, and hence, as soon as the ovens have been charged, an evolution of gas begins from that part of the coal which is contiguous to the hot walls, especially from the dust, as is evident from the smoke which issues from the open charging holes.

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* "Stahl und Eisen," 1894, Nos. 5 and 6, "Ueber den Verkokungsprocess."

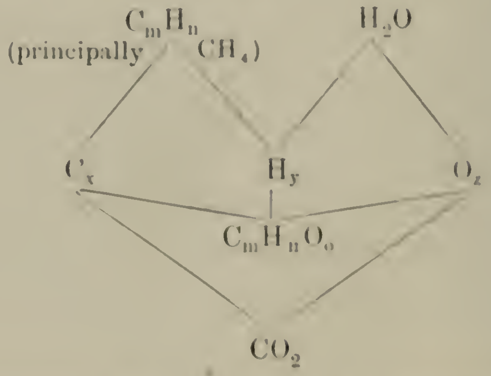
As soon as the mass of coal comes in contact with the heated walls, the surface of the charge becomes covered with a porous, molten crust, from which the melting proceeds towards the centre. This molten crust increases continually in thickness, and, in proportion as it does so, the production of gas from the central particles of coal slackens.

While the coking gradually progresses in the interior of the charge, a decomposition takes place by the action of the water contained in the coal and the air originally present in the oven. A series of new products is formed. The first part of the water goes off unchanged with the bulk of the oxygen present before a red heat is reached; but, owing to the low conducting power of the coal for heat, the other part, namely, the moisture present in the interior of the charge, is only expelled when the external portion of the coke mass is already at bright redness. In passing through the hot layers this water is decomposed, and carbonic acid and carbonic oxide are formed along with free hydrogen according to the equations,

$$H_2O + C = H_2 + CO$$
$$2H_2O + C = 2H_2 + CO_2$$

The evolution of gas begins at a temperature as low as 100° C., and increases with rise in temperature till the point of actual decomposition is reached, viz., a dark red heat. In the earlier stages of the process the gas comes off very violently, but afterwards the evolution proceeds with greater regularity. The "free hydrogen" unites with a portion of the carbon to form gaseous compounds, and there are formed in particular, marsh gas (CH_4), olefiant gas (C_2H_4), and liquid tarry products, even at a temperature of 500°-600°. Simultaneously with these, compounds of the three elements are produced, the boiling points of which lie far below the temperature at which they are formed, and which are in consequence at once evolved in the gaseous condition.

The highest temperature reached during the process of coking is about 1400° C., which subsequently towards the finish falls to about 800° C. when the coke is drawn. The following scheme in which for the sake of simplicity nitrogen and sulphur are omitted as negligible quantities, will sufficiently illustrate the coking process:—



With reference to the nature of the reactions which take place in the coking of coal and the extent to which they go on, accurate experimental work has still to be done; and indeed so long as the composition of coal is unknown, the peculiar internal reactions of coking will assuredly remain shrouded in obscurity.

The organic compounds which constitute the coal are destroyed by the heat prevailing in the coke oven, and the products of decomposition unite again with each other in new combinations, which are stable at the elevated temperature that exists. The nature of the volatile products thus formed depends, therefore, essentially upon the latter factor. The higher the temperature that prevails, and the longer they are subjected to the heat, the more completely will the products at first evolved in the form of vapour be converted into the condition of permanent gases, and the more varied will the latter be in composition. The form of the oven, as well as the temperature employed, exerts an influence upon the character of the products, according as it leaves the gases for a longer or shorter period in contact with the heated walls. The mutual affinities of the products themselves also determine to some extent the ultimate result. The character of the coal used for coking naturally plays the most important part. The larger the quantity of hydrogen, and the smaller the quantity of oxygen it contains, the more numerous will be the products of decomposition which the former gives with the carbon. The following are the compounds formed in the distillation of coal, arranged according to the classification adopted in Wagner's "Chemical Technology" (13th Ger. edit., 1889):—

I. Coke;

II. Illuminating gas:

(1) Illuminants or light givers:

(*a*) Gases:

Acetylene, - - - - C_2H_2

Ethylene, - - - - C_2H_4

Propylene,	C_3H_6
Butylene,	C_4H_8
Allylene,	C_3H_4
Crotonylene,	C_4H_6
Valerylene,	C_5H_8
(*b*) Vapours:	
Benzene,	C_6H_6
Thiophene,	C_4H_4S
Styrene,	C_8H_8
Naphthalene,	$C_{10}H_8$
Methyl naphthalene,	$C_{11}H_{10}$
Fluorene,	$C_{13}H_{10}$
Fluoranthene,	$C_{15}H_{10}$
Propane,	C_3H_8
Butane,	C_4H_{10}
(2) Diluents or light supporters:	
Hydrogen,	H_2
Methane,	CH_4
Carbonic oxide,	CO
(3) Impurities:	
Carbonic acid,	CO_2
Ammonia,	NH_3
Cyanogen,	$(CN)_2$
Methyl cyanide,	CH_3CN
Sulphocyanogen,	CNS
Sulphuretted hydrogen,	H_2S
Sulphurated hydrocarbons, carbon disulphide,	CS_2
Carbon oxysulphide,	COS (probably)
Nitrogen,	N
III. Ammonia liquor:	
(1) Chief constituents:	
Ammonium carbonate,	$(NH_4)_2CO_3$
Ammonium sulphide,	$(NH_4)_2S$

(2) Secondary constituents:

Ammonium sulphocyanide,	NH_4CNS
Ammonium chloride,	NH_4Cl
Ammonium cyanide,	NH_4CN

IV. Tar (according to Schulz and others):

(1) Neutral compounds:

(*a*) Hydrocarbons:

(*a*) Fatty series:

		M.P.	B.P.
Crotonylene,	C_4H_6	liquid	25° C.
Amylene,	C_5H_{10}	—	30
Hexylene,	C_6H_{12}	—	71
Hydrocarbon,	C_6H_{10}	—	85
O. Jacobsen's hydrocarbon,	—	—	159
Paraffin,	—	solid	about 400

(β) Aromatic series:

		M.P.	B.P.
Benzene,	C_6H_6	+ 3° C.	81
Toluene,	C_7H_8	liquid	111
Orthoxylene,	C_8H_{10}	—	141
Metaxylene,	C_8H_{10}	—	141
Paraxylene,	C_8H_{10}	15°	137
Styrene,	C_8H_8	liquid	146
Mesitylene,	C_9H_{12}	—	163
Pseudo-cumene,	C_9H_{12}	—	169
Hemellithene,	C_9H_{12}	—	175
Terpene,	$C_{10}H_{16}$	—	171
Cymene,	$C_{10}H_{14}$	—	175
Tetramethyl benzene,	$C_{10}H_{14}$	—	—
Naphthalene di hydride,	$C_{10}H_{10}$	liquid	205
Naphthalene,	$C_{10}H_8$	80	217

		M.P.	B.P.
α-Methyl naphthalene, -	$C_{11}H_{10}$	—	243° C.
β-Methyl naphthalene, -	$C_{11}H_{10}$	32·5	241·5
Diphenyl, -	$C_{12}H_{10}$	71	254
Berthelot's hydrocarbon,	—	85	260
Acenaphthene,	$C_{12}H_{10}$	99	280
Fluorene,	$C_{13}H_{10}$	113	294
Phenanthrene,	$C_{14}H_{10}$	100	340
Fluoranthene, -	$C_{15}H_{10}$	109	above 360
Pseudo-phenanthrene, -	$C_{16}H_{12}$	115	above 360
Anthracene, -	$C_{14}H_{10}$	213	above 360
Methyl anthracene, -	$C_{15}H_{12}$	200	above 360
Pyrene, - -	$C_{16}H_{10}$	119	above 360
Chrysene, -	$C_{18}H_{12}$	250	above 360
Chrysogen, -	—	290	above 360
Parachrysene,	—	320	above 360

(*b*) Other neutral compounds present in coal-tar:

Carbon disulphide, -	CS_2	liquid	47
Ethylic alcohol,	C_2H_6O	—	78
Acetonitrile, -	CH_3CN	—	82
Water, -	H_2O	—	100
Carbazol, -	$C_{12}H_9N$	238	355
Phenylnaphthyl carbazol, -	$C_{16}H_{11}N$	330	above 440

		M.P.	B.P.
Thiophene,	C_4H_4S	—	84° C.
Thioxene,	C_6H_8S	liquid	137
(2) Acids:			
Sulphuretted hydrogen,	H_2S	—	—
Hydrocyanic acid,	HCN	—	—
Carbonic acid,	CO_2	—	—
Acetic acid,	$C_2H_4O_2$	17	119
Phenol,	C_6H_6O	42	182
Orthocresol,	C_7H_8O	31	188
Metacresol,	C_7H_8O	liquid	201
Paracresol,	C_7H_8O	36	199
Xylenol,	$C_8H_{10}O$	—	—
Isodurol,	$C_{10}H_{12}O_2$	215	—
α-Pyrocresol,	$C_{28}H_{26}O_2$	—	195
β-Pyrocresol,	$C_{28}H_{26}O_2$	—	124
γ-Pyrocresol,	$C_{28}H_{26}O_2$	—	104
Benzoic acid,	$C_7H_6O_2$	121	249
(3) Bases:			
Ammonia,	—	gas	—
Pyridine,	C_6H_5N	liquid	115
Pyrrol,	C_4H_5N	—	126
α-Picoline,	C_6H_7N	—	134
Lutidine,	C_7H_9N	—	154
Collidine,	$C_8H_{11}N$	—	179
Aniline,	C_6H_7N	—	182
Parvoline,	$C_9H_{13}N$	—	188
Corindine,	$C_{10}H_{15}N$	—	211
Rubidine,	$C_{11}H_{17}N$	—	230
Chinoline,	C_9H_7N	—	239
Chinaldine,	$C_{14}H_9N$	—	240
Viridine,	$C_{12}H_{19}N$	—	251
Lepidine,	$C_{10}H_9N$	—	257
Cryptidine,	$C_{11}H_{11}N$	—	274

		M.P.	B.P.
Acridine, - -	$C_{12}H_9N$	107	above 360

(4) Asphalt-forming constituents, Empyreumatic resins; carbon.

A portion of these substances comes directly from the coal; the rest arise from the decomposition of the first products. Thus, in the cooler parts of the oven more particularly, a re-condensation of many of the vaporised bodies will undoubtedly take place, and these will, at a more elevated temperature, again break up into substances of different composition. Under these conditions hydrocarbon bodies decompose with separation of carbon to form marsh gas; indeed, such decomposition begins even at as low a temperature as 600° C. The richer these hydrocarbon bodies are in carbon, and the greater the heat to which they are exposed, the more abundant is the separation of carbon ($C_2H_4 = C + CH_4$). Probably the hydrocarbons of the methane series are the first to be formed in this way, and from them, by loss of hydrogen, other bodies are in turn produced ($C_2H_4 = C_2 + 2H_2$). (Cp. Wedding's "Theory," p. 29.)

Since the affinity of carbon for the gaseous elements is increased at a high temperature, a larger part of it is carried off by them, and, consequently, the compounds formed at elevated temperatures are richer in carbon, but poorer in hydrogen and oxygen, than those which result at a more moderate heat—that is to say, the mode of combination of the carbon atoms at high temperatures cannot be regarded as a simple one (different from the unsaturated bodies of the fatty series), nor the chain as open, but what we find is rather a closed carbon chain, with the carbon atoms combined in different ways. Among the products formed at a low heat, therefore, fatty bodies will predominate, and these, at higher temperatures, will undergo molecular condensation to form aromatic bodies. It is thus possible to modify the distillation process so as to meet the end in view.

The coking process is finished when flaming ceases, but the distillation is not by any means completed at the same time. Generally speaking, the latter process is never a complete one in the coking oven, since the temperature that prevails is much too low. It is only when a greater heat is employed, such as, for example, is obtainable in various types of blast furnace, that it is possible to get a coke from which the volatile matter is completely expelled. In the product of the coking process hydrogen and oxygen are always retained, partly in the occluded state and partly in the form of highly stable compounds of carbon and hydrogen. (Cp. following chapter—Hydrogen.)

The evolution of gases from the coal during the process of coking causes—as distinguished from the initial swelling up, which ceases at about 600° C.—a continuous contraction in the bulk of the coke produced from a certain quantity of coal, and this process goes on under ordinary conditions till the distillation is finished. The pores of the coke, which during the period of their formation are influenced to a certain extent by the gases contained in them, become towards the end of the process definite in shape and size, and this is not affected even by the subsequent operation of quenching. No credence can be given to the view that a diminution in bulk is produced by the quenching of the coke.

The packing of the coal in the ovens appears to exert an influence upon the coking process. The more loosely the coal is filled into the ovens, the larger is the quantity of air which remains in the chamber to produce those injurious effects, as regards loss of carbon, which have been indicated in the preceding chapter.

By means of the packing appliance of Quaglio the bulk of the coal is lessened to the extent of 25 per cent.; consequently, by the packing, it is made to fill a space only three-fourths of what it occupied in the loose condition, and the coke produced is about 25 per cent. more dense. By means of the packing the coal particles are made to lie more closely and smoothly upon one another, in consequence of which they cake together, when subsequently heated, much more readily than when they are only loosely filled into the ovens. Water acts as a binding material, but, that the time required for treatment may not be prolonged, it is desirable that only a small quantity of moisture should be contained in the coal.

With similar charges the period of treatment may vary according to the quality of the coal and the type of oven used (particularly with differences in the cross-section of the latter). As a rule, the period required for coking varies from twenty-four to seventy-two hours. The cross-section of the oven chamber is—

For 48-hour Coppée ovens, - 1·6 × ·6 = ·96 sq. metres.
„ 24 „ „ only 1·0 × ·5 = ·5 „
or 1·3 × ·4 = ·52 „

The time of treatment is therefore in direct proportion to the sectional area. For coals that swell up strongly narrow ovens are the most suitable, since in them the charge can be rapidly raised to a high temperature.

When the distillation is complete the coke consists of more or less firm aggregations of fixed carbon particles. In consequence of the shrinkage and splitting of the glowing prism of coke as it issues from the oven, the pieces are cleft asunder in a manner similar to basalt, the columns lying more or less irregularly in the direction of the lines along which the heat advanced.

The mass of coke got from Coppée ovens is found to be severed along the middle line, which is to be ascribed to the fact that coking proceeds from the walls towards the centre of the oven. The planes of cleavage are horizontal, and thus the length of the separate pieces cannot exceed half the width of the oven at most. If a uniform heat prevails, the plane of separation lies exactly in the centre, but if one of the side walls is more strongly heated than the other, the plane of separation is pushed further forward. If the plane of cleavage is not sharply marked, either the coking has been imperfectly performed at this point or the effects of the heated surfaces have interfered with one another; the coke is then frothy and coarse.

In the case of narrow ovens the plane of separation of the pieces abutting on the walls stands perpendicularly in the centre of the oven; in wide ovens it lies horizontally in the middle of the charge, and if the coke mass be approximately square in cross-section, and be heated uniformly on all sides, it is formed by the middle line of the coke, the cleavage planes passing radially from it. *Width of oven and temperature of coking stand, therefore, in a definite relation to one another* (Remy).

A section through the coke in a Coppée oven shows the varying effect of the heat as the coking proceeds. Part of the coal is carbonised mainly under the influence of the heat transmitted through the base, another part by that passing through the arch, and between these are situated certain portions which are coked by the heat of the side walls. The more strongly the oven is heated in any one of the above-mentioned parts, the further does the coking proceed on that side. *From the appearance of the coke body, therefore, it can be inferred whether the passage of the heat was uniform or not.*

In beehive ovens the coking process is a descending one, since the heating proceeds from above. The cleavage surfaces of the coke are consequently vertical, and hence it is that in beehive ovens very long columnar pieces of coke are got.

If the coking process proceeds normally, the sides of the coke mass exhibit the so-called "cauliflower heads." Black heads may usually be regarded as indicative of incomplete carbonisation. The black appearance may arise, however, from the fact that, when the coke is being drawn from the oven, certain portions of it always come to some extent in contact with air. The more rapidly the coke is quenched, the less frequently do such blemishes occur. If, on the other hand, the oven is working abnormally, the coke is formed in thick, massive pieces, it is "lumpy," and frequently appears molten, especially in the middle, where more or less bad uncoked portions are left. In this case the coke has very little hardness, and presents a dirty, black appearance, the latter being accompanied on the sides of the "heads" by a greenish lustre. These badly-coked portions are very prejudicial to the employment of the product in the furnace, since, on account of their inferior hardness, they are particularly exposed to the destructive action of the carbonic acid, and, at the same time, are unable to withstand the attrition to which the charge is subjected. This abnormal working is avoided by using greater heat. The increase of temperature promotes the passage of the heat to the interior of the oven, so that there the coking takes place under the influence of a higher temperature, and better coke is the result. The more uniform the coke is, the more useful is it for quick furnace work, *and for obtaining a uniform quality of coke, the maintenance of a uniform temperature, and a uniform distribution of gas and of air for combustion, is a necessary condition.*

In the manufacture of English round-oven coke ("Conditions of Coking") the coking process is not allowed to complete itself; more or less deep rents soon appear in the coke, so that all the carbon compounds are not coked, although it is not to be concluded in every case, where an excessive amount of oxygen and hydrogen is present, that the coking has been insufficient. Even well-burnt cokes frequently show 8-9 per cent. of hydrogen and oxygen together in the ash-free substance. In the former case the coke has usually a dull, graphite colour. When this happens, the temperature of the oven has undoubtedly been too low, or the period of treatment has been insufficient.

