General view of storage pile at Angus.

(Porter and Brunton)

CANADA

DEPARTMENT OF MINES

HON. LOUIS CODERRE, MINISTER; R. G. McCONNELL, DEPUTY MINISTER.

MINES BRANCH
EUGENE HAANEL, PH.D., DIRECTOR.

AN

INVESTIGATION

OF THE

COALS OF CANADA

WITH REFERENCE TO THEIR ECONOMIC QUALITIES:

AS CONDUCTED AT McGILL UNIVERSITY, MONTREAL,
UNDER THE AUTHORITY OF THE DOMINION
GOVERNMENT.

EXTRA VOLUME
SUPPLEMENTING REPORT No. 83

WEATHERING OF COAL

BY

J. B. Porter, E.M., Ph.D., D.Sc.,

ASSISTED BY

Stopford Lauder Brunton, A.M.,M.Sc.; Joseph B. de Hart, M.Sc.;
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and Edgar Stansfield, M.Sc.

LETTER OF TRANSMITTAL.

Eugene Haanel, Ph.D.,
    Director Mines Branch,
        Department of Mines,
            Canada.

Sir,—
    I beg to hand you, herewith, a report on the Weathering of Coal,
supplementing my report of November 7, 1910, on the Coals of Canada.

                    I have the honour to be, Sir,
                            Your obedient servant,
                                (*Signed*) **John Bonsall Porter.**

McGill University,
    December 28, 1914.

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PREFACE.

In the autumn of 1906 the Canadian Government through its Department of Mines—then the "Geological Survey of Canada"—undertook an extended study of the fuels of the Dominion; but inasmuch as the Government did not at that time possess suitable fuel testing laboratories, and a considerable amount of research work had already been done by the Mining Department of McGill University, the author was invited to undertake the larger investigation.

The main results of the above mentioned work have been published by the Mines Branch of the Department of Mines, under the title of "The Coals of Canada, An Economic Investigation—6 vols., Ottawa, 1912-13." This report presents, in great detail, a statement of the coal and lignite resources of the Dominion; a description of each of the important mines operating at the time; and the results of an extended series of experimental tests, on a semi-commercial scale, in coal washing, coking, steam-raising, and power gas producing. Each of these sections was prepared by a competent specialist, and contains a general discussion of its subject; a technical description of the tests made; a summary statement of the results of these tests; and an appendix giving full details of each experiment. The report, as a whole, then closes with a section devoted to the chemical methods employed, and their results.

In the above mentioned report attention was drawn to the fact that many coals oxidize rapidly in storage, and are liable to serious deterioration, or even destruction. Circumstances did not permit of an extended study of oxidation as a part of the original investigation; but the matter is especially important in Canada where climatic conditions necessitate the storage of large amounts of bituminous coal at central distribution points; and since the completion of the main report, the author and certain members of his staff have carried on a series of laboratory studies of the oxidation of coal at low temperatures. They have, moreover, made a study of the practical problem of coal storage, both at the mines and in Montreal, and also in other cities. These investigations have been by no means exhaustive, and no very novel conclusions have been drawn from them; but their results seem worthy of publication as a contribution to the literature of an important and difficult subject.

In addition to presenting reports on his own work, as above, the author has attempted in the present volume to bring together and summarize the more important writings of other investigators, and to present a somewhat extended discussion of the whole subject of the weathering of coal. He recognizes to the full the difficulty of his task and the impossibility of dealing adequately with it; but he hopes that his work will be of value to future students and investigators.

The literature of the subject is voluminous, but scattered, and often fragmentary and conflicting, and some of the most important contributions are in French or German or are in rare books and periodicals. The present work, which has been written in the spare hours of a busy life, makes no pretension to being a complete review of this literature; but it is believed that nearly everything of importance has been included, and, in the case of inaccessible or very important articles, full abstracts, or even extended quotations have been made, without hesitation.

In closing, the author wishes to acknowledge the valuable and most loyal aid of his several research assistants, whose names appear with his own on the title page. He also wishes to express his indebtedness to, and admiration for, the work of numerous investigators in the same field. It is impossible to name them all without repeating the bibliography; but especial reference must be made to the work of Dr. J. S. Haldane, F. R. S. of Oxford University, England; Professor W. S. Parr of the Engineering Experiment Station of the University of Illinois; and Dr. H. C. Porter of the United States Bureau of Mines, and to the research chemists working under their guidance.

McGill University,
    December 18, 1914.

THE

COALS OF CANADA:

AN ECONOMIC INVESTIGATION.

WEATHERING OF COAL.

BY

J. B. Porter, E.M., Ph.D., D.Sc.

AND OTHERS.

the main industrial population lies between them at a great distance from either. Industrial Canada may be said roughly to extend from Quebec to Sault Ste. Marie with its chief centres at Montreal and Toronto. These cities are 1,000 and 1,350 miles respectively from Sydney, Nova Scotia, which is the chief source of coal in eastern Canada, while Toronto is but 400 miles approximately from the centres of the anthracite and eastern bituminous coal fields of the United States.

From May until November, Nova Scotia coal can be sent to Montreal in large sea-going ships at rates of transportation averaging approximately one-third of those charged for rail shipments; and from Montreal, by a single transfer to smaller vessels, water transport becomes practicable not merely to Toronto, but as far west as Fort William.[1] Similarly, although to a less extent, American anthracite coal reaches Montreal by barge at rates which compare favourably with rail rates, and·tend to control the latter during the season of navigation.

For five months each year water transport is impossible and all fuel brought in has to pay the relatively high rates of winter traffic by rail. These rates from Sydney to Montreal for example are approximately two dollars per ton higher than rates by sea. The difference in favour of water traffic is sufficient to more than pay the cost both direct and indirect of shipping the great bulk of each year's supply in advance by sea and storing it until needed. The total amount so stored is immense; Montreal for instance being estimated to have had one million tons of bituminous coal and a very large amount of anthracite in store at the end of the season of navigation in November, 1913, while other cities and railway centres all similarly had great stores of fuel.

Canadian coals unfortunately do not differ from other coals of the same class in their liability to weathering, and while few if any of our coals are as troublesome as certain notorious coals in other lands, yet several of the best known and most valuable steam coals in eastern Canada are liable to spontaneous combustion, and large sums of money are spent each year in Montreal and other cities in guarding coal storage piles against fires, and still larger sums in fighting the fires which do occur, and making good the damage which results from the fires themselves, and that resulting from heating which does not quite reach the ignition point.

In view of the facts above set forth, it has seemed proper that a volume on the Weathering of Coal should be included in the general economic study of the Coals of Canada which was undertaken by the Department of Mines some few years ago, and entrusted, through the Director of Mines, to the senior author of the present work.

As already stated, the subject of spontaneous combustion has engaged the attention of several Royal Commissions, and there have been a very

[1] Very little sea-borne coal is actually shipped to Toronto and still less to Fort William, etc., because under the present tariff Pennsylvania and Ohio coals can be sold in most parts of Ontario at more favourable prices than Nova Scotian fuel. These American coals are, however, themselves transported by water to a considerable extent, and·the fact that water transport is possible for several months in the year has a very potent influence in keeping down rail freights to all competitive points.

large number of official and private investigations. During the last three or four years in particular an exceptionally large number of persons have been at work and scores of papers have been written; but the problem is one of extreme complexity and the great majority of the investigations which have thus far been carried out may be looked on as attempts to study specific aspects of the case rather than to deal with the matter as a whole.

The most important of the early investigations of the behaviour of coal in storage were carried out by Fayol[1] at Commentry in France. His report which appeared in 1878 is full of valuable information, but its most salient feature is the conclusive proof that when a pile of Commentry coal under ordinary conditions has attained a certain termperature (about 100°C.) autogenous[2] or self-propelled oxidation begins. The influences which tend to raise the temperature of coal to this point have engaged the attention of all investigators of spontaneous combustion since Fayol's time.

The senior author of the present volume has been interested for several years in the particular problem of the safe storage of Nova Scotian coal, and to this end has conducted a number of practical experiments both in Montreal and at the mines. He has, fortunately, also been able to assign the subject for four years in succession to one or another of his departmental research assistants, and thus to carry out a considerable amount of exact laboratory work on certain features of coal oxidation. All of this original work is, however, but a fraction of what will have to be done before the problem can be considered finally solved.

This experimental work must, therefore, be looked on merely as a contribution to the general investigation that is being carried on throughout the world, and under ordinary circumstances the account of it should have been published as a paper in the transactions of some suitable technical society. So much public interest has, however, been aroused of late in spontaneous combustion that it has seemed desirable both to the Director of Mines and the author to attempt to present in a single volume a general statement of what is now known on the subject, and a considerable part of the present work is, therefore, a review of the most important papers that have been published on coal weathering.

The author has tried to present this matter in logical sequence, and to state the views of the several writers as fairly as possible, although he has not refrained from comment or criticism where either seemed desirable. He recognizes, however, that his essay is by no means above criticism itself; the literature of the subject is very voluminous, and on the whole very unsatisfactory, and all that can be claimed for the present volume is that it is

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[1] Études sur l'Altération, etc., de la houille exposée à l'air. Paris, 1879.
This work has been reviewed and abstracted in English in the following publications:
Report New South Wales Royal Commission on ships carrying coal, 1897.
Review by Threlfall, Jour. Soc. Chem. Ind. Vol. 28, 1909, p. 763.
[2] This term autogenous oxidaton is frequently misunderstood. All natural oxidation is in a sense autogenous, but for coal which has been stored, there is some particular temperature for each particular coal and each particular condition of piling, above which the rate of oxidation is so rapid that the heat of the mass is no longer kept down by natural radiation, etc., but rises more and more rapidly until actual ignition takes place. This matter will be considered at length in another part of this book.

a sincere attempt to summarize in a comparatively small number of pages, matter culled from some thousands of pages of reports, bulletins, transactions, etc., most of which are only to be found in the great public libraries.

The book deals also with the individual experimental work of the author and his associates. This work was highly special and concerns only a few points in a very complex matter, but the results are offered for what they are worth. The author believes that they have definite value as settling one or two questions and casting light on some others on which opinions have been at variance.

ORIGIN AND COMPOSITION OF COAL.

The generally accepted theory of the formation of coal is as follows:—

Vegetable matter of all kinds, but particularly the remains of ancient Equiseta such as Calamite, and Lycopods such as Lepidodendron and Sigillaria with their huge root-like stigmaria, accumulated in thick layers and became massed together under conditions approximating those of swampy jungle of the present day. Eventually this vegetable matter was covered by the deposition of silt and mud, and this in turn by other stratified deposits often of great aggregate thickness. Through the agencies of heat and pressure in the earth's crust, the mass was next subjected to some sort of destructive distillation involving a gradual loss of water, oxygen and other constituents and resulting in the slow formation of coaly material, approximating more and more to pure carbon as time passed on. Anthracite is the last product which may be termed coal, further action of heat and pressure producing graphite. A coal which has arrived at the anthracite stage, will thus have passed through all the other stages during its formation: that is, first growing plants, then peat, lignite, bituminous coal and anthracite.

A great deal of light has been cast on the origin of coal by the study of thin sections under the microscope. By this means the original vegetable forms have been identified and studied, and the coaly material has been shown to consist very largely of accumulations of spores altered of course by heat and pressure, but still perfectly distinguishable.

Quite recently a very interesting contribution to this branch of the subject has been made by Lomax,[1] who has studied coals microscopically with especial reference to their liability to oxidation and spontaneous combustion. Still more recently a most valuable general work on the origin of coal has been published by the United States Bureau of Mines.[2]

As might be expected from its formation, the chief elements occurring in coal are also those which went to make up the plant body, although the proportions of course do not correspond, since the process of the formation

[1] (A). The Microscopical Examination of coal and its use in determining the inflammable constituents present therein T. I. M. E. Vol. XLII, 1911, p. 2.

(B). Further researches in the microscopical examination of coal especially in relation to spontaneous combustion. T. I. M. E. Vol. XLVI, 1914. p. 592.

[2] The Origin of Coal—by David White and Reinhardt Thiessen—with a chapter on the formation of peat by C. A. Davis—Bull. 38, U. S. Bur. of Mines, 1913, pp. 1-304 and 54 photographic plates.

of coal tends to the loss of oxygen and hydrogen more rapidly than the other constituents and therefore, to the relative increase in the proportion of carbon. The common elements in coal are: carbon, hydrogen, oxygen, nitrogen, sulphur, phosphorus, iron, calcium, magnesium, etc., the last four or five usually occurring in small proportions.

These elements are not merely linked up to form a few specific compounds. Many of the complex compounds, which existed in the plants from which the coal was derived, would each form whole series of degradation products during the slow transformation into coal. In every specimen of coal we get many compounds representative of some of the exceedingly numerous possibilities in the above series. There is no prima facie reason why any two different samples of coal should be alike in composition; for not only may different plants have gone to form their substance, but also the metamorphosis may have followed different lines. It can thus be easily understood that although a great amount of work has been done on the subject, very little is yet known of many of the actual chemical compounds existing in coal.