In coke from "lean" coal, transverse cracks often appear, especially in forced working. The product in such circumstances contains much "Knabbelkoks," similar to gas coke. In the case of very "fat" coal, and of coal which is very uneven in size, the cleavages of the coke, especially in isolated spots, are often fairly frothy, and in such places the so-called "coke-hairs" frequently appear also. The latter are—according to Wedding—formed of carbon separated at high temperatures from hydrocarbons rich in carbon ($C_2H_4 = C + CH_4$), while, according to Muck, they consist of solid compounds of carbon, hydrogen, and oxygen. (Cp. p. 81.)

Coke can be produced in large and small pieces, the size depending upon the height of the charge and on the degree of heat. Very heavy charges produce a large quantity of small coke; a low charge does the same, and yields only a small quantity in bars, which is the form desired by the blast-furnaceman. In practice, the height of the charge at Saarbrücken is 1·2 M. (47¼″) when the width of the oven is 1·2 M. (47¼″), and ·85 M. (33½″) with an oven width of ·9 M. (35½″). Moreover, the more intensely the ovens are heated, the more frequently do cleavage surfaces occur, and the smaller are the pieces of coke produced. In order to produce coke in large pieces, therefore, the temperature must not be allowed to rise above a certain definite limit. Powerful draught, admission of cold air, and, with it, rapid burning, cause likewise the splitting and crumbling of the coke on cooling. It is customary to give the ground used for quenching a slight inclination, and to cover it with a good layer of tiles or a smooth pavement, to prevent premature breaking-up of the mass of coke when it is drawn from the oven.

Coke which is manufactured in ovens is got in larger pieces than gas coke. The size of the latter is determined by the radius of the gas retort, for, since the retort is fired on every side, and the coking consequently proceeds from the periphery to the centre, no piece of coke can be of greater length than the radius of the gas retort. In addition to this, the unequal, and, for the most part, large size of the pieces of gas coal, which is usually introduced into the retorts simply as raw coal (Förderkohle—nuts and dross mixed), the shortness of the period of treatment and the rapidity of the distillation all operate to produce the same result. The process is not continued until all the gas is driven off—that which is evolved last being very poor illuminating gas, and useful chiefly on account of its heating power—but, after a certain time, the mass of coke still retaining gas is withdrawn from the retort and quenched. The rapid cooling, along with the action of the gases contained in the pores, causes it speedily to crack up. Gas coke varies, however, in the degree of friability it exhibits according to the quality of the coal used, and, of recent years, crushing machinery has been put down at the gas works to break the gas coal to pieces of a definite size.

To return to the question of oven coke, there is formed on the hard coke at both ends of the oven, where the doors are situated, a layer, more or less extensive, which is frothy in appearance and very friable. Such frothy coke results from the swelling-up of particles of coal in which the coking process has not been completely effected, owing to the cooling produced by the doors. It is advisable, therefore, to slope the charge forward in front of the two doors, since these are the coolest parts of the oven. This friable and brittle portion of the coke amounts, however, to only a few per cents. by weight, and under normal conditions of working well-burned coke should give only 4-6 per cent. of "small." This holds particularly for foundry coke.

Coke from ovens in which bye-products are recovered shows as much as 8 per cent. of spongy pieces, which must always be retained at the coke works. They appear principally in the upper layer, and next the doors, because at these places the gases are most rapidly sucked out.

The colour of coke is sometimes black and lustreless, sometimes light grey, with a brilliant metallic or silvery lustre, occasionally showing a play of rainbow colours. The latter is seen especially in coke from tar ovens, but also in ordinary coke, although less frequently and in smaller quantity. Pointing, as it does, to a high content of sulphur, its appearance is not regarded with favour. (Cp. p. 103.)

Good coke should appear silver white to light grey in colour, but when in the state of powder it has always a dark grey or black appearance. In the case of washed coke, the colour is uniform; unwashed coke, on the other hand, is traversed by more or less dingy-coloured streaks. On the surface of the mass of coke a white appearance is also frequently caused by the presence of ash where the carbonaceous constituents have been removed by burning. Where anthracite has been added, coke always shows small, bright, glancing plates, which consist of pure carbon.

Neither gas coke, nor that made in ovens from which the bye-products are recovered, possesses the silvery lustre, both being, for the most part, very dark coloured. This arises from the separation of carbon from those products of distillation which are very rich in carbon. In the case of ovens where the bye-products are not collected, air always gains access, and this prevents the separation of carbon, while the same fact explains why the coke made in round ovens has such a bright silvery colour.

Consequently it is not always possible to draw conclusions as to the quality of the coke from its colour. Westphalian Coppée coke, for example, is, both in respect of its chemical and physical properties, a more excellent material for blast-furnace work than round-oven coke, although it does not possess the fine silvery lustre that catches the eye.

If the coke, after it has been completely carbonised, be allowed to remain for any length of time at the temperature which prevails in the oven towards the end of the period of treatment, this has the effect of imparting to it a metallic glance or of increasing the latter when it is already present. On the other hand, the appearance of the finished coke is largely dependent on the quality of the water used for quenching. If the latter is dirty, the solid matter deposits upon the white surface of the coke and gives it a nasty foul appearance, especially if a heavy stream of water has been employed. The greater the purity of the water used, the brighter and more lustrous is the appearance of the coke. At the Westphalian mines, for the most part, a mixture of pure lake water or of that brought by supply pipes from the river Ruhr, with pit water previously clarified, is employed for quenching purposes, or preferably the former is used alone.

Should a great deal depend upon the appearance of the coke, it is best to perform the quenching in a shed erected on a sort of embankment in front of the oven. Quenching in the oven itself imparts a smooth surface and metallic lustre to the coke, but at the same time it causes a loss of carbon by the decomposition of the steam thus—

$$C_2 + 2H_2O = CH_4 + CO_2. \quad \text{(Cp. p. 97.)}$$

The surface of the mass of coke is generally rough, but frequently, except in coke quenched in the oven, that part of the charge which was next the wall is smooth and vitrified, and has a graphitic appearance.

In particularising the different kinds of coke, it is spoken of as hair-shaped, pipe-shaped, stalactitic, and cubical coke.

Good coke should have a metallic ring; a dull, heavy ring indicates inferior quality.

CHAPTER IV.

Chemical Composition of Coke.

Coke is generally regarded only as carbon contaminated with a certain amount of mineral matter. Such a view is, however, incorrect, since besides carbon and ash, coke contains hydrogen, oxygen, nitrogen, and organic sulphur. Underneath are given analyses of cokes of different composition—

ANALYSES OF TYPICAL EUROPEAN COKES.

Origin.	C.	Ash.	Sulphur.	H.	O.	N.	Analyst.
Germany (*a*).							
1. Westphalia,	85·060	6·400		·860	7·680	—	Dr. Muck.
2. ,,	91·772	6·933		1·255	·040	—	,,
3. ,,	83·487	10·309		·737	5·467	—	,,
4. Saar,	86·460	8·540		1·980	3·020	—	,,
Belgium (*b*).							
5. Seraing,	80·850	16·510		·510	2·130	—	I. L. Bell.
6. Mons basin,	91·300	6·200	—	·330	2·170		M. de Marsilly.
7. ,, ,,	91·590	5·890	—	·470	2·050		,,
England (*b*).							
8. Durham,	93·150	3·950	—	·720	·900	1·280	Richardson.
9. ,,	91·580	6·860		·230	1·310	—	I. L. Bell.
10. ,,	91·490	6·320		·460	1·730	—	,,
11. ,,	92·980	4·610		·300	2·110	—	,,
12. ,,	92·000	·700		·200	7·300	—	Baer.
13. ,,	93·040	5·090		·260	1·610	—	,,
14. ,,	84·360	9·150		·187	·303	—	J. Percy.

ANALYSES OF TYPICAL EXTRA-EUROPEAN COKES.

Origin.	C.	Ash.	Sulphur.	Moisture.	Vol. matter	Sp. Gr.	Analyst.
AUSTRALIA (*c*).							
15. N.S. Wales, -	88·086	10·456	·594	·538	·328	1·311	C. H. Mingaye.
16. ,, ,, -	90·880	7·930	·420	·310	·460	1·339	,,
17. ,, ,, -	84·210	14·050	·508	·698	·525	—	,,
AMERICA (*b*).							
PENNSYLVANIA.							
18. Connellsville, -	89·576	9·113	·821	·300	·460	Undet.	M'Creath.
19. ,, -	89·150	9·650	1·200	—	—	—	B. Crowther.
20. Irwin's, - -	88·240	9·414	·962	—	1·384	—	Carnegie Br's. & Co.
21. Allegheny Mts., -	87·580	11·360	1·060	—	—	—	M'Creath.
22. Blossburg, - -	84·760	13·345	·998	·175	·722	—	,,
23. Allegheny River,	85·777	11·463	2·107	·330	·623	—	,,
24. Beaver County, -	84·727	12·636	1·994	·100	·633	—	,,
WEST VIRGINIA.							
25. New River, - -	93·850	5·850	·300	—	—	—	J. B. Britton.
26. ,, ,, - -	92·180	6·680	·618	·110	—	—	,,
27. ,, ,, - -	93·000	6·730	·270	—	—	—	C. E. Dwight.
28. ,, ,, - -	92·220	7·530	·910	—	—	—	,,
OHIO.							
29. Leetonia, - -	93·750	5·380	·870	—	—	—	Prof. Wormley.
30. Steubenville, -	90·630	8·380	·270	—	—	—	Dr. Wuth.
TENNESSEE.							
31. Tracy City, - -	83·364	15·440	·142	—	—	—	Land.
32. Whitesides, - -	94·560	4·650	·790	—	—	—	Etna Coal Co.
33. Rockwood, - -	84·187	14·141	·182	—	—	—	Land.
ALABAMA.							
34. Warrior Field, -	88·224	11·315	·563	·362	·900	—	Prof. M'Calley.
35. Cahaba Field, -	84·035	15·216	·445	·083	·660	—	,,
ILLINOIS.							
36. Big Muddy, - -	88·180	10·070	·610	—	·930	—	T. M. Williamson.
COLORADO.							
37. El Moro, - -	87·470	10·680	·850			—	,,
38. Crested Buttes, -	92·030	6·620	—	1·85		—	,,
				1·35			

(*a*) Muck, "Steinkohlen Chemie."

(*b*) Weeks (*loc. cit.*).

(*c*) Report of the Geological Department Office of Mines, Sydney, 18th September, 1890.

Carbon.—The carbon of coke comes principally—

(1) From the carbon directly remaining from the coal: (further),

(2) From the carbon separated through the high temperature from hydrocarbons; and, finally,

(3) From the incompletely carbonised products of distillation.

A consideration of the different sources of the carbon which is contained in coke readily explains the variable composition of the specimens mentioned above.

In Westphalian coke the carbon amounts, as a rule, to 95-98 per cent. of the ash-free substance, although cases occur where the quantity of carbon is less, and, indeed, it may fall as low as 90 per cent. (Cp. Table I.)

Since, in the process of coking, a large quantity of hydrogen and oxygen, but relatively only a small quantity of carbon, is driven off, the coke that is left is naturally richer in the latter element and poorer in the former ones than the coal employed in its manufacture, so that in consequence the calorific power is considerably enhanced. By comparison, ash-free coking coal contains on an average only 82-84 per cent. of carbon—that is to say, about 10 per cent. less than coke.

Hydrogen and Oxygen.—The existence of hydrogen and oxygen in coke is to be explained by the circumstance that the coke is not completely carbonised in the coke oven, but retains gaseous bodies and especially hydrogen in no inconsiderable quantity. The longer the coking process lasts, and the higher the temperature at which it is carried out, the freer is the coke from hydrogen and oxygen, although these gases are, nevertheless, always to be reckoned with. Thus John Parry * succeeded, even after heating coke to redness in the Sefström oven, in extracting gas from it with the air pump. Twenty grms. of coke heated under these conditions yielded after—

	CO_2.	O.	H.	CO.	CH_4.	N.
1. 2½ hours, 301·5 ccs. gas of composition, - - -	22·8	·00	50·00	13·49	13·80	·00
2. 7 hours, 586 cms., - -	3·10	—	93·45	3·30	—	—
3. 1½ „ 65·60 „ - -	5·72	—	89·13	5·15	—	—
4. 1½ „ 80·00 „ - -	4·81	—	90·09	5·11	—	—
5. 1 hour, 62·50 „ - -	9·65	—	89·05	·70	—	—
6. 1 „ 21·60 „ - -	9·38	—	81·20	8·20	—	1·215

From three samples of coke which were different in physical properties, Parry obtained the following results:—

(1) Hard, well-burned coke; 20 grms., treated for two hours under the Sprengel pump, yielded 79·2 ccs. of gas of the following percentage composition:—

Carbonic acid, - - -	85·720	per cent.
Carbonic oxide, - - -	8·590	„
Hydrogen, - - - -	5·680	„
Nitrogen, - - - -	·000	„

(2) Hard coke made from a mixture of different varieties of coal gave, with two hours' heating under the air-pump, 42·4 ccs. of gas, containing—

Carbonic acid, - - -	57·413	per cent.
Carbonic oxide, - - -	28·562	„
Hydrogen and nitrogen,† -	14·025	„

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* "Chem. News," 25, 98; Dingler's pol. J., 204, 470; Muck, "Steinkohlen Chemie," p. 153.

† Both were present, the former being recognised by explosion, although not separated from the latter.

Analysis of the foregoing sample of coke:

Ash, - - - - -	12·100	per cent.
Sulphur, - - - -	1·400	,,
Loss at a red heat, - -	1·500	,,
,, under Sprengel pump, -	·586	,,
Carbon (by difference), - -	84·414	,,

(3) Ordinary coke which had lain for some time exposed to air; a badly-coked sample: 20 grms., in two hours under the Sprengel pump, yielded 91·7 ccs. of gas, which contained—

Carbonic acid, - - -	39·020	per cent.
Carbonic oxide, - - -	7·673	,,
Hydrogen, - - - -	53·317	,,
Marsh gas (CH_4), - -	trace	
Nitrogen, - - - -	·000	,,

Analysis of this sample of coke:

Ash, - - - - -	14·000	per cent.
Sulphur, - - - -	1·370	,,
Loss at a red heat, - -	4·820	,,
,, under Sprengel pump, -	1·000	,,
Carbon (by difference), - -	78·810	,,

Weak coke was found always to exhibit the largest quantity of hydrogen, while, on the other hand, it contained little or no nitrogen.

Parry held the view that the hydrogen retained by the coke is simply occluded like the gases enclosed by white pig iron. Muck, however, ascribes the presence of hydrogen and oxygen to the existence of solid carbon compounds, which are stable on heating, and in support of his contention points to the composition of the "coke-hairs." These consist, according to B. Platz, of—

95·729 per cent. C,
·384 ,, H,
3·887 ,, O, and
·815 surplus oxygen (over that required to satisfy the H.).

Since the coke-hairs contain no ash, they are undoubtedly something different from the remainder of the coke; they are, in fact, the carbonaceous residue of tarry products of distillation. The composition, indeed, is similar to that of the hard pitch from tar (Muck).

Dr. Thörner ("Stahl und Eisen," 1886, No. 2, p. 71, *et seq.*) likewise turned his attention to the gases retained in coke. Thörner dried samples of coke and wood charcoal, in pieces the size of lentils, at a temperature of 140° to 150° C., so that the hygroscopic water was driven off. Of these samples, similar quantities—about 1 grm. of coke and ·5 grm. wood charcoal—were heated to whiteness in a current of pure dry hydrogen for fully thirty minutes in a specially constructed apparatus (represented on p. 78 *loc. cit.*), by which means naturally all oxidising action was excluded. In these experiments Thörner observed the occurrence of larger or smaller losses—averaging in the case of coke 1·34 per cent.—which could have resulted only from the evolution of gas locked up in the pores. He also found that considerable quantities of hydrocarbons were present in the coke, and in the wood charcoal, carbonic acid and carbonic oxide as well.