When coals are consumed, whether that destruction be in the form of slow decomposition such as weathering, or more rapid decomposition as spontaneous combustion, or actual burning in the furnace, the action is primarily the oxidation of the combustible matter of the coal, that is to say (a) the coaly matter itself and (b) the pyrite, marcasite and other sulphur compounds which the coal contains. Other heat-giving reactions may occur to a small extent in some cases, but in a practical sense the only combustible elements are carbon C, hydrogen H, and sulphur S. Of these elements the carbon greatly predominates in heating value although its heat is largely augmented by that from the hydrogen, or in other words, the coaly matter proper provides enormously the greater part of the total heat, but as will be shown later the pyrite and other sulphur compounds are supposed by some observers to be the first to oxidize, and therefore to play a most important part in the early stages of combustion.

Harger[1] says in an address to the Liverpool section of the Society of Chemical Industry, that coals are conglomerates of four classes of bodies:

Approx. Composition and Calorific Value.

	Carbon %	Hydrogen %	Oxygen %	Cal. Val.
1. Carbon residuum	96	$2\frac{1}{2}$	$1\frac{1}{2}$	8,765
2. Resins	79	10	11	9,130
3. Humus bodies	63	5	32	6,480
4. Hydrocarbons	75–85	25–15	0	12,000

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[1] Society of Chemical Industry. Vol. XXXI, February 1912, pp. 413-416.

1. *Carbon residues* contain little volatile matter; occur largely in anthracites and hard steam coals, and in bituminous coals to a lesser amount.

2. *Resin bodies* contain very little hydroscopic moisture, melt and decompose between 300°C and 400°C; and below 500°C they yield soft coke; heated above 500°C they decompose rapidly, yielding hydrogen, hydrocarbon gases and hard coke.

These resin bodies and their derivatives, the humus bodies, are believed by many authorities to play a major part in the spontaneous combustion of coal. This matter will, however, only be touched upon here as it is dealt with at some length in another section.

There are two classes of these bodies (a) unsaponifiable by alkali, not oxidizable by warm air, and insoluble in pyridine; (b) soluble in pyridine, saponifiable by alkali, and oxidizable to humus bodies by warm air. These are the bodies upon which Parr worked, using phenol as a solvent. He says that they are oxygenated compounds which exist in coal and can be removed by phenol, and that they are unsaturated, and can take up oxygen. After distillation the distillates are equally active with respect to oxygen. They have definite melting points. The resin bodies are those whose presence decides the coking power of a coal; if too great a quantity is present the coke as it forms will swell and burst itself, just as sugar does when heated: if excessively resinous coals are to be coked they should, therefore, be mixed with some inert carbonaceous substance such as coke breeze.

The origin of these resin and humus bodies, and the part they play in spontaneous combustion is dealt with from the microscopical point of view by Lomax.[1]

Fayol classes coals which are liable to heat in the following natural order: Lignite, Bituminous, and Anthracite. It can be readily understood that bituminous coals containing large quantities of easily attacked resin bodies are the ones which generally heat most readily; peaty lignites, and some lignites themselves, also heat readily, but this fact is of theoretical interest only as they contain so much oxygen, water, etc., that they keep very badly, and having a very low calorific value there is little commercial reason for storing them. On the other hand coals approximating to anthracite resemble carbon more and more in their stability when exposed to air.

Dennstedt and Bünz[2] ascribe increase of absorption of moisture by coal to the humic acids which are gradually formed as oxidation of the resin bodies proceeds. They state that the last products of the reaction are mainly humic acids, and the quantity of these acids present is, therefore, an indication of the heating tendency of a coal.

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[1] Same reference as ([1]A and B) on page 4.
[2] Zeitschrift für ang. Chemie. (1908). Vol. 35, pp. 1825-35.

The above mentioned resin bodies are presumably those to which Parr and Kressmann[1] refer when they speak of the avidity of freshly mined coals for oxygen, which gas enters into combination with the unsaturated hydrocarbons of the coal.

Fischer[2] made use of the oxidizability of these resins as an indication of the liability of a coal to heat. He heated a weighed sample with a definite quantity of an oxidizing agent like bromine water.

Stansfield[3] draws attention to the similarity between the production of acids by oxidation of aldehydes, and the production of acids (humic) by oxidation of coal.

3. *Humus bodies* are similar in chemical composition to woody fibre, they retain a considerable amount of water which is only removed at 105°C; they have a lower percentage of carbon than shown in the table (p. 5) as Harger's figures are calculated free of nitrogen, ash and water. Large quantities occur in peat and lignites, lesser quantities in cannels and bituminous coals, and none in true anthracite.

Boudouard[4] worked on these bodies, and shows that the chemical constituents of the humic substances obtained by extraction from coal by means of potassium hydroxide solution, correspond with one or more of the following formulæ:—

1. $C_{18}H_{14}O_6$ (Berthelot and Andre)
2. $C_{18}H_{14}O_9$ (Malaguti)
3. $C_{18}H_{14}O_{11}$

and that the effect of oxidizing the coal is to diminish the percentage of carbon, and increase the hydrogen and oxygen content of the humic substances.

Treatment with potassium hydroxide, hydrochloric acid and Schweizer's reagent completely destroyed the coking power of a coal, probably because the cellulose-like substances were removed.

Boudouard also points out that the humic acids are probably the carbohydrates of the original coal in a condensed and polymerized condition, just as polyatomic alcohols, sugars, etc. furnish resins by treatment with alkalies, acids, or by heat.

Chemically similar humic substances, artificially prepared, resemble those extracted from peat and lignite, which adds credence to the theory of the formation of coal aforementioned.

4. *Hydrocarbons* chiefly methane, occur in large quantities in some coals, ethane and higher paraffins may also occur; but these constituents need not be further discussed here.

[1] University of Illinois Exp. Sta. Bull. 46 (1910).
[2] Die Brennstoffe Deutschlands, etc. Braunschweig, 1901, pp. 1-107.
[3] Jour. Can. Mining Inst. Vol. XIII, 1910, p. 196; and Coals of Canada, Vol. VI, 1912, pp. 95-120.
[4] Bull. de la Societe Chimique, Ser. 4, Vol. V, 1909, pp. 365, 372, 377, 380.
Compte Rend. 147, p. 986; 148 p. 284 and 348—1909.