The experiments of I. L. Bell ("Stahl und Eisen," 1885, p. 300) established the fact that a diminution in weight takes place at a temperature of about 510° C., a result which can be ascribed only to the loss of volatile bodies. Bell obtained the following numbers:—

(1)	Coke from beehive ovens, -	1·41	per cent. loss.
(2)	,, ,, -	1·41	,,
(3)	,, ,, -	1·41	,,
(4)	,, Simon-Carvès ovens,	2·40	,,

It is thus evident—seeing that in the process of coking a temperature prevails at least as high as that employed by Thörner and Bell in their investigations—that Muck's objection to the view of Parry that hydrogen and oxygen are occluded cannot be looked upon as the last word in the matter. The conclusion seems rather to be that hydrogen and oxygen are retained in coke in two forms—

(1) In the form of solid carbon compounds, which are stable on heating;

(2) In the form of hydrocarbons, &c., which are enclosed in the pores.

According to Thörner the gases retained in the pores cannot, by reason of their low tension, make their escape from the hard-baked mass of coke in the interior of the oven; but this, naturally, they have no difficulty in doing in the case of the material used for investigation, which is broken to the size of lentils. The view which Thörner goes on to express that "the pores in the pasty coke mass that has undergone reaction are substantially larger, and only afterwards, on cooling, become contracted," is one that cannot be assented to. (Cp. p. 66.)

The following table gives the losses found by Thörner in his experiments:—

(1)	Retort coke,	·25	per cent. loss.
(2)	Dannenbaum, near Bochum,	·75	,,
(3)	Ordinary Coppée coke, Cologne, Müsener Union,	1·13	,,
(4)	Pressed coke, Cologne, Müsener Union,	1·15	,,
(5)	Pressed coke, Cologne, Müsener Union,	1·40	,,
(6)	Coke from Karlsglück and Planetenfeld, Dortmund field,	1·55	,,
(7)	Coke from Maas, Tief Bau, Maas Mine,	1·70	,,
(8)	Coke from Westhausen, near Bodelschwingh,	1·70	,,
(9)	Beech charcoal,	11·80	,,
(10)	Oak ,,	13·20	,,
(11)	Birch ,,	13·20	,,
(12)	Pine ,,	17·90	,,
(13)	Meiler coke,	29·70	,,

This loss in weight is smallest in the case of gas retort coke, and largest in the case of meiler coke, The more complete the carbonisation of the coal the less will be the loss. Hence it is evident that in the case of tar coke, where the evolution of the gases is assisted artificially by exhausters, the enclosed gases will be present in appreciably smaller quantity than in Coppée coke.

The following sentence with which Thörner concludes his observations has considerable interest:—

"The fact is worth noting in connection with these researches, that the fuels which are known to give the best reducing effects in the blast furnace, viz. wood charcoal and meiler coke, are generally those which yield the largest quantities of volatile hydrocarbons or products of decomposition."

Of the hydrogen which is contained in coke, only that which is "free" evolves heat, the combined hydrogen conducting itself as if it were already in combination with the quantity of oxygen necessary to form water. This water is called "chemically combined" water, as distinguished from the hygroscopic. Not only does this combined hydrogen itself yield no heat, but it also uses up a part of the heat evolved by the carbon.

The oxygen which is present in coke is equally deserving of attention, since, in the operations of the blast furnace, where the end in view is to secure the combination of the oxygen of the ore with the carbon of the carbonic oxide produced from the coke, the heating power of a coke containing much oxygen is reduced. In consequence of this, a coke of great purity, so far as ash in concerned, has less heating power if the quantity of oxygen and water which it contains is greater in proportion, since in this case not only is the percentage of carbon diminished, but heat is consumed over and above.

In the case of Westphalian coke, the amount of hydrogen retained in the coke varies from ·2 to almost 2 per cent. English cokes show less. Oxygen varies in quantity from a trace up to about 8 per cent.

Hygroscopic Water.—Coke is very slightly hygroscopic, notably less so than wood charcoal; even a few per cents. of water resulting from the quenching process, or from access of rain, make the coke sensibly wet. This water resides in the pores of the coke, and when the latter is broken into small pieces it evaporates very quickly to a small fraction of a per cent. Completely dry coke does not absorb more than 1-2 per cent. of water from air saturated with moisture.

The quantity of hygroscopic water increases with the size of the pores, and, to a less extent, with the number of the pores. Dense coke has always less moisture than porous, yet the latter has at the most only 1 per cent. more than dense coke.

The unequal porosity of different pieces of the coke mass naturally involves a very variable absorptive capacity for water. Thus, the moisture in the upper part of the coke mass is appreciably higher than towards the middle (in the case of Coppée coke). In two different makes of coke O. Simmersbach found at the top about 6 per cent. of water, and in the middle only ·25 per cent.

The following are the exact numbers:—

I.	II.
Top, 5·92 per cent. moisture.	5·41 per cent. moisture.
5·49 ,,	4·78 ,,
·30 ,,	·42 ,,
·23 ,,	·26 ,,

To obtain comparable results careful attention must be paid to the sampling of the coke. For estimation of water in coke, see,* among others, W. Thörner ("Stahl und Eisen," 1888, p. 591).

The quantity of water contained in the coke is of great importance. In stuff which is being put on the market the moisture should not exceed 4 per cent.; no great error will be committed, however, in taking the average as being from 5 to 6 per cent. Higher numbers are exceptional. Round-oven coke, with an almost smooth surface, takes up the smallest quantity of water, and, on account of the gases enclosed in it, and its smooth surface, it swims on water.

The hygroscopic water is driven off in the blast furnace at about 100° without any further decomposition of the fuel. In effecting the vaporisation, a part of the heat is rendered latent and the calorific value is correspondingly lowered; in fact, the daily consumption of coke is increased or diminished by about ·125 ton for every 1 per cent. of water in the coke. (Cp. Lürmann, "Stahl und Eisen," 1884, No. 5.) The greatest possible care must therefore be taken to ensure the dryness of the coke.

In consequence of this, attention must be paid to economy in quenching. A great deal depends especially upon the manner in which this is done. If a heavy stream of water be employed, the coke is wetter than if quenched by sprinkling or from above. The coke-burner continues the quenching till the coke no longer appears red hot in daylight; when the quenching is done at night, however, the redness is apparent for a

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* A detailed sketch of the various methods of estimation is given in Chap. vii.; reference may also be made to the abundant literature on the subject. (Cp. p. 49.)

greater length of time, and an excessive quantity of water may very easily be used under these circumstances, so that coke quenched at night contains more moisture than that quenched during the day (Muck). About 1 cubic metre of water is usually reckoned necessary for the quenching of one ton of coke.

Nitrogen.—The nitrogen contained in coal comes principally from previous access of air, but also from nitrogenous substances associated with the cellulose (albuminoid or proteid bodies) which have escaped destruction, and partly from animal remains which are known to be present in the coal.

The nitrogen is present in quantities ranging from ·4 to 2·49 per cent.

Coal from	Westphalia	shows	·84—1·77	per cent. N.
,,	Upper Silesia	,,	2·49	,,
,,	Ostrau	,,	·90—1·76	,,
,,	England	,,	1·14—2·37	,,
,,	N. America	,,	1·20—2·00	,,

Coal usually contains more nitrogen the greater the quantity of volatile constituents, and especially of oxygen. Professor Andrews found a relatively large amount of nitrogen in the case of a coal from Ohio. Analysis of the coal gave the following composition:—

Carbon, - - - - -	76	per cent.
Hydrogen, - - - - -	5·75	,,
Water, - - - - -	5·25	,,
Oxygen, - - - - -	9·53	,,
Nitrogen, - - - - -	2·15	,,
Sulphur, - - - - -	·75	,,
Ash, - - - - -	5·80	,,

(Cp. p. 54, No. 19.)

In the Franco-Belgian area, according to Rossigneux,* the quantity of nitrogen in "semi-fat," and especially in "lean" coals, falls as low as ·7 per cent., and even ·44 per cent.; in England it is otherwise, the "lean" coal of Wolverhampton containing 1·84 per cent. N.

With reference to the nitrogen contained in coal, a distinction is made between the carbon- and the ammoniacal-nitrogen; the former remains permanently in the coke, the latter goes to form ammonia.

As regards the carbon-nitrogen, Dr. Knublauch states ("Stahl und Eisen," 1885, No. 8) that 31-36 per cent. of the total nitrogen contained in the coal remains behind in the coke, as is seen from the following table:—

	Nitrogen contained in coal.	Nitrogen contained in coke.	Proportion of N. to corresponding wt. of coal.	Proportion of N. of the coal left in the coke.
(1)	1·612	·737	·508	31·5 per cent.
(2)	1·555	·677	·480	30·9 ,,
(3)	1·479	·774	·532	36·0 ,,

Of the total nitrogen present in the coal, 31-36 per cent. was thus found to be retained in the coke, 10-14 per cent. appeared as ammonia, 1·5-2 per cent. as ferrocyanide, 1·00-3 per cent. was contained in the tar, while the remainder passed off with the gases as free nitrogen.†

In connection with the latter fact, it may be appropriate to quote here the following results of Schondorff, who experimented on the oven and chimney gases of the Mansuy Coke Works:—

Number of Experiments.	CO_2.	CO.	N.	CH_4.
Mean of experiments on oven gases,	10·2	5·6	75·5	8·7
,, ,, 6 experiments on chimney gases,	9·9	6·0	75·5	8·7

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* Rossigneux, Ueber Koksfabrikation, Bull. de la soc. de l' ind. minerale, 1891, p. 387.

† See further Knublauch, "Jr. Soc. Chem. Ind.," 1896, pp. 106, 107.

Nitrogen is generally present in coke in quantities ranging from 0·4-1·5 per cent. Its amount bears no definite proportion to that of the original coal, since the nitrogen from some classes of coal combines more readily with the hydrogen, that from other classes less readily (Jičinsky, "Oesterr. Ztsch. für Berg- u. Hüttenwesen," 1888, p. 529). Corresponding to this, moreover, the nitrogen contained in the coal is not by any means proportional to that in the coke or to the ammonia obtained on distillation, as is specially evident from Nos. 1 and 3 of the following list given by Foster. Foster found nitrogen in coke from

		Per cent.		Per cent.
(1)	Durham coal, -	·842 = 48·7	of the N. in the coal	(1·730)
(2)	Yorkshire coal, -	1·099 = 62·8	,, ,, ,,	(1·750)
(3)	,, ,, -	1·101 = 65·9	,, ,, ,,	(1·670)
(4)	English cannel coal,	·875 = 52·7	,, ,, ,,	(1·660)
(5)	Scotch ,, ,,	·661 = 51·6	,, ,, ,,	(1·280)

According to this statement, therefore, 48-66 per cent. of the nitrogen contained in the coal remains behind in the coke ("Stahl und Eisen," 1885, p. 362). Hilgenstock ("Stahl und Eisen," 1885, p. 420) found less nitrogen in bright, silvery, hard coke than Foster. His figures were—

1st Experiment, - - -	·087 per cent. N.
2nd ,, - - -	·088 ,,
3rd ,, - - -	·287 ,,
4th ,, - - -	·227 ,,

The nitrogen can only with great difficulty be separated from the carbon, and is set free only by the complete combustion of the coke. The method of coking has a distinct influence upon the quantity of nitrogen which is thus retained. Watson Smith, for example ("Jr. Chem. Soc.," 1884, p. 144; also "Chemiker Zeit.," 36, p. 635), who investigated three kinds of coke, obtained the following results:—

Kinds of Coke.	Per cent. N.
Ordinary gas retort coke, - - - -	1·375
Oven coke from beehive ovens, - - -	·511
,, ,, Simon-Carvès ovens, -	·384

It follows from this that the strong heat of short duration in the gas retorts is less effective for the destruction of certain very stable nitrogen compounds of the coal than that of the Simon-Carvès oven, which is similar in degree but is maintained for a longer period.

According to J. Parry (*loc. cit.*) hard coke always contains more nitrogen than weak. (Cp. p. 80.)

The nitrogen of the coke has a detrimental effect in the blast furnace, since it dilutes the active gases and thereby hinders the reduction; it is found also in the furnace gases as ammonia. In the manufacture of soda the quantity of nitrogen in the coke is of importance, inasmuch as it causes the formation of cyanogen compounds.

The nitrogen in coke is most conveniently estimated by the method of S. Schmitz ("Stahl und Eisen," 1886, p. 47). Cp. also G. St. Johnson and A. Eilvart ("Chem. News," 53, p. 76).

Ash.—In the process of coking, the earthy and, generally speaking, all non-volatile substances are left behind; the residue is the ash. The quantity of ash in coke, therefore, is greater than that in the original coal, and is determined by the amount of coke obtained. Assuming a coke yield of 75 per cent., it will require about 140 parts of coal to produce 100 of coke; and, consequently, coking coal with 6 per cent. ash gives coke with $6 \times 1{\cdot}40 = 8{\cdot}40$ per cent. ash; 6-7 per cent. ash in the coal yields 8·40-9·80 per cent. ash in the coke, giving a mean of 9 per cent., which is a percentage that should never be exceeded in good coke.

In Westphalia, on an average, washed coke shows an ash of 7-10 per cent., half-washed coke has 9-12 per cent., and unwashed coke 12 per cent. and upwards of ash.

The greater part of the coke manufactured in Belgium is made from riddled coal: the ash contained in this riddled coal is from 12-15 per cent., so that the amount of ash in the coke manufactured from it often rises as high as 17 per cent.

Recourse is therefore had to mixing with washed coal which contains 5-7 per cent. of ash. In Belgium samples of this "coke lavé" have shown as much as 9 per cent. ash, "demi lavé" as much as 15 per cent. ash + water, and "ordinaire" over 15 per cent. ash + water, the latter amounting to 3 per cent.

With reference to American coke * a large number of analyses of Connellsville, representing 150,000 tons, showed ash falling within the limits of 9·11-10·91 per cent. 9·75 per cent. may therefore be regarded as the

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* See also p. 37.

mean quantity of ash contained in good Connellsville coke. The following table will serve to indicate the ash present in American coals and cokes:—

	Per cent.		Per cent.	
(1) Connellsville (Pa.), - -	8·233	in the coal,	9·113	in the coke.
(2) Allegheny Mounts. (Pa.), -	6·930	,, ,,	11·360	,, ,,
(3) ,, River (Pa.), -	7·340	,, ,,	11·463	,, ,,
(4) New River (West Virginia),	4·680	,, ,,	5·850	,, ,,
(5) Leetonia (Ohio), - -	1·800	,, ,,	5·380	,, ,,
(6) Tracy City (Tennessee), -	7·800	,, ,,	15·440	,, ,,
(7) Warrior Field (Alabama), -	5·416	,, ,,	11·315	,, ,,
(8) Big Muddy (Illinois), -	1·810	,, ,,	10·070	,, ,,
(9) Crested Buttes (Colorado), -	3·100	,, ,,	6·620	,, ,,

Selected pieces of coke from the top and bottom layers are, in consequence of partial burning, considerably higher in ash than that from the middle layer, a fact which must be kept in view in sampling. Determinations made by O. Simmersbach in two samples of coke showed the following decrease in ash from the top to the middle of the charge in the oven:—

I.	II.
8·91 per cent.	10·54 per cent.
8·17 ,,	8·85 ,,
7·69 ,,	8·63 ,,
6·94 ,,	8·55 ,,

The chief influence of the ash upon the value of the coke consists in its diminishing the quantity of carbon contained in it—that is to say, its heating power. In the operations of the blast furnace, the ash requires an equal bulk of limestone to slag it, and to melt the slag thus produced from the ash necessitates a quantity of pure fuel, equal to at least a quarter of the weight of the ash: in addition to this, the cost of blast and steam, and the loss of time involved, must be considered.

According to Lürmann (*loc. cit.*) the daily consumpt of coke in the blast furnace is increased or diminished by ·5 ton for every 1 per cent. of ash, more or less. Blast-furnace coke must therefore be as free as possible from ash.

If the coke is being employed only to obtain the most complete using up of the heat generated that is possible, at a relatively low temperature—for example, in the heating of drying chambers, in evaporations, &c. —the ash must be regarded as a reservoir of heat which has a beneficial influence on the utilisation of it. In such a case, therefore, a coke which is high in ash will give a greater economic advantage, if it is cheaper in price in proportion to the quantity of ash it contains, than one which has less ash, but is dearer. Regarding the estimation of ash, reference may be made, among others, to F. Stolba, "Jahresbericht über d. Leistung der Chem. Techn.," 1888.

It is not, however, sufficient to ascertain only the total quantity of ash; the constituents of the latter may be of such a character as to exercise a distinctly adverse influence upon the smelting process, and upon the quality of the iron alike in the blast furnace and in the cupola.