HISTORICAL SURVEY OF PREVIOUS INVESTIGATIONS ON WEATHERING OF COAL.

In the following six pages an attempt is made to summarize very briefly the statements of a number of the more important writers in chronological order. The literature of this subject is very voluminous, and only a fraction of the papers are mentioned. In subsequent pages several of the papers referred to and others not mentioned here will be extensively quoted or abstracted and their conclusions discussed. A much more complete bibliography will be found at page 184 et seq.

The earliest authoritative discussion of the causes of weathering and particularly of spontaneous combustion seems to have been in a series of three reports to the British Parliament by **De la Beche and Playfair,** (1846-50) on "Steam Coals for the Royal Navy". They discuss the probable causes of heating and give analyses and arguments leading to the conclusion that considerable quantities of fines or dust in the coals are more likely to give trouble than the mere presence of pyrite.

Regnault[1] (1855), experimented with coals which he analysed, sealed up in corked flasks and set aside for twenty years; on re-analysis he could detect no alteration, probably because his chemical methods were not sufficiently delicate. Regnault, no doubt following Berzelius, however, states that pyritic coals are known to weather.

Marsilly[2] in his "Etude des houilles consommeés sur la marche de Paris," notes that he believes that coals from gassy mines suffer change on exposure to air, but he does not venture to express an opinion regarding non-gassy coals. Marsilly also notes that coal dust exposed to air loses hydrocarbons, and also some of the substances which determine coking power.

Grundmann[3] (1862) conducted extensive experiments on the weathering losses of coal, and found that large pieces weather less than small; he also found that increase of temperature accelerated the weathering. His experiments on the loss in weight of coal were chiefly of use in that they attracted attention to the subject, his high apparent losses being probably due to poor sampling.

Percy[4] (1864) was apparently the next observer to ascribe spontaneous combustion of coal chiefly to oxidation of the carbonaceous matter of finely divided coal (dust) rather than to the pyrite as had commonly been assumed.

Varrentrapp[5] (1865) kept coal at a constant temperature of 284° C, and claims that it was soon completely oxidized, the coal itself, however, must have risen to a much higher temperature.

[1] (A). Annales des Mines, 3rd Series t. XII, 1837, pp. 161-240.
(B). Rapport sur la fabrication des gaz—Annales des Mines, 5th Series t. VIII 1855, pp. 1-67.
[2] Étude des houilles consommeés sur la marche de Paris, Annales des Mines, 5me Series t. XII, 1857, pp. 347-416
[3] Carnall's Zeitschrift. Vol. X, 1862, p. 236.
Kerperly Bericht, 1866, pp. 32, 33.
Zeitschrft fur Berg Hütten. u. Salin, Vol. X, 1862, pp. 326-332. Vol. XIV, 1866, pp. 52-72.
[4] Chemcal News, Vol. X, 1864, p. 19.
"Metallurgy". Vol. Fuel I, 1875, pp. 289-298.
[5] Dinglers Poly. Journal, Vol. 175, 1865, pp. 156-158.
Dinglers Poly. Journal. Vol. 178, 1865, pp. 379-384.

Fleck[1] (1865) analysed six coals which had weathered for some years, and noted a decrease in carbon and available hydrogen, accompanied by an increase in oxygen and non-disposable hydrogen.

Thompson[2] (1865) noted that in six months a dry coal lost 13% of its calorific value, but that if the coal was moist, the loss was much greater.

Reder[3] (1866) followed up Grundmann's work and using the same kind of coal found small increase of weight, but no practical changes. In a German coal he found a loss of calorific value of about 4%.

Richters[4] (1868) concluded that oxygen was absorbed by coal, part being again given off as carbon dioxide and water while the rest remained in combination. He found that the absorption was at first rapid, but later became very slow; he thought that the only effect of moisture is to disintegrate the coal when pyrite is present.

Pechin[5] (1872) stated that bituminous and semi-bituminous coals weather most severely, the former losing 10 to 25 per cent of its carbon upon exposure to the atmosphere, but he gives no figures to prove his statement, which is undoubtedly incorrect or rather very greatly exaggerated.

Rothwell[6] (1873) says from his experiments that no losses were noted in the cases of anthracite and bituminous coals, except when using small sizes of the latter.

The English Royal Commission[7] (1876) ascribed spontaneous combustion to pyrites, condensation of oxygen on the surface of the coal, and to oxidation of the coal matter itself.

Haton[8] (1878) says the cause of heating lies in the combustible itself, possibly aided by the presence of pyrites. He notes also that air must be present.

Kimball[9] (1879) discusses loss of coking power due to weathering, and thinks the weathering of marcasite and pyrite is of as much importance as the weathering of the coal itself.

Fayol[10] (1879) ascribes the main cause of heating to the coal itself.

Admixture of extraneous pyrites with the coal did not appear to hasten the spontaneous heating.

Adverse weather had no injurious effect upon the coal stored in piles, in so far as could be detected.

Coal piled to a depth of less than two metres did not suffer spontaneous combustion.

[1] Die Steinkohlen Deutschlands, 1865, Vol. II, p. 221.
  Abstr. Percy—Fuels, 1875, pp. 290-2.
[2] London Journal of Arts. June 1865, p. 321 (P. and K.)
[3] (A) Zeit. Verein deutsch. Ing. Vol. X, 1866, p. 698.
  (B) Oest. Zeitschrift fur Berg und Hutton., Vol. XV, 1867,
[4] Dinglers Poly. Jour. Vol. 190; 1868, p. 398.
  Dinglers Poly. Jour. Vol. 193; 1869, pp. 54 and 264.
  Dinglers Poly. Jour. Vol. 195; 1870, pp. 315 and 449.
[5] Trans. Am. Inst. Min. Eng. Vol. I, 1872, p. 285.
[6] Trans. Am. Inst. Min. Eng. Vol. II, 1873, pp. 144-152.
[7] English Royal Commission, "Spontaneous Combustion of Coal in Ships," 1876.
[8] Rapport de la Commission d'études des moyens propre à prevenir les explosions de gison; 1878.
[9] Trans. Am. Inst. Min. Eng. Vol. VIII, 1879, pp. 204-225.
[10] Études sur l'altération et la combustion spontanée de la houille exposée à l'air; 1879.

Haedicke[1] (1881) thought that pyrites is the primary cause of heating in coal.

Lewes[2] (1890) discussed the effects of the presence of inorganic matter in coal; he also discussed spontaneous heating in general, especially with regard to the occurrence of the same in ships. Lewes concluded that pyrites played a large part in spontaneous heating.

Erdmann and Stolzenberg[3] (1907) think that humic acid is the prime cause of heating, especially where ozone is present in the air as at sea. They record some very interesting experiments.

New South Wales Commission[4] (1897-8). In the evidence heard before the Commission the question of depth of storage piles was shown to be one of great importance. This had, of course, been conclusively shown by Fayol previously.

Haldane and Meachem[5] (1898) show from experiments that mine air is usually at a higher temperature than the seam and strata through which it circulates; they also sealed coal in flasks and obtained a reduction in pressure, the residual gas being nitrogen. Haldane and Meachem arrived at the following conclusions:—

"1. The rate of absorption of oxygen is proportional to the partial pressure of the oxygen present.

2. The rate of absorption of oxygen is doubled for every 30° C rise.

3. The rate of absorption of oxygen decreases as time goes on.

4. Absorption goes on at the coal surface and does not penetrate very deeply."

Hale and Williams[6] (1899) found that a bituminous coal lost from one-half to one per cent of its calorific value in eleven months.

Fischer[7] (1901) concluded that weathering of coal is due to oxidation, that actual wetting hastens the weathering of pyrite and marcasite, and that many coals contain organic sulphur compounds. Fischer proposes as a test that a gramme of any finely powdered coal be shaken with 20 c.c. of half normal bromine solution for five minutes, and if any smell of bromine remains, the coal may be safely stored.

Macaulay[8] (1903) after conducting steaming tests with locomotives, concluded that English coal depreciates ten to twelve per cent per year in storage.

Doane[9] (1904) concluded that the amount of moisture left on air drying is an indication of liability of coal to heat when stored.

[1] Dinglers Poly. Jour. Vol. 239; 1881, pp. 148-9.
[2] Trans. Inst. of Naval Arch. Vol. XXXI, 1890, pp. 204-228.
Jour. Soc. Arts. Vol. 40, 1892, pp. 352-365.
[3] Braunkohle Vol. VII, 1908, p. 69.
[4] New South Wales Royal Commission on Ships carrying Coal; 1897-8.
[5] Trans. Soc. Min. Eng. Vol. 16; 1898, p. 457.
[6] Trans. Am. Soc. of Mech. Eng. Vol. XX, 1899, pp. 333-341.
[7] Die Brennstoffe Deutschlands, etc., 1901, pp. 1-107.
[8] Practical Engineering. Vol. XXVIII, 1903. pp. 318-320.
Engineer (London), Vol. 96, 1903 p. 415.
[9] Engineering News, Vol. 52, 1904, p. 141.

Durand[1] (1883) thought spontaneous heating was induced in coal piles by the pyrites present first taking fire. This as already explained is an old opinion which is no longer held by the majority of observers. It is, however, no doubt true of some coals.

Heideprin[2] (1907) stored coal under water, and states that during seven months it lost from $0\cdot8\%$ to $8\cdot5\%$ of calorific value. The losses for coal in the air are reported as being very little more than this. These results are contrary to the observations of all other experimenters, and it is probable that something went wrong either with his sampling or his calorimetric .work. Possibly however, the coal tested was abnormal.

A German gas engineer (1907) is quoted by Porter and Ovitz[3] as having claimed that he found a loss of $1\cdot7\%$ of calorific value per week for fine coal. This statement could only be true of a very exceptional coal; but it typifies a very prevalent and exaggerated opinion as to the rate of loss.

Fessenden and Wharton[4] (1908) claim that the percentage of volatile matter is an indication of the liability of a coal to heat. This statement is only to be taken in a very broad sense. It could not be trusted as between any two individual coals.

Dennstedt and Bunz[5] (1908) passed oxygen through coals at elevated temperatures. They found that coals which have been thoroughly wet, kindle more rapidly than those that have been kept dry; also they state that "self ignition increases in a ratio corresponding to the amount of moisture in air-dry coal." They further point out that coals which contain the most oxygen are most liable to heating, and describe several chemical methods of predetermining the liability of coal to spontaneous combustion.

Parr and Hamilton[6] and Parr and Francis[6] (1908) studied the weathering of coal and the changes which take place in coal when subjected to low temperature distillation. Their conclusions will be quoted later.

Parr and Barker[7] (1909) found that after mining, coal commenced to absorb oxygen at the same time evolving methane; and that after two months all the methane had passed away, but absorption of oxygen continued.

Boudouard[8] (1909) working from the chemical side of the question of loss of coking power, proved the formation of humic acids caused by oxidation of the coal matter and showed that the presence of these acids is very detrimental.

Parr and Wheeler[9] (1909) experimented on the weathering of bituminous coals from Illinois. Their report which covers a large amount of experimental work will be freely quoted in the body of the present work.

[1] Journ. Soc. of Chem. Industry, Vol. 2, 1883, p. 325.
[2] Power, Vol. 27, 1907, p. 437.
[3] Tech. Paper 16, U.S. Bureau of Mines, 1902, p. 4.
[4] Bull. Univ. of Missouri, Eng. Series, Vol. I, 1908.
[5] Zeitschrift fur Ang. Chemie, Vol. 35, 1908. pp. 1825-35.
[6] Bull. No. 17 and 24, Univ. Ill. Exp. Sta., 1908.
[7] Bull. 32 Univ. of Illinois Exp. Sta., 1909.
[8] Bull. de la Societe Chimique, Ser. 14, Vol. V, 1909, pp. 365, 372, 377, 380.
   Compte Rendu. 147, 1908, p. 986; 148, 1909, pp. 284 and 348.
[9] Bull. 38, Univ. Illinois Exp. Sta. 1909.

Porter, Ovitz[1] and others (1910) have been engaged for some years on the study of the constitution and decomposition of coal. Their results, which have in the main appeared in publications of the U.S. Bureau of Mines, are of very great value and numerous quotations and abstracts from their work will be found in the following pages.

A distinction should be noted between H. C. Porter whose work is here referred to and J. B. Porter, the senior author of the present volume.

Parr and Kressmann[2] (1910) experimented on bituminous coals from Illinois to determine their rate of heating under various conditions. Their report, on the Spontaneous Combustion of Coal, is a very valuable work, and its conclusions will be referred to repeatedly in the following pages. They also supplement the description of their own tests with an extended review of the literature of the subject.