Speaking generally, the ash of coke corresponds in composition to the ash of coal. Certain mineral constituents of the coal are indeed volatilised in the process of coking—for example, a part of the sulphur, the water of hydration present in silicate of alumina,

&c. Many substances, moreover, enter into new combinations; thus, calcium and magnesium carbonate remain in the coke ash for the most part as compounds of silicic acid, and not as oxide. In the ash both of coal and of coke, the constituents which preponderate are found to be—silicic acid, alumina, oxide of iron, lime, magnesia, sulphur, and phosphorus; of these, sulphur, iron, phosphorus, and silicic acid are the most important, and exercise the greatest influence.

The composition of the ash of coke may be gathered from the analyses subjoined. See table given below.

The composition of the ash from various samples of coal may also be given here by way of comparison (Muck, "Steinkohlen Chemie," p. 70).

Ash from	Westphalian coal.	Lower Silesian coal.	Dowlais coal.	Anthracite from U.S.A.
	Per cent.	Per cent.	Per cent.	Per cent.
Silicic acid, - -	27·365	31·300	35·730	53·600
Alumina, - - -	22·552	8·310	41·110	36·690
Oxide of iron, - -	46·900	54·470	11·150	5·590
Lime, - - - -	2·686	3·440	2·750	2·860
Magnesia, - - -	·000	1·600	2·650	1·080
Potash, - - - -	·300	·070	not estim.	not estim.
Soda, - - - - -	·237	·290	not estim.	not estim.
Sulphuric acid, -	traces	·520	·290	0 ?
Phosphoric acid, -	·541	not estim.	2·000	0 ?

Sulphur.—The sulphur of coals has its origin in the large amount of the element contained in the plants that went to form them. Dieulafait * on investigating the surviving species of the families of

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* "Comptes rendus," 1885; "Engin. and Min Jr.," vol. 41, p. 264; "Berg- u. Hüttenm. Ztg.," 1886, p. 276.

coal plants, especially the equisetaceæ, found in them a considerably greater quantity of sulphur than is found in plants now living.

Sulphur appears in coal in three forms, and is usually found as—

(1) Pyrites,
(2) Sulphate (gypsum), and
(3) Organic sulphur, *i.e.*, combined with carbon, hydrogen, and oxygen.

No definite relations have been established between the quantity of sulphur present in coal and that in the coke obtained from it, but the amount contained in the latter is always found to be less than was originally contained in the coal which entered into its composition.

In the preparation of coking coal in a pulverised condition, the coal, in virtue of its lower specific gravity, is floated off from the heavy pyrites; a not inconsiderable quantity of pyrites, however, always remains behind in the coal.

In the coke-burning process itself, under favourable conditions, half of the sulphur is volatilised, provided organic sulphur is not present in excessive quantity. The sulphur that is thus expelled comes partly from that which is present in the form of organic compounds, and partly from that contained in the pyrites, the latter going off even at a low temperature as sulphur vapour ($7FeS_2 = Fe_7S_8 + 6S$).

The organic sulphur remains for the most part in the coke; a part of the volatile sulphur will also be retained by certain constituents of the ash, especially compounds of iron (carbonate, oxide, and

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silicate), calcium and magnesium. According to Muck ("Stahl und Eisen," 1887, No. 7), these compounds of iron are reduced in the process of coking by compounds of carbon to the metallic condition, and this even at a low red heat. The reduced iron, in virtue of its powerful affinity for sulphur, again forms FeS with a part of the sulphur set free from the FeS_2. Moreover, carbon compounds containing sulphur, which are formed in the coke oven—for example CS_2—will undoubtedly form sulphides with iron and with the red-hot oxides of the alkali metals. Sulphates which are present, especially $CaSO_4$, will be partially reduced to sulphides (CaS) in the oven. *Consequently it is never possible to produce from coking coal, even when the quantity of sulphur it contains is small, a coke low in sulphur, if the ash of the coal is rich in iron, lime and magnesia, especially in iron.*

With the theoretical knowledge of these facts, however, it is necessary that practical skill go hand in hand. A great deal depends, above everything else, on the skill and judgment of the coke-burner. If, for instance, in the coking process, the caking proceeds too quickly, or if the development of heat goes on irregularly, or with over-much vigour, the desulphurisation of the coke will be less complete. Overheating, in fact, promotes certain chemical reactions in which the sulphur forms compounds with other bodies on which heat has no effect.

In the quenching of freshly made coke with water, yet another part of the sulphur is expelled as sulphuretted hydrogen ($FeS + H_2O = FeO + H_2S$); at the same time it follows from the structure of coke—and this holds especially of the denser varieties—that desulphurisation by steam cannot be complete. For one thing, the mass of coke cools very quickly.

The same principle enters when the quenching of the coke is performed in the oven itself; H_2S is evolved in this case, but the steam is at the same time decomposed by the carbon, with production of combustible gases ($H_2O + C = CO + H_2$). Frankland (Percy, vol. 1), for example, found in the gases evolved from Derbyshire coke and steam—

$H + CH_4$	56·9
CO	29·3
CO_2	13·8
	100·0

(Cp. p. 76.)

According to Dr. Muck ("Post, Chemisch-technische Analyse," p. 38) sulphur is not by any means invariably present in coke in the form of sulphide of iron; indeed, it is not always present as sulphide, for while some cokes, on treatment with hydrochloric acid, evolve considerable quantities of sulphuretted hydrogen, others, containing as much sulphur, scarcely give any trace of it, and consequently undergo no desulphurisation with the acid. In the latter case the sulphur contained in the coke comes from organic sulphur in the coal.

The sulphur contained in coke has a considerable effect when the latter is used for the production of iron. Sulphur and iron are the greatest enemies of one another. Coke containing much sulphur makes the iron white, hard, and brittle, yet, in the case of foundry coke, a certain quantity of sulphur may improve the iron by rendering it more malleable without making it brittle. It is certain that sulphur in the cupola furnace reduces the quantity of graphitic carbon, and so promotes a speedy cooling of the molten foundry iron. In this connection, analysis of the iron is always quite as important as that of the coke; only too often the fault is attributed to the coke, without any reason, when it ought to be looked for in the iron, &c.

In the cupola the sulphur which is contained in the coke is, to a certain extent, burned and evolved with the gases—Fischer found in 1 cubic metre of the gases escaping from the cupola 67 ccs. of sulphurous acid; the bulk of it, however, remains in the furnace unburnt, and passes into the iron, unless this is prevented by the formation of a slag rich in lime.

With regard to the part which sulphur plays in the formation of blast-furnace slags, reference may be made to the following conclusions of Elbers.* "In the zone of carburisation the charge comes in contact with sulphurous gases which are ascending from the zone of melting and of combustion. The gases consisting principally of sulphurous acid are reduced with formation of metallic sulphides, chiefly sulphide of calcium and sulphide of iron. Calcium sulphide is formed according to the following formula:—$4CaO + 4S = 3CaS + CaSO_4$. If the temperature is very high, carbon disulphide is also formed, which likewise

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* "Eng. and Min. Jr.," 31st March, 1894; also "Berg- und Hüttenman Zeitg.," No. 42, p. 366.

produces calcium sulphide: $2CaO + CS_2 = 2CaS + CO_2$. Both modes of forming calcium sulphide involve a higher temperature than the formation of sulphide of iron. At a high temperature in the zone of carburisation calcium sulphide principally is formed, while, if the temperature at this point is insufficient, sulphide of iron is the result. At a later stage the uncombined lime unites with the ash of the fuel, which consists principally of silicates of alumina mixed with pyrites. In the hearth calcium sulphide remains with the slag, while the sulphide of iron, in consequence of its higher specific gravity, goes into the metal. If the iron is highly carburetted, and be strongly heated, the sulphide of iron may be decomposed by the carbon of the iron: $Fe_4C + FeS_2 = 5Fe + CS_2$. The carbon disulphide is oxidised in the zone of combustion, and augments the quantity of the sulphurous gases already mentioned.

When the molecules of slag are being formed, the molecules of metallic sulphides, which have a low specific gravity, thrust themselves between these, and combine with them. Since, however, the metallic sulphides do not constitute a factor in the chemical reactions, to which the continually accumulating mass of silicates are subjected, they can only act as an impediment, and hinder the process. Therefore the fluxing effect of slags containing sulphur is far less than that of slags of similar composition which contain no metallic sulphides.

To what extent iron takes up the sulphur contained in the coke has not yet been ascertained; the iron, however, is useless if the coke contains 1·5, and indeed, even 1·25 per cent. S.

It is thus a matter of prime importance to the iron-smelter to produce a coke as low as possible in sulphur, the more so since, in the operations of the blast furnace, where an effort is made by addition of lime to transfer the sulphur of the coke to the slag, even a large excess of lime is scarcely able to remove the deleterious ingredients that have already entered the iron, and, for the most part, its action is restricted to promoting a prior union of the particles of ash and sulphur with those of the lime.

In accordance with these facts, an endeavour has also been made to reduce the sulphur contained in coke to the utmost. Various means of betterment have been resorted to. Calvert and Chenot add common salt in coking to form chloride of sulphur; Bleibtréu mixes the small of caking coal with powdered lime in order that thereafter, by using the limed coke thus obtained in the furnace, the sulphur contained in it may be carried into the slag. Kopp quenches the coke with dilute hydrochloric acid, washes out the soluble salts, and dries the wet coke in the air, or by heat from the ovens. Hoffmann employs for the same purpose a solution of chloride of manganese. Grandidier introduces compressed air at a temperature of 250-300° C. into the ovens, whereby the carbon is set on fire and the sulphide of iron is oxidised.

All these methods, however, have failed to overcome the difficulty of producing a coke low in sulphur. The best remedy is careful selection of the coal—due regard being paid to its quality, and to the quantity of ash, and especially of iron, it contains. For it is not always the coal that contains least sulphur which yields the coke purest in this respect; much depends upon the form in which the sulphur is combined, and the character of the mineral matter determines to a considerable extent whether much or little sulphur is evolved with the oven gases or remains behind in the coke.

Westphalian coke very seldom contains less than ·8 per cent. of sulphur—most of it contains from ·8 to 1·5 per cent.; larger quantities are rare. Out of sixty-two determinations* of sulphur in Westphalian coke, eleven showed under 1 per cent. of sulphur (minimum ·83 per cent.), and fifty-one over 1 per cent. Of the latter, forty-three showed between 1 per cent. and 1·2 per cent. of sulphur (mean, therefore, 1·10 per cent.); eight analyses gave 1·20 to 1·47 per cent. S. (the latter figure as maximum). Consequently, no great error is committed in regarding 1·06 per cent. on an average as the quantity of sulphur contained in Westphalian coke.

In English coke and in that of the Ruhr district the quantity of sulphur varies between ·80-1·30 per cent. The best Connellsville coke (Pa.) also shows ·82 per cent. of sulphur. Foundry coke contains in general ·75-1·0 per cent. of sulphur—1 per cent. being regarded as the maximum, although instances are known in which it rises as high as 1·25 per cent.

The following is a list of various cokes, showing the quantities of ash and sulphur they contain:—

Coke from	Ash per cent.	Sulphur per cent.
(1) Eschweiler Bergwerks Verein (Anna), - - - -	10·81	·860
(2) Vereinigungsgesellschaft, Maria Pit, main shaft (Aachen), -	10·65	·893

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* From the laboratory of the "Westfälisches Kokssyndikat," at Bochum.

Coke from	Ash per cent.	Sulphur per cent.
(3) Vereinigungsgesellschaft, Maria Pit, shaft 1, - - -	10·02	·863
(4) Obernkirchen, - - -	6·02	1·27
(5) Marihaye (Lüttich), - -	11·06	1·54
(6) Strépy Bracquegnies (Centre),	11·32	·67
(7) Chevalières de Dour (Mons), -	6·96	·80
(8) Roche la Molière,* - -	13·00	·300-·400
(9) Houillères de Saint Etienne, -	13·00	·300-·405
(10) Montcell (Saint Etienne), -	11·00	·270-·400
(11) Montmartre (Saint Etienne), -	11·00	1·37
(12) Tilleur (Belgium), - -	12·00	·50
(13) Donetz (Russia), - - -	6·00	·27

American coke ("Glückauf," 1892, p. 76) shows the following quantities of ash and sulphur:—

	Ash per cent.	Sulphur per cent.
1 Sample of Big Stone Gap coke, from Virginia, - - -	4·74	·588
3 Samples of Connellsville coke (Pa.),	9·74	·810
4 ,, ,, Chattanooga coke (Ten.),	16·34	1·595
4 ,, ,, Birmingham coke (Alab.),	10·54	1·195
3 ,, ,, Pocahontas coke (Virg.),	5·74	·597
8 ,, ,, New River coke (West Virginia), - - - -	7·21	·552

As regards English coke, that from Durham, according to Weeks (*loc. cit.*), contains the following:—

	Ash per cent.	Sulphur per cent.
Hamsteels Mine, - - - -	6·36	·81
Consett ,, - - - -	6·91	·84
Whitworth ,, - - - -	6·69	1·21
South Brancepeth Mine, - -	5·30	·91

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* No. 8-13 according to Rossigneux (*loc. cit.*).

Coke that is high in sulphur, after exposure to air even for a short period, shows brown spots, the edges of which present a more or less distinct play of colours. Frequently in such places the coke appears exactly like pyrites. The author has always found in such spotted pieces of coke an appreciably larger quantity of iron and about ·30 per cent. more sulphur than in bright coke from the same works.

With reference to the estimation of sulphur in coke, see, among others, L. Blum, "Zeitschr. für Anal. Ch.," 1888, p. 445; also F. Stolba, "Jahresbericht über d. Leist. d. Chem. Techn.," 1888.

The only means by which it is possible to get an indication of the quantity of sulphur likely to be contained in a coke which it is proposed to manufacture, is, according to Muck, to make a test coke from the coal in question and to determine the sulphur in it.

Iron.—The iron contained in coal is the product of a series of secondary reactions. According to Ochsenius ("Glückauf," 1894), acids are formed by the decomposition of plants, which, acting in the constant presence of a supply of moisture, tend to dissolve the finely-divided iron in the subsoil. In this way slimy solutions of iron are formed, which cover the whole ground, together with the roots, and at length convert the metal into the form of salts of ulmic, humic, carbonic, and phosphoric acids. From such deposits the iron has been readily introduced into coal, where it has been converted for the most part into carbonate of iron. In addition to the carbonate, coal contains both the oxide and silicate of iron. The changes which these compounds undergo in the coke oven and the influence they exert upon the combination of sulphur have been considered in the preceding section.

The iron in the ash of coke has a striking effect in causing the latter to clinker, and that, indeed, at a comparatively low temperature. This troublesome formation of clinker in the grate arises from the fact that the peroxide of iron in the ash is easily reduced when in a thick layer to the state of protoxide, and as such unites with the remaining constituents of the ash to form a very readily fusible silicate. (Cp. p. 110.)

In generating carbonic acid in the lime kiln in the ammonia-soda process, the effect of this property of iron can be observed in the vitrification of the lime which takes place, when the former is present in excessive quantity.

The quantity of iron contained in coke is very variable, and is generally in inverse ratio to the alumina present in the ash.

Of forty analyses* of Westphalian coke

3	Samples	gave	under	·5	per cent.	Fe.
5	,,	,,	between	·6 and ·7	per cent.	Fe.
8	,,	,,	,,	·8 and ·9	,,	,,
6	,,	,,	,,	·9 and 1·	,,	,,
5	,,	,,		1·	per cent.	Fe.
7	,,	,,	under	1·2	per cent.	Fe.
3	,,	,,	over	1·2	,,	,,
2	,,	,,	,,	1·3	,,	,,
1	,,	,,	,,	1·4	,,	,,

The mean is thus approximately ·90 per cent. Fe.

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* "Westfälische Kokssyndikat."

In the Westphalian coal basin the phenomenon is generally observable that the quantity of iron varies with the depth of the seams, and that, particularly, it increases alike in the coal and in the coke from the top downwards—that is to say, from the "fat" coals to the "lean" coal. A series of cokes from the Ruhr coal basin contained—

(*a*) From the Gelsenkirchen district (best "fat" coal),	·722	per cent.	Fe.
	·913	,,	,,
	·944	,,	,,
	·984	,,	,,
(*b*) From the Langendreer district (smithy coal),	·853	,,	,,
	1·070	,,	,,
	1·099	,,	,,
(*c*) From the districts of Witten and Sprockhövel (smithy and "lean" coal),	1·300	,,	,,
	1·414	,,	,,
	1·590	,,	,,

The larger amounts of iron in the cokes contained in division (*c*) may probably have a genetic connection with the presence of beds of spathic iron ore in the "lean" coal division of the Ruhr.

Coke from the Aachen basin contains a smaller quantity of iron—namely, about ·6 per cent.

Coke of the Eschweiler Bergwerks V., Anna pit, - - -	·628	per cent.	Fe.
Coke of the Vereinigungs gesellschaft, Maria pit, main shaft,	·559	,,	,,
Coke of the Vereinigungs gesellschaft, Maria pit, shaft No. 1,	·610	,,	,,

Edm. Jensch (Dürre, *loc. cit.*) reckons the metallic iron in the pyrites present in the small and dust of Upper Silesian coal at 17·28 kilos. per ton (metric) of coal. The loss of iron annually—in 1885 the production was 12,734,000 tons—is thus estimated at 220,000 tons. In individual instances it may readily happen that the iron of the coke goes completely or partially into the blast-furnace slag; in this case the quantity of lime added has been too small.

Phosphorus.—The principal carriers of the phosphorus contained in coke are, according to M. Carnot (Compt. rend., 99, 154), the spores and pollen grains which are easily observable under the microscope in the accumulation of decomposed vegetable matter. The cryptogams—that is to say, ferns, equisetums, and lycopods (lepidodendra and sigillaria)—along with some conifers (cordaites), constitute the bulk of the carboniferous flora, and these contain, as a group, a more or less considerable quantity of phosphorus. Carnot attempted to trace a connection between the quantity of phosphorus contained in coals and the nature of the plants of which they are composed. In the same deposit he could detect no appreciable differences, but those coals which contained a large number of spores, such as cannel coal, were found to contain the largest quantities of phosphorus. The amounts found varied from ·00572 to ·06275 P. in 100 parts, while ·02 might be regarded as the mean.

At the Denain Iron Works, according to Rossigneux (*loc. cit.*), a comparison was made of various coals belonging to that locality with reference to the quantity of volatile constituents and of phosphorus they contained. Nothing definite, however, was arrived at. At Anzin the quantity of phosphorus varied in different seams in the proportion 1 : 6, and the "half-fat" coals contained a half less phosphorus than the "fat" coals. Generally speaking, the quantity of phosphorus is very variable.

In the process of coking the phosphorus of the coal goes completely into the coke. In Westphalian coke the phosphorus varies between several thousandths of a per cent. and a few hundredths, the limit being about ·05 per cent.

Of 56 analyses* of Westphalian coke—

4	Samples showed less than	·01	per cent. P.
41	,, ,, between	·01–·02	,,
10	,, ,, ,,	·02–·03	,,
1	,, ,, over	·03	,,
	Approximate mean,	·016	,,

As is the case with the iron, the quantity of phosphorus in the Ruhr area increases generally from the "fat" coal to the "lean" coal, as may be seen from the annexed table:—

(*a*) Coke from the Gelsenkirchen district (best "fat" coal),	·0145	per cent. P.
	·0154	,,
	·0185	,,
	·0129	,,
(*b*) From the Langendreer district (smithy coal),	·0110	,,
	·0120	,,
	·0125	,,
	·0180	,,
(*c*) From the districts of Witten and Sprockhövel (smithy and "lean" coal),	·0248	,,
	·0210	,,
	·0230	,,

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* "Westfal. Kokssyndikat."

The larger quantity of phosphorus in (*c*) is apparently to be explained by the heavier precipitate of phosphate of iron, which, in the lowest coal seams, has been exposed to most pressure from the overlying strata.

With regard to Aachen coke, there is contained in that from—

Eschweiler Bergwerk Verein (Anna),	·0207	per cent. P.
Vereinigungsgesellschaft (Maria) main shaft,	·0208	,,
Vereinigungsgesellschaft (Maria) No. 1 shaft,	·0140	,,

Pennsylvania coke shows on an average ·01 per cent. of phosphorus, that from Mingo Mountain (Tenn.) ·008 per cent., and Pinneville coke only ·007 per cent. P. A larger quantity is found in coke from West Virginia which has ·027 per cent., while that from Illinois contains ·033 per cent. In coke from Upper Freeport coal (Allegheny River), M'Creath found phosphorus to the extent of ·1085 per cent., the coal itself containing ·0684 per cent.

In the blast furnace the phosphorus of the coke, at the high temperature prevailing and under the influence of the silicic acid which is present, is taken up into the body of the iron.* Phosphorus diminishes the elasticity and tenacity (Festigkeit) of the iron, and has the property of making it harder, in consequence

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* Under certain conditions, a small part of the phosphorus contained in the whole charge may go into the slags and also be carried off through the throat. For particulars see "Stahl und Eisen," 1882, vi., 232; 1894, xviii., 873.

of which great importance is attached in the iron works to the amount of phosphorus contained in the coke; its influence upon the quality of the iron is not so powerful, however, as that of sulphur.

For the manufacture of fine castings in foundries, a somewhat high percentage of phosphorus is not regarded with disfavour, because phosphorus lowers the melting point and renders the iron more fluid, so that it fills up the moulds completely and gives fine, smooth surfaces to the castings.

Silica.—The silica comes from the usual accompaniment of coal, the coal shale. The preponderance of silica in the coal ash, as well as the circumstance that the alkalis therein are present as silicic acid compounds, points to the matter of the fireclay having been partly introduced into the body of the coal.

In earlier days the silica was credited with exercising a great influence in the blast furnace by expelling the sulphur. This view has been proved, however, to be erroneous, although at the same time it is not without effect in determining the melting of the slags in the furnace.

In the melting of soda ash, silicic acid is very objectionable. When coke is used as a fuel a large quantity of silica prevents slagging of the ash in the grate, while a low or medium quantity of silicic acid along with large quantities of oxide of iron and lime has a very pronounced slagging effect.

The relation which the quantity of silica bears to the strength of the coke is very important, for it is found that the hardness of the coke varies inversely to the amount of silica present. For further particulars see the following chapter.

The following analyses show, according to Dürre,* the silica in various cokes made from washed coking coals of the Ruhr basin:—

Coke from		Ash per cent.	With SiO_2 per cent.
Präsident Mine,	-	10·19	30·86
Carolinen Glück Mine,	-	12·15	43·93
Centrum ,,	-	10·93	38·56
,, ,,	-	12·65	41·48
Graf Schwerin ,,	-	11·08	34·60
,, ,, ,,	-	9·08	33·78
,, ,, ,,	-	9·71	53·91
Westhausen ,,	-	13·21	37·33
,, ,,	-	11·01	39·33

According to Weeks' report there is contained on an average in—

Connellsville coke,	44·64 per cent. SiO_2	and in
Big Muddy coke,	47·00 ,,	,,

Impurities of Minor Importance.—In addition to sulphur, iron, phosphorus, and silica, other impurities are found in the ash of coal and coke, and, although their amount is so small that in practice they may be entirely neglected, it will yet be worth while to mention them.

The coke manufactured from Ruhr coal, according to B. Platz ("Stahl und Eisen," 1886), contains copper, and, as a matter of fact, twelve samples taken monthly are stated to have shown ·017-·046 per cent., or an average of ·032 per cent. copper. Larger quantities of copper than those mentioned occur only rarely,

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* "Anlage und Betrieb der Eisenhütten."

for the most part in coals exceptionally rich in pyrites, the ash of which, when moistened with hydrochloric acid, shows the copper reaction. Since any copper which may be contained either in the ores or in the fuel finds its way ultimately into the pig iron, it follows that, assuming one ton of coke containing 10 per cent. of ash to be required for the production of one ton of pig iron, the quantity of copper in the latter will amount to about ·0032 per cent. With such minute quantities, however, no injurious effect on the quality of the iron need be feared.

The blue flame which makes its appearance when salt is sprinkled upon glowing coke was ascribed by Smith ("Chemical News," 39, 141) to hydrochloric acid. Since then, however, according to G. Salet (Compt. rend., 110, 280-283), it has been proved to be due to a small quantity of copper, which was recognised, spectroscopically, by introducing a steel needle into the Bunsen flame after it had been dipped in the acid extract of the ash in question, and heated to redness with hydrochloric acid (Muck, "Steinkohlen Chemie.").

In coal from Newcastle Daubrée found both arsenic and antimony; in Saarbrück coal ·003 per cent. of arsenic; and in a sample of coal from Villé (Bas Rhin), besides traces of antimony and copper, ·0415 per cent. of arsenic. Coal from Nottinghamshire likewise contained appreciable traces of arsenic. Percy discovered galena in coal from Bedworth (Warwickshire). Oxide of lead and oxide of zinc are also frequently present, as is indicated by the white or yellow incrustations found above the doors of the coke ovens and also on the pieces of coke themselves.

Platz* investigated two specimens of volatilised dust, which had been deposited from coke-oven gases on boilers heated by them. On the hotter parts a yellow deposit had been formed, and on the cooler part a white one, the composition of which was as follows:—

White.

	Per cent.
Sulphate of zinc,	63·01
,, lead,	11·23
,, soda,	4·82
Persulphate of iron,	12·22
Insoluble residue,	1·62
	92·90

Yellow.

	Per cent.
Oxide of zinc,	58·43
Sulphate of lead,	4·24
Lime,	1·12
Magnesia,	·75
Alumina,	8·40
Peroxide of iron,	5·49
Silica,	17·78
	96·21

In the flues of a boiler at Zankeroda heated by coke gases, according to H. Schulze ("Jahresbericht Leist. d. Chem. Techn.," 1886), a deposit was formed which had the following composition:—

	Per cent.
Sulphate of zinc,	58·41
,, ,, lead,	20·86
,, ,, thallium,	·57
,, ,, cadmium,	2·60
,, ,, iron (ferric),	2·24
Oxide of iron,	·92
Sulphate of calcium,	·42
,, ,, lithium,	·72
,, ,, sodium,	·65
,, ,, potassium,	2·08
Water,	8·37
Insoluble residue (coal, mortar),	2·50
	100·34

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* Muck, "Steinkohlen Chemie.," 2nd ed., 1891.

CHAPTER V.

Physical Properties of Coke.

Hardness.—When the use of coke began to be substituted for that of wood charcoal, the form and size of the charcoal furnaces originally employed was at first retained. Since these were only of small height and were fed with cold or only moderately-warmed air, the aim was to produce a light and porous coke, which in physical properties would not be very different from vegetable fuels.

The low power of resistance possessed by this coke naturally placed great restrictions upon its use in the blast furnace, and hence, when the working of the latter came to be forced, in order to secure a largely augmented output, some remedy had to be sought for this defect. For use in the huge blast furnaces of to-day, which are fed with a blast of air at from 700-800° C. under high pressure and produce as much as 300 tons of pig iron per twenty-four hours, it is necessary, above everything else, that the coke should be strong.

Until about eleven years ago the height of the blast furnace was regarded as being determined by the resistance of the coke to crushing, since it was assumed that the weight of the column of matter contained in the charge would crush the coke to a greater or less extent. Calculation, however, shows this view to be quite untenable.

According to Wedding,* 1 cubic metre of coke = 450 kilos.; 1 cubic metre of wood charcoal = 140 kilos.; and 1 cubic metre of ore + fluxing material = 1800 kilos. If, therefore, we take 3 parts by weight of the charge and 1 part by weight of coke, it gives—

450 kilos. coke, - - -	1	cubic metre.
1350 kilos. charge, - - -	·75	,,
Total, - - -	1·75	,,

And

140 kilos. wood charcoal, -	1	cubic metre.
420 kilos. charge, - - -	·23	,,
Total, - - -	1·23	,,

In the first case, therefore, 1 cb. metre $=\frac{1800}{1\cdot75}=1028$ kilos; in the second case 1 cubic metre $=\frac{560}{1\cdot23}=455$ kilos. So that if the height of the charge in the blast furnace be 30 metres, the weight on each square metre of the base is, in the case of a furnace using coke, 30 × 1028 kilos. = 30,840 kilos., and, in one using wood charcoal, 30 × 455 = 13,650 kilos., or, per square centimetre, in the first instance 3 kilos., and in the second 1 kilo.—that is to say, a weight very much less than coke or wood charcoal, even of the lowest

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* Wedding, "Die Berechnungen für Entwurf und Betrieb von Eisenhochöfen," p. 80.

resisting capacity, would be able to bear. It follows from this that it is not the resistance offered to a crushing stress, but the friability of the fuel that is a factor in determining the height of the blast furnace.

The friability of coke is connected principally with the condition of the walls of the pores—that is to say, it depends on the carbonaceous material. Coke is always more or less porous in structure. These pores are nothing more than the passages through which the volatile products that result along with the coke in the process of coking make their escape. If the walls of the pore spaces are hard, the coke is generally called "hard": if they are soft, the coke is called "soft."

On the other hand, the friability is also dependent on the density of the coke—that is to say, upon the size of the pore spaces, inasmuch as, where the pore walls are equally hard, a dense coke is less friable than a porous coke: the exception to this is where, in the latter case, the deteriorating effect of the large pore spaces is again compensated by increased thickness of the partition walls between the pores.

Consequently, the friability determines also the relative size of the pieces in the various sorts of coke. The denser the coke is, the larger the pieces that can be employed, while, under similar conditions, increased porosity necessitates the use of smaller pieces.

The hardness of the pore walls of coke is what determines the resistance offered by the latter to attrition. Hard coke may show a very small amount of friableness, without being in the least dense; on the other hand, dense coke must, in every case, be hard as well if it is to be of any use.

The disadvantage of a friable coke is seen even in the transport of it, where, between the loading of the waggons and making-up of the trains, no inconsiderable part is lost as refuse. As a general rule, 6 per cent. of dust will be found associated with it at the point of unloading.

In the blast furnace itself, the pieces of coke turn about and rub against the materials which form the charge. In the case of very friable coke, pieces are thus very readily broken off, and these form with a part of the charge dense masses which the gases are unable to penetrate, and which thus inevitably lead to interruptions of the smelting process.

It is, moreover, no uncommon result when friable coke is employed, that small particles of it are carried off unburnt in considerable quantity by the gases escaping from the upper part of the furnace, or are removed with the slag.

A further disadvantage of friability, connected more particularly with the weakness of the pore walls, bears upon the combustion in the interior of the blast furnace. The coke in its descent is surrounded by a hot layer of carbonic acid. This gas has the power of oxidising the carbon, which, however, is not attacked in all its forms to the same extent by carbonic acid. Hard coke withstands its destructive influence to a greater degree than soft coke. In an experiment of thirty minutes' duration, Lowthian Bell* found the loss in weight by oxidation in the case of soft coke to be six times as great as in the case of hard coke. Every bit of the coke that is used up by carbonic acid in the upper parts of the blast furnace constitutes a double loss—on the one hand, by the lowering of temperature at the place where such action is going on, and on the other, in consequence of the serious loss of coke which is consumed before it reaches the crucible of the furnace. This loss of heat is accompanied at the same time by a more or less considerable disturbance of the working of the furnace.

In practice, the friability of the coke is determined indirectly by testing the hardness of the pore walls—that is to say, the resistance offered by the coke to pressure, and from the figures obtained for the carrying power, conclusions are drawn regarding the friability. If a shorter method of estimating the value of different cokes in this respect is desired, the samples in question are simply rubbed against one another; that kind is the best which gives the smallest loss on rubbing. In this case, obviously, a similar degree of purity in the cokes is presupposed.

If we consider more fully the hardness of the pore walls of coke—that is, the resistance they offer to pressure—we find that the latter depends on the quality of the coal, the quantity of ash in the coke, and particularly the quantity of silica it contains; also upon the temperature employed in coking, the width of the oven, and the duration of the coking process.

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* "Berg- u. Hüttenm, Zeitg.," 1884, p. 551.

Obviously, the greatest attention must be paid to the quality of the coal, since, although with a bad oven it is easy to manufacture a bad coke even from a good coal, it is impossible to obtain good coke from bad coal—at least, by the present methods of manufacture. Caking sinter coals or sinter coals are scarcely in a condition to yield coke. Even in the case of the coking coals, properly so called, more or less considerable differences are seen in the hardness-number.

Herr Simmersbach investigated coke made from both kinds of coal found in the Westphalian coal range, viz., smithy and "fat" coal—the latter being again divided into light coking coal and "high fat" coal, rich in gas. The result was—

Coke from smithy coal,	- 80–115	kilos carrying capacity	per sq. cm.
,, light fat coal,	- 120–160	,,	,,
,, best ,,	up to 175	,,	,,

The hardness of the coke appears, therefore, to stand in a definite relation to the caking power of the coal, for the smithy coal, which borders on the "lean" division, yields a coke the hardness of which is only 115 kilos. per sq. cm. In one case, where a better smithy coal was coked, the hardness of the product rose to 143 kilos.; while coke made from the best "fat" coal possesses a far higher hardness, which may be fairly placed at about 170 kilos. when the average quantity of ash is under 9 per cent. The bulk of the coke which is produced in Westphalia will bear a weight of 115-170 kilos., so that, in point of fact, 120 kilos. is regarded as the standard for cokes produced from light coking coal. A series of experiments carried out some time ago by the Westphalian Coke Syndicate at Bochum gave likewise, as a mean, the number 120 kilos. This number appears to hold for Durham coke as well.

In experimenting on the hardness, cubes of coke 1 cm. in height were employed along with the apparatus shown below, which is so simple as to require no further description. (Cp. p. 14.)