Habermann[3] experimented with coals at 50° C. in a fire-brick retort, and, supplying them with air at 26° C., ignition occurred in 36-39 hours. He found that the most easily oxidizable coals were those which were attacked by bromine with greatest avidity.

Dennstedt and Schaper[4] (1912) experimented with coals in a current of oxygen at a temperature of 150° C. They concluded that coals which show no tendency to increase in temperature under these conditions are absolutely safe; that coals which may heat locally, but do not heat generally in one hour are safe enough for transport in ships, and for storage in piles; that those which ignite within one hour are unsafe; and that those which ignite when subjected to the same tests at temperatures below 150° C. are exceedingly dangerous.

They also note that the greater the percentage of oxygen in the coal the greater will be the liability to give trouble.

Lamplough and Hill[5] (1913) after experimenting on several English coals, chiefly from the Barnsley seam, came to the conclusion that pyrite plays a larger part in spontaneous combustion than the majority of recent students have believed. Their paper and its discussion and criticism are of considerable interest and will be dealt with later.

Winmill[6] (1914) describes the first of a series of experiments which are now being carried on for the Doncaster Coal-owners Association. He discusses the relative rates of oxidation of various parts of the Barnsley seam, the effect of size of the coal dust particles on the rate of oxidation, the effect

[1] (a)   Losses in storage of coal (H. C. Porter) Journ. Ind. and Eng. Chem. Vol. II, 1910, pp. 77-83.
    (b)   The volatile matter of coal (Porter and Ovitz) Bull. No. 1. U. S. Bureau of Mines, 1910.
    (c)   The escape of gas from coal (Porter and Ovitz) Technical Paper No. 2, U. S. Bureau of Mines, 1911.
    (d)   Deterioration and spontaneous heating of coal in storage. Tech. Paper No. 16, U. S. Bur. of Mines, 1912.
    (e)   The Spontaneous Combustion of Coal, 8th International Congress of Appl. Chem. Vol. X, 1912, pp. 251-267.
    (f)   The weathering of the Pittsburgh coal bed (Porter and Fieldner) Tech. Paper No. 35 U. S. Bur. of Mines, 1914.
    (g)   A study of the oxidation of coal (Porter and Ralston) Tech. Paper 65, U. S. Bur. of Mines, 1914.
[2] Bull. 46 Univ. of Illinois Exp. Sta. 1910.
[3] Schillings Jour. für Gasbel. Vol. XLIX, 1906, pp. 419-422.
[4] Zeit f. Ang. Chemie Vol, 51., 1912. pp. 2625-2629.
[5] "The Slow Combustion of Coal Dust and its Thermal Value." T. I. M. E. Vol. XLV, 1913, pp. 629-657
[6] "The Absorption of Oxygen by Coal." T. I. M. E. Vol. XLVI, 1913, pp. 559-591.

of temperature on the rate of oxidation and the effect on the rate of oxida-
tion of variations in the oxygen content of the air current.

Lomax[1] (1911 and 1914) whose work has already been referred
to on page 4 studied coals under the microscope with reference to their com-
position and liability to spontaneous heating.   He finds that coals which
are particularly troublesome almost always contain dull-looking bands
of amorphous material, and he believes that fires usually start in this
material which is particularly pulverous.   He suggests that these bands
may be the result of forest fires at the time that the coaly matter was being
laid down.   He also discusses the effect of pyrite which he does not consider
a primary cause of combustion in most cases.   His papers are very inter-
esting and suggestive.

Morris[2] (1914) discusses the experience of Lydbrook Colliery in the
Forest of Dean with reference to underground fires.   The seam is partic-
ularly liable to spontaneous combustion, and the method of mining had to
be modified with a view to meeting this difficulty.   Ordinarily the coal
or gob took fire about seven weeks after its first exposure, but the length
of time depended upon the degree of pressure and also of course upon the
amount of very fine material.   When the compression was very great so
little air entered that little or no heating occurred, but if, even after some
months of these conditions, the pressure was reduced or a new way opened
up for the admission of air, heating immediately took place.   He also notes
that material which has once started to heat and has been checked is
particularly liable to heat again.

SUMMARY OF CONCLUSIONS.

From the results as set forth by all investigators dealing with the subject
of weathering, the main causes seem to be the following:—

(1)   The presence in the coal of complex and more or less unstable
carbonaceous compounds such as resins, humus, etc., which oxidize readily.

(2)   The presence of pyrite and marcasite in the coal, these minerals
being effective both as disintegrating agents and also as actual sources of
heat.

(3)   The presence of moisture, which, whether or not it aids in the
oxidation of the coal itself, certainly hastens the decomposition of pyrite
which is always present to some extent.

(4)   The physical condition of the coal itself is of vast importance as
oxidation is largely superficial, and fine coal, and particularly coal dust, pre-
sents an immense surface to the air as compared with an equal quantity
of lumps.

[1] (a) "The Microscopical Examination of Coal and its use in determining the inflammable constituents
present therein."   T. I. M. E. Vol. XLII, 1911, p. 2.
(b) "Further researches in the microscopical examination of coal, especially in relation to spontaneous
combustion."   T. I. M. E. Vol. XLVI, 1914, p. 592.
[2] "Notes on gob fires, etc."   T. I. M. E. Vol. XLVII, 1914, p. 195.

(5)   The presence of air as the source of oxygen is of course essential to oxidation, but a great excess of air, while facilitating oxidation of certain constituents, will also carry off the heat generated, and thus keep the coal cool and in this way prevent the coal from reaching the high temperature necessary for very rapid oxidation.   It is thus possible to prevent oxidation altogether by absolutely excluding air, or to prevent undue heating by ensuring thorough ventilation.   When, however, a limited, but sufficient, supply of air reaches the coal the destructive action is most rapid.   In this connexion also, the physical condition of the coal is important, as dust, while it retards the passage of air, does not by any means prevent it.

(6)   The way in which the coal is stored is of great importance in connexion with the last named points.   A low thin pile ordinarily receives enough air to keep it cool; a high pile by its own weight compresses its lower portion and reduces the voids.   There is thus a level or zone in any very high pile in which the conditions for heating are at a maximum while the deeper parts of the pile may get too little air and the portions near the surface too much for dangerous heating.

(7)   The individuality of the coal is a factor of prime importance, for although certain types such as resinous lignite and bituminous coal are of course most easily oxidized, and other types such as anthracite and semi-bituminous are very slightly affected, yet chemical analyses and physical appearances alone do not always suffice to enable us to determine the relative susceptibility to weathering, and of any two coals which are apparently alike in composition and condition, one may prove to weather very much more rapidly than the other.

CHAPTER II.

A GENERAL DISCUSSION OF WEATHERING.

WEATHERING IN NATURE.

Weathering in nature takes place at and near the outcrop of coal seams, and in some cases this action has even resulted in spontaneous combustion, and considerable quantities of coal have been completely or partially destroyed in place in the beds.[1]   Ordinarily, however, the natural weathering of seams is too slow to cause fire, and all that happens is the disintegration of the coal, accompanied by the loss of part of its combustible matter, and a more than equivalent increase in ash.   Outcrop coals are thus almost always of poor quality, but fortunately the damage rarely penetrates far into the seam, and coal as ordinarily mined shows little or no sign of oxidation in the destructive sense in which the term is used in this discussion.

The artificial or commercial weathering of coal begins the moment the miner's pick exposes its surface to the air of the mine, and this weathering continues with increasing, or decreasing intensity, depending on circumstances as long as the coal is exposed to the air.   Weathering may thus be considered as taking place (a) in or near outcrops or fissures in nature; (b) in the coal mines; (c) on the surface during preparation and in transit; (d) in storage while awaiting use.

The first case is of little interest or importance except to the geologist and will not be discussed in this report, but the other cases are all deserving of separate consideration, although the general phenomena of weathering are alike in all.

WEATHERING ACTION TAKING PLACE IN THE MINE.

Changes undoubtedly commence to take place in coal immediately upon mining, owing to the alteration of conditions.   Coal in situ is under pressure due to the superincumbent strata, and it is also absolutely removed from contact with the atmosphere, but as the mining operations approach the coal the gases, which it ordinarily contains under pressure, begin to escape.   This evolution of gas becomes more rapid when the coal is actually broken down, and for a time probably almost protects it from oxidation, but both oxidation and desiccation no doubt commence almost immediately and increase as the escaping gases decrease, and cease to protect the coal from the action of the air.

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[1] The Burning of Coal Beds in place, by A. Bowie, Am. Inst. Min. Eng. Bull. 86, pp. 195-204, February (1914).

Evolution of Gas.

Parr and Wheeler have shown that a combustible gas is given off by coal immediately upon mining; they sealed coal up in air-tight jars, and found that after ten months the vessels were filled with a combustible gas under pressure.

Taffanel states that it is during the first ten days after mining that the greater part of the available methane is set free; he obtained a liberation of 14—22 c.c. per grm. of coal. These figures do not include the methane evolved during the period elapsing immediately after breakage at the face.

Porter and Ovitz believe that methane is formed by slow decomposition of the coal, and they quote the work of Chamberlin, in which he crushed coal under a high vacuum, obtaining only a quantity of gas equal to one-fourth the volume obtained by bottling for six months. During two weeks after mining they found that a certain coal lost three-fourths of its own volume of gas, and after five months it has lost an amount equal to one and three-fourth times its own volume. They seem to think that this is a great deal, and in a chemical sense it may be, but from the practical standpoint it is of little importance except in the case of coal carriage in ships. If we consider the huge volume of air which sweeps constantly through a mine and the amount of gas given off by the coal during development work and before it is mined, this gas from the mined coal is unimportant: although, of course, immediately bad ventilation comes in, we have an entirely different situation. The loss in calorific value due to the escape of this $1\frac{3}{4}$ volumes of methane if calculated out, is seen to be negligible as compared with other weathering losses.

Taffanel draws attention in his paper to the evolution of methane from coal in the mine, he, however, attacks the subject chiefly from the point of dust explosions; he gives figures for the quantities of gas given off by the samples upon which he experimented.

In this, as in every other action which we are to study in connexion with this subject, every coal has its own individuality, due in part to the particular condition of pressure, water, associated strata, etc., in the mine; and in part to the exceedingly complicated organic compounds, resins, albuminoids, etc., of which it is composed.

Absorption of Oxygen and Oxidation.

This subject will be taken up at length in subsequent pages, but we may perhaps here quote certain observers who have particularly studied underground conditions. Porter and Ovitz following various earlier writers, state that "the air in a poorly ventilated section or closed portion of a mine is deficient in oxygen, and contains much less carbon dioxide than it would if all the oxygen that must have been removed from the air by the coal were immediately split off in combination with carbon." This absorption of oxygen is due in part to the coal left in the walls and pillars,

but in most cases the chief absorption is by the broken coal and carbo-naceous shale, and particularly by the coal and shale dust which is always produced in mining.

Parr and Wheeler state that pillar coal in a particular district after 25 years loses only 2·5% of its calorific value; this illustrates the imper-viousness of unbroken coal to the air. The main deterioration in pillar coal is found, however, to be due to its increased friability resulting chiefly from the heavy pressure to which it has been subjected.

Interesting figures are given by Haldane and Meachem,[1] to show that 80% of the heating which air undergoes while passing through a mine, can be accounted for only by the weathering of the pyrite and the coal itself. Their experiments which are described below were carried out at the Hamstead colliery, South Staffordshire, where the "Thick Seam" is worked at a depth of about 2000 feet below the surface, and their obser-vations and conclusions are so interesting that no apology need be offered for summarizing them at some length.

They noticed that the general effect of opening up the mine was to warm both the coal and the strata adjacent to the workings. The average temperature on the surface at Hamstead is 49° F. At the bottom of the intake shaft the temperature is much more constant than at the surface and averages 60° F. The air is compressed as it descends the shaft and this compression would account for a gain in temperature of 10°. A little moisture is taken up by the air in the shaft, and this must tend to cool the walls so that some heat is transmitted to the air from the strata.

From the pit bottom the air steadily increases in temperature at the rate of about 6° for every 3000 feet. In the workings the temperature is generally about 80° to 85°. In the return airway there is a relatively slow though steady fall of temperature from the face to the upeast shaft. The average temperature in the main north return airway is 77°. Analysis of the air shows that this fall in temperature is probably due to the leakage of air from the intake to the return airway.

To determine the temperature of the undisturbed coal a maximum and minimum thermometer was inserted into the end of a 10-foot borehole in freshly cut coal. The hole was then closed with clay and left undisturbed for at least several days. Several such experiments showed the temperature of the coal to be 66°. Similar experiments were made in coal which had been long exposed. They showed that coal behind such an exposed surface gradually rises in temperature. Thus at two places in the side of a main road the temperature at the ends of 10-foot boreholes were taken in 1894 and 1898. In 1894 the temperatures were 66° and in 1898 they were 93° and 90°.