A high percentage of ash naturally affects the hardness of the coke, but the degree of the latter is dependent pre-eminently on the quantity of silica present therein, as is evident from the following experiments carried out by Herr Simmersbach:—

No.	Type of Oven.	Width of Oven.	Period of Coking.	Ash Content	SiO_2.	Hardness per sq. cm.	No. of Experiments.
		m.ms.	hours.	per cent	per cent	kilos.	
1	Dr. Otto, - - -	600	48	10·14	66·00	98	4
2	,, - - -	600	48	9·17	60·25	115	4
3	,, - - -	500	36	9·97	25·7	160	6
4	Brunck (tar oven), -	500	36	8·11	28·36	170	6
5	Dr. Otto ,, -	525	48	9·2	28·59	175	4
6	,, - - -	600	48	7·79	25·28	175	7

According to these results, the effect of silica in the ash seems to be that, with an increase in its amount, the hardness-number falls, and *vice-versâ*. From experiment No. 3 it follows further that the brand of coke which is freest from ash does not always possess the greatest hardness, even when the quantities of ash and silica are, generally speaking, in the same proportion.

The predominating influence of the silica is seen especially in the case of the Australian cokes, which, on account of the large quantity of silica they contain, have a much lower hardness than Westphalian coke.

The effect of temperature upon hardness is strikingly noticeable at different points in the same oven charge. At the sides of the coked charge the hardness is considerably greater than in the middle, because at the centre the temperature cannot act so powerfully, since the heat which the arch of the oven takes up and reflects upon the charge of coal is to some extent not at the disposal of the coke in the middle. The same holds good of the large amount of heat generated by the surface burning of the coke, which likewise acts most powerfully on the sides of the charge.

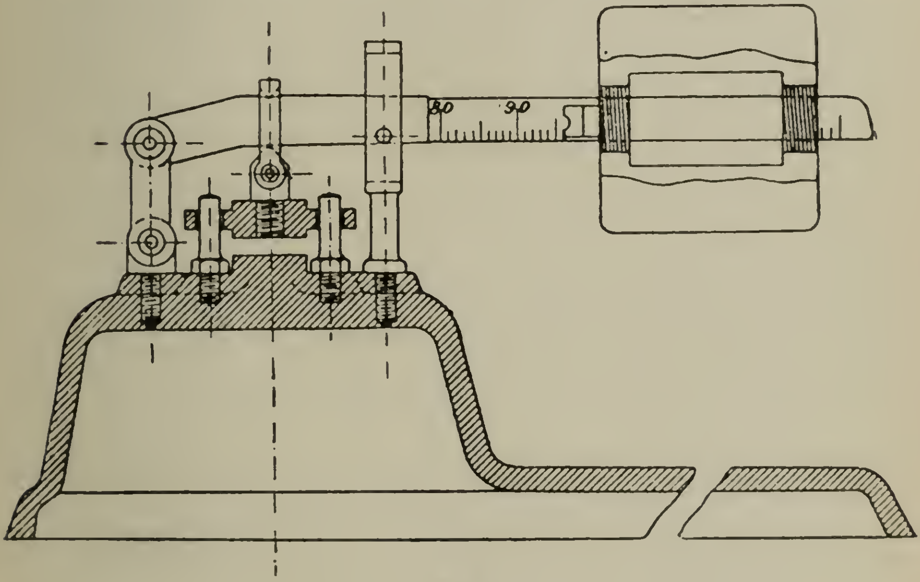

Fig. 1.

According to Rossigneux (*loc. cit.*), with Belgian ovens of 450 mms. diameter, using a mixture of "fat" coal and "half-fat" coal, with 21 per cent. volatile constituents, the hardness of the coke next the oven walls amounted to 120 kilos., while, in the neighbourhood of the perpendicular axis of the oven, the number fell to 80 kilos.

Herr Simmersbach investigated round-oven coke made from the best Westphalian coking coal and containing 9 per cent. of ash, and found that the carrying power diminished continuously from top to bottom. The hardness-number fell from 175 kilos. to 170, 123, and finally to under 80 kilos.

Every coke-burner, moreover, is aware that coke becomes harder if it is heated for some time after its formation. But the manner of conducting the coking process, permitting as it does a uniform or non-uniform heating, also admits of considerable differences in the hardness of the product.

The beneficial action of heat is shown in the case of ovens of different widths and with varying periods of treatment. The narrower the oven is, the more speedily does the charge become heated to redness through and through, and the longer, accordingly, is the period for which the coke is exposed to a red heat.

Experiments carried out at the Bessèges Iron Works, on samples of coke made in Carvès ovens, gave the following figures for the resistance of the cokes to pressure:—

From ovens of 700 mms. width	- 66·40 kilos.
660 ,, ,,	- 79·72 ,,
500 ,, ,,	- 92·32 ,,

It is obvious, therefore, that the hardness increases with decrease in the width of the ovens. The knowledge of this has had the effect that, in the more recent types of oven, the width is always diminished as far as possible.

With reference to the period of treatment, it holds that an extension of the time produces harder coke, because the coke is acted on longer and more powerfully. Thus the 48-hour working of ovens generally produces a harder coke than the 24-hour, and, on the other hand, the 72-hour yields a harder product than the 48-hour treatment—complete treatment being presupposed in both cases.

According to Wedding*

70-hour coke from beehive ovens at Connellsville, -	gave	284	lbs. per	sq. inch.
48-hour coke from beehive ovens at Connellsville, -	,,	249	,,	,,
24-hour coke from closed ovens at Johnstown, -	,,	245	,,	,,

For the production of blast-furnace coke at Connellsville the coal is treated for forty-eight hours, while for foundry coke the period is extended to seventy-two hours; because by extending the period of coking the cokes become harder, and at the same time are got in larger pieces. In this case, moreover, a special selection is made, and the inferior pieces picked out are not sold as foundry coke.†

For 48-hour coke the carrying power is reckoned in

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* Wedding, "Nord Amerikanisches Eisenhüttenwesen, Zeitsch. für Berg- Hutten- und Salinen-Wesen," vol. 1876, p. 409.

† Wedding, "Stahl und Eisen," 1893, p. 21.

Westphalia at 80-120 kilos. per sq. cm., for 72-hour coke at 120-140 kilos. In America (round-oven coke with 72-hour treatment) the hardness is taken at 150 kilos. per sq. inch.

The recovery of bye-products from the coal is not detrimental to the carrying power of the coke. Coke ovens with recovery of tar and ammonia produce quite as hard coke as ordinary ovens, as is evident from experiments 4 and 5.

Herr Simmersbach's experiments show further that width of oven and length of treatment, as factors in the production of good coke, are always subordinate to the right choice of the coking coal and to the quantity of silica in it. (Comp. Experiments, 1, 4.) From inferior coking coal it is never possible to produce harder coke, even with the smallest width of oven and with the longest period of treatment, than can be got from the best fat coal which contains little silica, even with a greater width of oven and a shorter period of treatment.

In experiments upon hardness it is by no means safe to rest satisfied with the result of a single test; it is essential that a considerable number of experiments be made and the average taken. It is of great importance that good and, above all, uniform samples should be chosen.

On the basis of the mean hardness as thus determined, however, only approximate conclusions can be drawn as to the quality of the coke, because a coke in large solid pieces of 20-30 cms. in width without cracks will give better results than another coke of equal hardness but in smaller pieces, but more especially for the reason that the experiments have not been carried out at the high temperatures which the coke must be subjected to in practical working.

In this connection comparative experiments on hardness in the cold and in the heat were made by P. Holtzer (Rossigneux, *loc. cit.*) with metallurgical coke containing 14 per cent. ash made from coal from St. Etienne. The hardness in the cold amounted to 95 kilos. and at a red heat fell to 87·8 kilos.

Further experiments of this kind have unfortunately not been carried out, so that the question whether the hardness of coke in the heat is in all circumstances and for all kinds of coke proportional to the hardness at ordinary temperature still remains an open one.

Porosity.—The porosity is not connected with the nature of the pore walls but is based upon the capacity of the pore spaces, it is therefore independent of the hardness. According as the pore spaces are large or small, the coke is called porous or dense. Coke can be porous and yet hard, if the pore spaces are large but the walls of the pores are hard; conversely, it can be dense without possessing hardness—that is to say, its pore spaces are indeed small but the walls surrounding them are weak.

As already mentioned in Chap. II., under "Preparation," the size of the particles of coking coal has an influence upon the porosity of the coke. The finer and more uniform the grain of the coal, the denser is the coke, and *vice versâ.* In addition to this, the kind of coal and the duration and method of coking stand in the closest relation to the porosity of the coke.

The more volatile constituents a coal contains—that is to say, the more gases it evolves on being coked—and, further, the more rapidly the same coal is heated, the more porous is the coke produced. According to Dr. Thörner (*loc. cit.*), by the employment of more moderately heated new systems, the sum total of the pore spaces fluctuates between 29-35 per cent., while vigorously coking types of oven can produce as much as 40-50 per cent. of pores; in the case of meilers and open ovens or stalls it is least, falling as low as 15 per cent.

The higher the pressure—that is, the column of coal (for example, under the charging holes)—the denser does the coke become, and the more difficult is it to push out.

The density likewise increases with the temperature, because with increase of temperature the tarry products of distillation are in large measure destroyed within the coke.

The various parts of an oven give cokes of quite different density, as is seen from the following figures *:—

Closed oven of the Cambria Iron Co. at Johnstown.

	Coke per cent.	Cells per cent.
Upper part of the oven, -	63·41	36·59
Middle ,, -	69·00	31·00
Lower ,, -	73·98	26·02

Closed oven, Cap Furnace, near Hollidaysburg.

	Coke per cent.	Cells per cent.
Upper part of the oven, -	63·80	36·20
Middle ,, -	65·50	34·50
Lower ,, -	70·42	29·58

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* Wedding, "Nord Amerikanisches Eisenhüttenwesen, Preussische Ztschr.," vol. 1879, p. 409.

Open heaps, Böckhill Coal and Iron Co. (washed coal).

	Coke per cent.	Cells per cent.
Upper part of the heap, -	56·51	43·49
Middle „ -	47·66	42·44
Lower „ -	61·89	38·11

The upper part of the oven consequently always yielded coke appreciably more porous than the lower part.

In one and the same charge, moreover, quite different densities result at different places; top and bottom layers are always more porous than the middle layer.

Dr. Thörner has made interesting microscopical investigations on the form and size of the pores, and the stoutness of the pore walls in coke and wood charcoal, in which he prepared similar thin sections from the samples to be compared, and from these, by equal enlargement by means of a microphotographic apparatus, obtained photographs, which he used as the material for comparison. (Cp. p. 13.)

In the case of wood charcoal the vegetable structure was found to present a series of long extended pore tubes, but no closed pores or groups of cells.

Coke contained both small and large, separate and connected, pores of the most various shapes. All are scattered haphazard through one another, and there is no sign of any structure. The coke substance forming the walls of the pores is always fused together to a solid vitreous mass, the specific gravity of which is variable.

In meiler coke the structure was still retained to some extent, and in it the matter of the coke showed least evidence of fusion. Oven coke had an irregular porous structure, and was fused together to a dense vitreous mass. Furthest removed in structure from the wood charcoals stood the gas-retort cokes, in which moderate-sized pore walls alternated with large cells, while the substance of the coke was fused to a dense, impenetrable, vitreous mass.

The table on p. 129 gives a synopsis of Thörner's investigations.

According to these, the largest amount of pores is contained in retort coke with 61·6 ccs., the smallest in meiler coke with 28·4 ccs.; between them lies oven coke, while the porosity of wood charcoal varies between 96·2 ccs. and 200·4 ccs. in 100 grms. of coal. Round-oven coke is generally more porous than Coppée coke. As regards the former, West Virginia coke is considerably more porous than round-oven coke from Pennsylvania, without, at the same time, showing any greater friability.

Coke made under pressure shows the largest number, but also the smallest pore spaces. The pressure to which the coke was subjected in the coking process consequently does not affect the density of the carbon, but rather under its influence a compression of the pores takes place, as is clearly indicated by the 3rd and 4th experiments in the table.

The density of the carbon, the real coke substance, varies within narrow limits, viz., between 52·4 and 56 ccs. in 100 grms. of coke. Among wood charcoals, that made from pine shows the smallest bulk occupied by the carbonaceous matter, viz., 61·6 ccs., and that from oak the largest, viz., 74·2 ccs.

The amount of ash in coke has nowhere any appreciable influence on the density of the carbon. (Cp. Nos. 4 and 8 of the table.)

Kinds of Coal and Coke.	In 100 grms. Coke.			Vol. of 100 grms in ccs.	Microscopical Condition.
	Ash.	Ccs. occupied by Pores.	Ccs. occupied by Coke Substance.		
1. Retort coke, Pluto mine,	3·8	61·6	54·8	116·4	Large pore cavities with bulky walls.
2. Retort coke, Friedrich der Grosse mine, -	7·5	60·0	55·2	115·2	
3. Pressed coke, Köln Müsen, - - -	7·7	47·6	54·0	101·6	Many, mostly smaller pores.
4. Pressed coke, Köln Müsen, - - -	6·9	47·2	56	103·2	
5. Ordinary Coppée coke, -	7·99	54·8	53·2	108	Fewer small and large pores.
6. Carlsglück and Planetenfeld, - - -	7·8	55·2	54·8	110	
7. Maassener Tiefbau, -	7·3	58·4	54	112·4	
8. Westhausen, nr. Bodelschwingh, - - -	10·6	54·8	54	108·8	
9. New Iserlohn, nr. Langendreer, - - -	8·8	60·4	54	114·4	Numerous smaller and much larger pores.
10. Dannenbaum, nr. Bochum, - - - -	8·45	59·6	52·8	112·4	Smaller and larger pores.
11. Germania iron works at Grevenbrück, - -	7·6	58·4	52·4	110·8	Mostly somewhat large pores.
12. Heinrichshütte Company, - - - -	7·6	49·0	53·0	102·0	
13. Meiler coke, - - -	2·9	28·4	67·2	95·6	Numerous small pores with clearly recognisable longitudinal direction.
14. Pinewood charcoal, -	2·9	200·4	61·6	262·0	Few microscopic small regularly arranged cells, tubular in longitudinal section.
15. Oak charcoal, - - -	2·45	96·2	74·2	170·4	Fewer large cells, tubular in longitudinal section.
16. Beech charcoal, - -	2·10	100·8	67·6	168·4	Like No. 14, but larger cells.
17. Birch charcoal, - -	1·65	132·5	74·0	206·5	Like No. 14, but larger and apparently more irregularly arranged cells.
18. Anthracite Piesberg, -	9·3	3·6	60·0	63·6	
19. Coal Borgloh,- - -	8·3	1·4	75·6	77·0	

Specific Gravity.—A distinction is made between the apparent and the real specific gravity. The former is usually accepted as meaning the specific gravity of the coke free from pores—that is, of the coke carbon (+ash); the real specific gravity then means that of the pore-containing coke—that is to say, of the coke carbon + pore space (with air). (But Cp. Chap. VII., p. 154).

The apparent specific gravity depends on the quantity of ash in the coke and on the density of the carbon, while the number and also the size of the pores has an effect on the real specific gravity. The more pores the coke contains, and the larger these are, the lower is the specific gravity.

In practice what is called above the "apparent specific gravity" is generally that referred to. This varies in the case of European brands of coke between 1·2 and 1·9; while for American coke the average is 1·5, although here too values as high as 1·9 are not infrequent. The lower specific gravity of American coke, as compared with Westphalian, is explained by the predominance of the beehive type of oven in America. Beehive coke has a very low specific gravity, and is much lighter than an equal bulk of Simon-Carvès coke. Compared with these, the specific gravity of wood charcoal is ·20-·50, and that of coal 1·25-1·75.

The weight of a cubic metre of coke in the form of pieces is from 350-450 kilos., varying with the amount of ash and the density and size of the pieces; 420 kilos. may be taken as an average. Coal weighs 700-900 kilos. per cubic metre, while the weight of air-dried wood charcoal amounts to only 190 kilos. per cubic metre. By stamping and by pressure, &c., during coking, the volume of coke can be diminished by about 25 per cent. Westphalian coke is reckoned at about 2 cubic metres to the ton (metric). A 15-ton waggon, 7·7 metres long, 2·84 broad, and 1·50 deep, holds about 32·7 cubic metres. With large coke the waggon is filled exactly, and in the case of broken coke to within 4-5 cms. of the edge.

PHYSICAL PROPERTIES.

		Standard Coke.	Pinneville.	West Virginia.	Broad Top.	Clearfield.	Cumberland.	Alabama.	Illinois.
1 cb. inch contains grms.	dry,	15·47	14·10	13·76	11·76	14·79	12·76	13·30	11·06
	moist,	23·67	22·24	21·19	20·18	19·86	21·63	18·29	17·09
1 cb. foot contains lbs.	dry,	58·98	52·75	52·54	44·81	56·35	48·61	50·70	43·02
	moist,	87·34	84·73	81·56	77·88	76·69	82·41	69·01	65·09
Percentage volume of	coke,	49·96	50·37	64·3	58·3	74·4	59·	73·8	63·8
	cells,	50·01	49·63	35·7	41·7	25·6	41·	26·2	36·2
Crushing strain in lbs. per inch,		301	227	258	240	319	215	225	180
Height of column in furnace which the coke stands without crumbling,		120	91	103	96	128	86	87	70
Hardness,		3·5	3·	3·15	3·35	3·60	3·	3·5	3·2
Specific gravity,		1·89	1·71	1·5	1·342	1·56	1·75	1·493	1·215
		CHEMICAL COMPOSITION.							
Carbon,		87·46	94·66	92·18	89·28	89·86	89·86	89·86	89·77
Moisture,		·49	1·14	·11	·11	·54	·54	·54	·12
Ash,		11·32	3·37	6·88	8·66	9·41	9·41	9·41	9·58
Sulphur,		·69	·59	·618	1·06	1·06	1·06	1·06	·93
Phosphorus,		·029	·007	·027	·027	·027	·027	·027	·033
Volatile constituents,		·111	·041	·350	·350	·667	·667	·667	·667

For determining the specific gravity and the porosity of coke, the volumetric method of Dr. Thörner, "Stahl und Eisen," 1884, p. 594, may conveniently be employed. See also C. Reinhardt, "Stahl und Eisen," 1884, p. 521, and W. Carrick Anderson, "Jr. Soc. Chem. Ind," 1896, p. 20.

The foregoing table, giving an interesting comparison of the physical properties and chemical composition of certain American cokes, may find a place here;[*] the experiments were carried out by Fulton, manager of the Cambria Iron Works.

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[*] From F. M. Simmersbach, Mittheilungen über den Kohlenbergbau und den Kohlentransport in den Vereinigten Staaten von Amerika (published as a handbook in 1891). Also "Iron," 1884, No. 602; "Berg und Hüttenman. Ztg.," 1884, p. 551.

CHAPTER VI.

Combustibility and Calorific Value of Coke.*

THE inflammability of coke shows great variations, so that it is a difficult matter to make a statement regarding it that would apply universally. Besides this, different metallurgical processes demand a greater or less degree of inflammability, according to the circumstances of the case.

For the ignition of coke a bright red heat, about 700° C., is required, while coal will ignite at a temperature as low as 326°. Coke burns only when placed in a thick layer, and requires for complete combustion a lively draught of air; a single piece taken out of the fire cools very rapidly in the air on account of the high temperature of ignition.

The inflammability of coke depends upon the size and shape of the pieces, and also upon the moisture it contains. It decreases with increase of carbon, and *vice versâ;* a flame that will blaze up instantly, or one that can be speedily extinguished, naturally cannot be obtained by the use of coke. The carbon, which by

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* Belani, "Stahl und Eisen," 1885, p. 603; 1886, p. 302; Kutscher, "Stahl und Eisen," 1885, p. 794; Van Vloten, "Stahl und Eisen," 1886, p. 42, and 1886, p. 241; Jantzen, "Stahl und Eisen," 1886, p. 83.

itself is difficult to ignite, is rendered more combustible by the presence of a larger proportion of easily combustible hydrogen; consequently the inflammability is increased by the addition of bitumen. Since carbon has a much higher specific gravity than hydrogen, coke of low specific gravity will burn more readily than that which is heavier. Further, the looser its condition, the more inflammable the coke usually becomes. Coke differs from wood charcoal in having a high conductivity for heat, which is an advantage not to be under estimated, since the heating of the charge in a blast furnace is, to a certain extent, due to the direct conduction of heat from below. When used in stoves also for the heating of rooms, &c., the proportionally high conductivity for heat possessed by coke is a distinct advantage.

As regards the behaviour of coke towards a heated air blast, the combustibility stands to that of wood charcoal, on an average, in the proportion 1 : 1·6. The denser the coke is, the higher does this numerical ratio become, while it diminishes conversely with increase in the porosity.

According to Thörner * the ratio of combustibility is as follows:—

Ordinary coke to birch charcoal,	= 1 : 1·97
,, ,, ,, pine charcoal,	= 1 : 1·97
,, ,, ,, meiler coke,	= 1 : 1·72
,, ,, ,, beech charcoal,	= 1 : 1·58
,, ,, ,, oak charcoal,	= 1 : 1·55
,, ,, ,, coal,	= 1 : 1·45
,, ,, ,, anthracite,	= 1 : 0·89

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* "Stahl und Eisen," 1886, p. 71, *et seq.*

From this it appears that cokes burn more rapidly than anthracite, while, on the other hand, they are more difficultly combustible than wood charcoal. They remain longer, therefore, in the furnace than the latter, and are better heated up when they come to be burned, so that their efficiency is enhanced. By increasing the pressure and temperature of the blast the combustibility can be increased.

The capacity of the fuels to resist the action of heated air is very variable, and similarly they show different degrees of affinity for carbonic acid.

Lowthian Bell [*] compares the different degrees in which various forms of carbon attack carbonic acid with the different inflammabilities of wood charcoal, coke, and diamond, which, when completely burned in oxygen, liberate almost exactly equal quantities of heat, and holds that this small discrepancy between the different forms of carbon is due to the fact that the quantity completely burned to carbonic acid in each case must be different.

The wood charcoals are most powerfully attacked by carbonic acid, and burn with greatest rapidity. Meiler coke comes next, and lastly, the different varieties of coke. On soft coke, carbonic acid acts six times as powerfully as on hard. (Cp. p. 117.) Dr. Thörner (*loc. cit.*) obtained the following figures for combustibility in carbonic acid:—

Ordinary coke : gas-retort coke, - - - = 1 : 1·4
,, : pressed coke from Köln-Müsen, = 1 : 1·7
,, : coke from Neu Iserlohn, - = 1 : 1·4

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[*] "Stahl und Eisen," 1885, No. 6.

Ordinary coke : meiler coke, - - - - = 1 : 5·6
,, : oak charcoal, - - - = 1 : 10·5
,, : beech and birch charcoal, - = 1 : 11·7
,, : pine charcoal, - - - = 1 : 11·9

With regard to these experiments, it must always be taken into consideration that in the blast furnace the carbonic acid is diluted by the presence of carbonic oxide, and especially of nitrogen, and consequently the carbonic acid cannot have so wide a range of attack in the blast furnace as it has in laboratory experiments.

Coke serves, as pointed out in Chapter I., both as a melting and reducing agent. The blast furnace is at once a melting and reducing furnace, while in the cupola furnace the function of reducing is omitted. Accordingly, blast-furnace coke serves for the production of heat and for reduction—that is to say, for the formation of carbonic oxide; whereas foundry coke is employed only for the production of a high temperature by means of the most complete combustion, namely, to carbonic acid. As is known, the formation of carbonic oxide proceeds according to the following equation:—

$$2C + 2O = 2CO ;$$

the formation of carbonic acid thus—

$$C + 2O = CO_2.$$

Consequently, in the formation of carbonic oxide double the quantity of carbon is burned by the same quantity of oxygen as in the formation of carbonic acid. *Hence the physical structure of the coke—that is to say, the surface it presents—has an essential bearing on its employment as blast furnace or as foundry coke.*

Porous coke occupies a larger space in proportion to its weight than dense coke, consequently it exposes a larger surface to the oxygen of the air—that is to say, essentially a greater number of carbon molecules stands at the disposal of the oxygen, so that carbonic oxide is more readily formed. Besides this the action of the oxygen is increased by the greater rapidity with which the gases can pass through, and thus on all sides—not only on the outside, but at the same time also within—exercise their oxidising effect. But the more rapidly the free oxygen and the carbonic acid that is also to some extent produced are converted by the carbon into carbonic oxide, the more favourably does the blast-furnace process proceed.

In the case of dense coke, on account of the smaller space it occupies, the amount of surface reached by the oxygen of the air blast is considerably less, and consequently the latter can act only on a smaller number of carbon molecules; the intensity of the action is likewise essentially less, inasmuch as the coke burns only on the surface, the gases being unable to enter or to penetrate through the dense structure. In this way increased density of the coke tends to promote the formation of a large quantity of carbonic acid in combustion. Foundry coke must accordingly be as dense as possible.

If dense coke be employed in the blast furnace, it is necessary, in order to obtain a sufficient quantity of reducing gases, to have recourse to a hotter blast under increased pressure, consequently a more energetic working of the furnace. The hotter blast has much less oxygen for the same bulk than a colder one, and thus the preponderance of carbon particles is promoted —that is to say, the formation of carbonic oxide. A result of the increased pressure is that the blast seeks to penetrate as far as possible into the pores of the coke, whereby the surface of carbon is further augmented. Certainly, by the higher pressure, the speed of the blast is also increased, and thus the air on the surface of the coke is more quickly renewed, so that, so far as the formation of carbonic oxide is concerned, the effect of the increased pressure must be regarded as less important than the employment of the hot blast.

In the cupola furnace, on the other hand, the use of porous coke will only aggravate the evil of incomplete utilisation of the fuel: and the greater the amount of carbonic oxide produced in the cupola, the larger will be the consumpt of coke.

The extent to which the surface of the coke determines the character of the combustion, and especially the formation of carbonic acid or of carbonic oxide is indicated by the experiments of Lowthian Bell,* in which a current of dry carbonic acid at a bright heat was led in the first instance over wood charcoal, then over porous, and finally over dense coke. The resulting gaseous mixtures were found to contain CO_2 and CO in the following proportions:—

Wood charcoal,	35·20	per cent.	CO_2 and	64·80	per cent. CO.
Porous coke, -	69·81	,,	,,	30·19	,, ,,
Dense coke, -	94·56	,,	,,	5·44	,, ,,

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* "Journal of the Iron and Steel Institute," 1872, i., p. 74; repeated in Bell's "Principles of the Manufacture of Iron and Steel," London, 1884, p. 287; further, "Ledebur, Die Gasfeuerungen für Metallurgische Zwecke," Leipzig, 1891.

Now, in the blast furnace the carbonic acid is always converted into carbonic oxide according to the equation $CO_2 + C = 2CO$; in this process, however, coke is consumed which is thereby prevented from reaching the crucible, and is thus completely lost so far as the production of heat is concerned. Since 1 kilogram of carbon in burning to CO_2 evolves 8080 heat units, and in burning to CO only 2473, the loss of heat for every kilogram of carbon which is oxidised by CO_2 to CO is $8080 - 2 \times 2473 = 3134$ units.

Wood charcoal by reason of its porous structure readily produces large quantities of carbonic oxide in the blast furnace which, when coke is used, must be produced artificially by hot air blast, &c. On the other hand, dense coke yields more carbonic acid than wood charcoal, which explains the fact observed even in the earliest cupola furnaces that the consumption of fuel was less where coke was used than where wood charcoal was employed.

At the Connemaugh blast furnaces carefully conducted experiments with porous and dense coke gave, according to Fulton (*loc. cit.*), a diminished production to the extent of 11 per cent. when dense coke was used without any admixture.

Speaking generally, the efficiency of the Connellsville coke in the blast furnaces stands to that of dense anthracite in the proportion of 8 : 5; between coke and wood charcoal the ratio is as 1:1·3.

From this it is evident that the employment of what, so far as its chemical composition is concerned, might be regarded as an excellent coke for blast furnace or foundry work, may prove to be uneconomical according as the coke is dense or porous.

In any variety of coke, it is obvious that the smaller the size of the pieces, the larger will be the surface exposed to the action of gases. For this reason coke in small pieces would be more suitable for the production of a gas rich in carbonic oxide than when in large pieces. Since, however, such decrease in the size of the pieces increases the resistance offered to the ascent of the gas, the use of coke in too small pieces is impracticable. When, on the other hand, the size of the pieces is too large, the air blast by means of the large interstices penetrates too deeply, thereby extending the zone of combustion and so causing the heating effect to be diminished. Pieces of uniform size and not exceeding a certain weight appear to be the most suitable.

The calorific value of different cokes is compared partly with reference to the quantity of heat and partly with regard to the temperature produced, and a distinction is made accordingly between "absolute" and "pyrometric" heating effect.

By absolute heating effect is understood the quantity of heat which the unit weight (1 kilo.) of coke evolves on combustion, expressed in calories or heat units.

A calorie is that quantity of heat which is required to raise the temperature of 1 kilo. of water from 0° to 1° C.

The absolute heating effect can be calculated from the chemical composition of the fuel with sufficient accuracy for all practical purposes. For details see Ost, "Lehrbuch der Technischen Chemie"; Post, "Chemisch-technische Analyse"; Muspratt's, "Chemistry," 1893, under heading "Fuels"; Mills and Rowan, "Fuel," pp. 336-338; and others.

The following is a comparative statement of the heating power of the solid fuels. (Cp. Bernoulli's "Dampfmaschinenlehre," Chapter "Verbrennung"):—

Wood with ·20 water,	3200	heat units.
,, ,, ·10 ,,	3600	,,
,, dry,	4000	,,
Peat, dry,	5000	,,
Brown coal, dry,	6000	,,
Coal with ·20 ash,	6250	,,
,, ,, ·10 ,,	7050	,,
,, ,, ·3 ,,	7600	,,
Wood charcoal with ·07 water,	7050	,,
,, ,, dry,	7580	,,
Coke with ·15 ash,	6600	,,
,, ,, ·10 ,,	7000	,,
,, ,, ·5 ,,	8000	,,
Anthracite,	7900	,,

The evaporating power, according to P. W. Brix,[*] is

For Prussian coke (average) dried,	7·81
,, ,, coal ,,	7·39

Very important in practical working is the pyrometrical heating effect of the coke—that is to say, the temperature resulting from its combustion, since upon it depends the possibility of carrying out many metallurgical operations.

The more dense the coke is, the higher is the temperature that can be attained, because, other things

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[*] Brix, "Untersuchungen über die Heizkraft der wichtigeren Brennstoffe des Preussischen Staates," Berlin, 1853.

being equal, the fuel that generates the most powerful heat is that in which the carbonic acid formed by its complete combustion is converted to the smallest extent into carbonic oxide gas by contact with a portion of the glowing carbon. If the combustion be accelerated by air pressure, a more rapid oxidation of the carbon ensues, on account of the presence of a larger quantity of oxygen. Previous heating of the air, &c., further assists in raising the temperature of combustion, for, in this case, the blast carries with it a certain quantity of heat into the furnace which, under these circumstances, does not involve the consumption of any part of the coke already there. On the other hand, the water contained in coke, by reason of its high specific or latent heat, has a considerable effect in lowering the temperature of combustion (sp. heat of steam = ·4750). Similarly, the pyrometric heating effect diminishes with increase in the quantity of air introduced to support the combustion, because the nitrogen, which constitutes four-fifths of it, only consumes heat, so that, in this way, a considerable waste of heat results, as the following comparison indicates :—

C burned in pure O to CO_2 evolves 9870° C.
C ,, air ,, 2450° C.

The pyrometric heating effect is determined by means of a suitable pyrometer, or is calculated from the chemical composition of the fuel. See, among others, Jüptner, "Heizstoffe"; Post, "Chemisch Technische Analyse"; Mills and Rowan, "Fuel," pp. 348-352.

The following may be regarded as the conditions that ought to be fulfilled by a coke which is to be employed in the smelting of iron, and which may be said to hold for Westphalia, Belgium, France, and England :—

(1) 1 per cent. sulphur, - -
(2) ·018 per cent. phosphorus, -
(3) 4 per cent. water, - - } *As maxima.*
(4) 9 ,, ash, - - -
(5) 6 ,, dust (on delivery),
(6) 40-50 per cent. pore space (in foundry coke 25-40 per cent.).
(7) The coke must possess a hardness of 80 kilos. per sq. cm.
(8) The weight of 1 cc. of the coke (dried at 100° C.) should be 800-900 mgrms.

On the value of the fuels as a class, many views have been expressed in the literature dealing with the subject. Fischer[*] refers to their origin. The solid fuels have arisen from cellulose, from which, by separation of H_2O, CO_2, and CH_4, residues rich in carbon are left behind. Cellulose is formed by the action of the sun's rays from carbonic acid and water; $6CO_2 + 5H_2O = C_6H_{10}O_5 + 6O_2$; while, by the combustion of cellulose, the same substances are regenerated: $C_6H_{10}O_5 + 6O_2 = 6CO_2 + 5H_2O$. In the formation of 1 kilo. of cellulose, 5200 heat units must have been supplied by the sun's rays. In using coal or coke we are thus making use of the sun's heat that has been stored up for thousands of years—a store of heat which, without doubt, with the increasing

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[*] "Zeitsch f. angew. Chemie," 1888, p. 351.

cultivation of the soil, will diminish day by day, and gradually become exhausted. In the year 1892, Germany produced 7,700,000 tons of coke; and, if 1 kilo. of coke be reckoned as equivalent to 8000 heat units, it follows that Germany alone consumes annually in the shape of coke about 61,600,000,000,000 heat units from this store.

If it be remembered, moreover, that in Germany in the first half of 1894 the production of pig iron amounted to 2,649,071 tons, and that this material cannot for the present be produced generally without the use of coke, it is evident how important, from an economic point of view, every achievement is which tends to effect a saving in its consumption.

To be enabled therefore to manufacture a more uniform and efficient product from the coking process, and at the same time to lessen the, by no means small, loss of combustible material, ought to serve as an inducement to gain something more than a superficial acquaintance with the chemistry of coke, as well as with the technical contrivances for its improvement.

CHAPTER VII.

Chemical and Physical Examination of Coal and Coke.*

FROM what has been said in the preceding chapters it is evident that the term "coke" covers a series of substances, of varied chemical and physical properties, which are employed for purposes entirely distinct. Gas coke—the fixed product got by distillation of gas coal in closed retorts—is a substance essentially different from metallurgical coke, which is obtained by the carbonisation of "coking coals" in ovens and meilers. Although produced in very large quantity, retort coke is for the most part a bye-product, and endeavours after the improvement of its quality must, in almost every case, be subordinated to the main end of getting the maximum yield of gas of high illuminating power. It it otherwise with the coke which is produced in ovens. Whether the latter be adapted for the recovery of tar, ammonia, &c., or not, the quality of the coke itself demands the first consideration. To begin with, since it is to be employed in metallurgical operations, it must be as free as possible from impurities, and especially from such as, apart

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* Cp. W. F. Keating Stock, "Jr. Soc. Chem. Ind.," 1897, p. 304.

from their merely negative effect in diminishing the total quantity of heat-giving constituents, may exercise a distinctly injurious influence upon the metals with which they come in contact in the furnace. Of these the most important are sulphur and phosphorus. In addition to this, in order to determine its value as a fuel, the coke must be examined for moisture, ash, and volatile constituents, while, if the manufacture is being conducted with recovery of bye-products, it will frequently be necessary to make a determination of the not inconsiderable percentage of nitrogen which, under all circumstances, remains in combination with the fixed carbon. Moreover, oven coke is usually manufactured for either one or other of two definite purposes. It may be designed simply as a heating agent to be employed for the melting of iron in cupola furnaces (foundry coke), or the intention may be to use it at once as a heating and a reducing agent for the production of metals, *e.g.*, iron, from their ores (blast-furnace coke). It has already been stated at length (Chap. VI.) that, to perform these two operations economically, necessitates a different physical structure in the cokes used—that is to say, a greater or less degree of porosity is required; while, in both cases, the hardness or strength of the coke must reach a certain standard to enable it to withstand the attrition to which it is continually exposed in the furnace.

The methods of testing coal and coke, which are given below, will be found convenient alike by those manufacturers who are striving to adapt the character and quality of their product to serve a special purpose, and by consumers who wish to protect themselves in the market against impure fuels of low heating power, as well as against many brands of coke which, excellent as they may be for one purpose, are, in virtue of the degree of hardness and porosity which they possess, of comparatively low efficiency when applied to another. Fuels, whether natural or artificial, are so variable in character and quality that their production and employment alike should invariably be controlled by a systematic scientific examination.

Sampling.—The sampling of coal and coke must be done with the greatest possible care to ensure that the sample is an average one. In the case of coal, a complete section of the seam, or a fair selection of "large" and "small" from a train of waggons, should be taken—amounting in all to about 5 cwts. Coke, when lying on the bench in front of the ovens, is sampled by filling average pieces from the whole length of the charge, and particularly in equal quantities from the top, middle, and bottom of the latter into a barrow, until from 3-5 cwts. have been collected. According to Stock, if the coke is in waggons at the iron works, the waggons are run up on to the gauntree over the storage bunks, and two doors on one side of each waggon are let down. This admits of half the load being seen from top to bottom, so that an idea can be formed as to the relative proportions of "large," "small," and "breeze." Portions of the coke are selected from top, middle, and bottom, and this is done for, say, ten waggons, which should give a bulk sample of 3-5 cwts. The samples got as above are knocked down on clean iron plates until reduced to the size of road metal. The pieces are thoroughly mixed, spread in a square and quartered. Two opposite quarters are removed, and the dust carefully swept away. The remaining quarters are mixed, and the size of the pieces further reduced. The process of quartering is repeated, and is always followed by thorough mixing, until finally a sample of about 300-500 grms. is got, which, in small quantities at a time, is reduced to fine powder in a Wedgwood or agate mortar. Careful mixing of the whole concludes the process.

CHEMICAL ANALYSIS.

Moisture and Ash.—3 grms. of the finely-ground coal or coke in a platinum basin is heated in an air bath at 105° C. for one hour (in the case of coke till constant in weight), afterwards cooled completely in a good desiccator and weighed quickly. The loss in weight $\times \frac{100}{3}$ = per cent. of moisture. The sample is then incinerated, and the residue weighed after cooling in a desiccator. Weight of residue $\times \frac{100}{3}$ = per cent. of ash. The ignition may be done over a powerful argand Bunsen or, better, in a muffle furnace. Under all circumstances, and particularly in the case of cokes, which retain small quantities of carbon in the ash for a long time, the ignition must be continued until the weight is constant to ± 1 mgrm.

Volatile Matter and Fixed Carbon.—1 grm. of the coal or coke sample is ignited in a platinum crucible, with close-fitting lid, for two minutes over a large Bunsen burner and then (without allowing to cool) for three minutes over a good blast lamp. Muck recommends that the crucible be placed 3 cms. above the top of an ordinary Bunsen burner with a flame at least 18 cms. in length, and heated till combustible gases cease to be evolved.* The time treatment, as above, gives a better result, although at the best the experiment cannot be regarded as affording an exact indication of the percentage of coke that the coal will yield in any type of oven. In the case of certain coals, the results, even when obtained under conditions as nearly as possible identical, vary considerably; three determinations should be made and a mean taken.

Sulphur.—1 grm. of the sample is intimately mixed in a platinum crucible with 1 grm. of pure calcined magnesia and ·5 grm. dry sodium carbonate (free from sulphate), by means of a stout platinum wire. The mixture is heated in the open crucible over a good argand Bunsen burner for one hour, or until it is quite white, the incineration being promoted by stirring with the platinum wire at intervals of about five minutes. The crucible is allowed to cool, and 1 grm. of powdered ammonium nitrate is added and well mixed with the residue, which is afterwards heated to bright redness for ten minutes with the lid on. After cooling, the sintered mass is transferred to a beaker, and covered with 200 ccs. of distilled water.

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* The Committee of the American Chemical Soc. on Coal Analysis in their preliminary report ("Jr. Amer. Chem. Soc.," 1898 [4], 281-285; "Jr. Soc. Chem. Ind.," 1898, pp. 608-609), recommends that the coal be heated in a platinum crucible weighing 20-30 grms. supported on a platinum triangle with its bottom 6-8 cms. above the top of a Bunsen flame, 20-25 cms. high when burning free. It is thus heated for seven minutes in a place free from draughts.

The particles adhering to the crucible are removed as far as possible by heating several times with a few ccs. of water, which is added to that in the beaker. A small quantity of dilute nitric acid is warmed in the crucible to dissolve the residue, and this solution is diluted and passed through a filter, which is then washed till free from acid. The beaker containing the bulk of the fuse is meanwhile boiled for half an hour, and the solution passed through the same filter. The residue is well washed with hot water, and filtrate and washings concentrated to about 150 ccs. The latter is acidified with nitric acid, boiled, and precipitated at the boiling temperature with a slight excess of barium chloride. The boiling is continued for ten minutes, the ppt. allowed to settle in the heat, filtered, washed with hot water till the washings are free from chloride, dried in a water bath, incinerated in a platinum or porcelain crucible, and finally ignited over a strong Bunsen flame for twenty minutes. Weight of ppt. $\times \cdot 1374 \times 100 =$ per cent. of sulphur.

Phosphorus.—10 grms. of coal or coke is ignited in a platinum basin till all organic matter is removed. The residue is finely ground in an agate mortar, and digested in an 8-oz. covered beaker with 20 ccs. of brominised hydrochloric acid for one hour at a temperature little short of boiling. The bulk of the acid is then removed by evaporation, and the solution diluted with 20 ccs. of water and filtered. The residue on the filter is washed with distilled water—filtrate and washings should not exceed 45 ccs.—15 ccs. of strong ammonia are then added, and this is cautiously neutralised by nitric acid from a small pipette. When re-solution takes place, dilute ammonia is dropped in till a faint opalescence appears, and this is taken up with a few drops of nitric acid. All these operations are carried out at a temperature approaching boiling. To the faintly acid solution 2½-3 ccs. of strong nitric acid are added, and then 5 ccs. of a 10 per cent. solution of ammonium molybdate is quickly projected from a small measure (not a pipette) into the solution, which is meanwhile briskly agitated. After a second or two the yellow ammonium phosphomolybdate makes its appearance in a granular form, which rapidly settles. The flask is heated to about 90° C., with constant shaking for five minutes; the ppt. filtered off on a hardened filter paper, washed three times with 1-50 nitric acid, dried on the water bath for a half to three-quarters of an hour, and finally brushed into a balance scoop and weighed. Weight of ppt. $\times \cdot 163 =$ per cent. of phosphorus. (Stock.)

This method, though a convenient and rapid one for general use, rarely gives the total phosphorus present in the coal or coke. For most purposes the determinations thus obtained are sufficiently exact, but if the total phosphorus be required, fusion of the ash should, as a rule, be resorted to.

Nitrogen.—1 grm. of the finely-powdered coal or coke is placed in a pear-shaped flask of good potash glass, which should be of about 250 ccs. capacity, and have a long neck (Kjeldahl flask). The sample is covered with 20 ccs. of concentrated sulphuric acid (free from N), and thoroughly moistened with the latter. The mixture is then heated to boiling over a small flame—the flask being held in a slanting position and protected by wire gauze—10 grms. of pure potassium sulphate is added, and the boiling continued till the solution is colourless, which, in the case of most coals, takes place in two and a half to three hours. Metallurgical cokes take longer. If their complete decomposition is unduly delayed, it is advisable to add to the mixture 2 grms. of powdered permanganate of potash in small quantities at a time to hasten the oxidation. When the operation is finished, the partially-cooled contents of the flask are dissolved in water and transferred to a round-bottomed flask of 16-24 oz. capacity. The solution is cooled completely, mixed with 100 ccs. of a 20 per cent. solution of pure sodium hydrate (free from N), and, after addition of a few small fragments of zinc to prevent bumping, the ammonia is distilled off through a Liebig's condenser, and collected in 30 ccs. of $\frac{N}{10}$ sulphuric acid, contained in a 500 ccs. Erlenmeyer flask. A trap arrangement should be fitted between the neck of the distilling flask and the condenser to prevent the carrying over of small quantities of caustic soda. The distillation is continued for a half to three-quarters of an hour with brisk boiling, and the ammonia afterwards determined by titration with a deci-normal solution of sodium carbonate, a carefully neutralised solution of litmus being employed as indicator. The method described is preferable to that of Schmidt ("Jr. Soc. Chem. Ind.," 1886, p. 506), in so far as it does not involve the use of sulphide of soda.

Silica.—10 grms. of the coal or coke is incinerated completely in a platinum crucible, and the ash mixed intimately with 5-6 grams. of "fusion mixture" (Na_2-$CO_3 + K_2CO_3$). The mixture is fused over the foot blowpipe for thirty minutes with the lid on, and, after cooling, crucible and contents are transferred to an evaporating basin of 5″-6″ diam., and covered with hot water. A clock-glass is placed over the basin, and solution of the melt is hastened by warming with small quantities of hydrochloric acid. When solution is completed, the crucible is removed and carefully washed. The solution (which may contain some flocculent silica) is evaporated gently to dryness, the final stage being completed on the water bath with constant breaking up of the hard crusts by means of a glass rod. The residue is gently heated to render the silica insoluble, and, after cooling, moistened with HCl, and digested with hot water. When the soluble matter has been dissolved, the solution is passed through a filter, the silica washed several times by decantation, afterwards thrown on the paper and washed with hot water till free from chlorides. After drying in the oven, the silica and filter paper are ignited together in a tared platinum crucible. Weight of silica × 10 = per cent. silica in the sample.

Iron.—10 grms. of the coal or coke is incinerated, and the ash fused and treated as described above for separation of the silica. The filtrate and washings are concentrated to about 300-400 ccs., a slight excess of ammonia added, and the solution saturated with H_2S. The precipitate is filtered off, dissolved in dilute sulphuric acid in an Erlenmeyer flask, and the solution boiled till free from H_2S. As soon as the H_2S is completely expelled, the solution is cooled as rapidly as possible, with limited access of air, and titrated with a standard permanganate of potash, of which 1 cc. = ·0056 grm. Fe. Fe. × 10 = per cent. iron in the sample.

PHYSICAL PROPERTIES OF COKE.

Hardness.—The method of determining the hardness of coke has already been described on p. 120.

Real Specific Gravity.—To determine the real specific gravity 3-3½ grms. of the finely-ground average sample of coke (previously dried) is weighed out in a tared specific gravity bottle of 50 grms. capacity. The sample is then covered with about an inch of water, and the bottle is immersed in a beaker of water kept at a temperature of 90°-100° C. The neck of the bottle is attached by a tube to a Bunsen water-pump with a good supply of water to exhaust the air, and the exhaustion is kept up for two and a half hours, a gentle ebullition being meanwhile maintained. The tube is then detached, the bottle filled up with water, brought to the correct temperature, and finally dried and weighed. This gives what is strictly the "real specific gravity"—*i.e.*, the specific gravity of the matter of the coke.

$$\text{Real sp. gr.} = \frac{\text{Weight of dry sample}}{\text{Weight of (bottle + sample + water content of bottle)} - \text{final weight of (bottle, sample, and water required to fill)}}$$

Apparent Specific Gravity.—The "apparent specific gravity"—that is, the specific gravity of the coke matter and enclosed gases together—can be rapidly and accurately obtained by means of the simple "volumenometer" shown in fig. 2. The instrument consists of two parts, one of which (A) is a receiver capable of holding 25-100 ccs. of water. This is closed at the top by an accurately-fitting, hollow, glass stopper, which is prolonged upwards into a narrow tube closed by a stopcock. The receiver is connected at the bottom by means of a piece of thick-walled indiarubber tubing with the measurer (B), which is an ordinary glass burette capable of being read to $\frac{1}{20}$ cc., and the whole instrument is clamped to a suitable stand. To obtain the specific gravity of a sample of coke, the measurer is moved up and down so as to fill the receiver with water exactly to the level of the stopcock, which is then closed, and the reading on the measurer taken. The stopcock is next opened, and part of the water in the receiver caused to flow into the measurer, and the stopper is then removed to admit the weighed sample. The dry sample, brushed free from dust, should be from 5-30 grms. in weight, and in fairly large pieces. When the sample has been

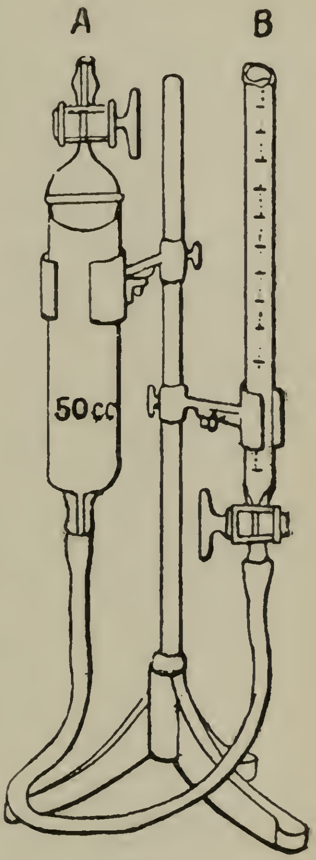

Fig 2.

gently placed in the receiver, the stopper is replaced, and the water caused to return to the level of the stopcock, which is then closed. The instrument is next shaken briskly to detach adhering air bubbles, which are allowed to escape, and a new reading is taken. Ten minutes, or at least equal intervals of time, should be allowed to elapse before taking each reading, to admit of the liquid running down. The difference of the two readings gives the volume of the sample in ccs., which, at the ordinary temperature, may be assumed with sufficient accuracy to represent an equal number of grms. of water, and therefore—

$$\text{Appar. sp. gr.} = \frac{\text{Weight of sample in grms.}}{\text{Volume in ccs.}}$$

Porosity.—The porosity of coke, by which is meant the percentage of its volume occupied by the pores, is readily obtained by combining the figures for the real and apparent specific gravities—

$$\text{Porosity} = \frac{(\text{Real S.G.} - \text{appar. S.G.}) \times 100}{\text{Real S.G.}}$$

The volume of pores in ccs. per 100 grms. of coke is got by dividing the porosity by the apparent specific gravity.

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