It was impossible to correctly calculate the total heat generated in the mine since there must have been large radiation losses through the walls, roof and floor. The amount of heat, which escaped by the return airway,

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[1] Trans. Inst. of Min. Eng. Vol. 16, 1898, p. 457.

could, however, be calculated. Such a calculation shows that the total heat carried away per minute by the air-current was 48,000 B. Th. U., each cubic foot of air passed through the mine, therefore, carried off with it approximately one B. Th. U. of heat.

Summarizing Haldane and Meachem's paper further there are several possible sources of heat in a mine. Of these the most obvious are the presence of men and horses and lights. The heat from these sources is, however, approximately determinable and in the case of the particular mine under very careful calculations showed that it could not have exceeded 7% of the heat leaving the mine. Another possible source of heat is the friction due to the settling down of the roof and consequent grinding of the coal and other material by the pressure of the superincumbent strata. The depths of the Hamstead workings is 2,000 feet. Assuming the specific gravity of the strata to be 2, the authors arrived at a pressure of 250,000 lbs. per square foot or about 0·8 tons per square inch. The average output of coal from the north side of the pit was about 15 cubic feet per minute and the average rate of settling down of the strata could not exceed this. The heat liberated could therefore not exceed the heat equivalent of $15 \times 250,000$ ft. lbs. of work, i.e. 4,850 B. Th. U. Even if this were all given up to the mine air it would only be about 10% of the total heat leaving the mine. The friction of the air current passing through the mine also produces heat,— the amount which could have thus been generated could, however, never exceed 1·7% of the total heat withdrawn from the mine.

It is clear then, that the main portion of the heat generated in the mine was due to some cause other than any of those mentioned, and the obvious conclusion is that it is due to the chemical action of the air on the coal. Haldane and Meachem[1] made a large number of experiments on the subject and a copy of a sketch plan of the entries at Hamstead Colliery is reproduced (Fig. 1) to show the positions of the points where some of the air samples, referred to below, were taken.

Table I shows the analyses of ten samples of air taken in the mine. The figures are calculated by deducting the actual oxygen percentage found from that given by the same gas burette for pure air, and then deducting from the result the deficiency due to dilution with firedamp. For carbonic acid the figures shown are obtained by deducting from the actual result the percentage of carbonic acid in the pure air, (0·030 per cent.)

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[1] Ibid.

SKETCH PLAN OF THICK COAL-SEAM
HAMSTEAD COLLIERY

THE RECORDED TEMPERATURES WERE TAKEN ON
FEBRUARY 17TH 1897

Scale 800 Feet to 1 Inch

Working Face
Lady Shafts
F

No (1) Road

Return Airway · 83°Fahr
Intake Airway
D
83°Fahr
D
Working Face

B 71°Fahr
North Intake Airway
5850 Feet from Shaft
North Return Airway
B 78°Fahr.
7920 Feet from Shaft
75°Fahr
C
Working Face
C
80°Fahr

G   H
H   G

Main North Intake Airway
Main North Return Airway

55°Fahr A   A 74°Fahr
Upcast Shaft
Downcast Shaft
E   E
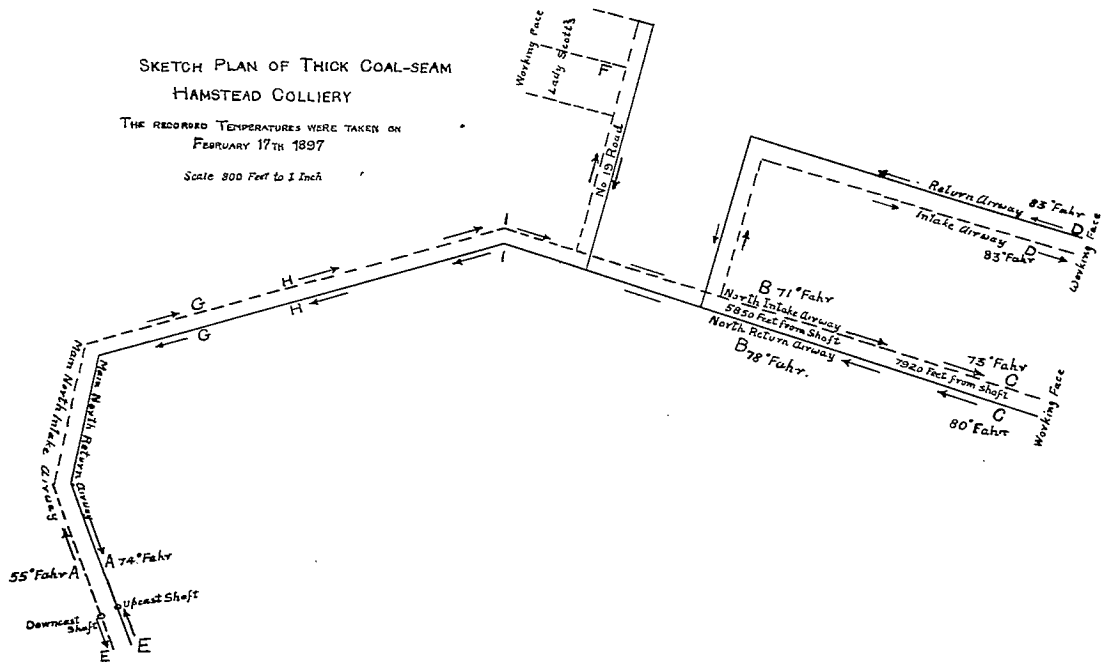
Fig. 1.   Map of Hamstead colliery.

(From Haldane and Meachem)

TABLE I.

Analyses of Some Samples of Air Taken in the Mine

(Haldane and Meachem)

No. and position on plan	Name of road	Distance from shafts	Temperature	Deficiency of oxygen	Carbonic acid in excess	Fi da
		Feet	Degs. Fahr.	Per Cent	Per Cent	Per
A........	Main North Intake Airway..........	150	55	0·00	0·000	0·
A........	Main North Return Airway..........	150	74	0·37	0·100	0·
B........	North Intake Airway.............	5,850	71	0·16	0·090	0·
B........	North Return Airway.............	5,850	78	0·36	0·100	0·
C........	Intake Airway......	7,920	73	0·25	0·095	...
C........	Return Airway.....	7,920	80	0·77	{0·250 / 0·280	0·
D......	Intake Airway......	9,150	83	0·88	{0·310 / 0·330	0·
D......	Return Airway.....	9,150	83	1·70	{0·470 / 0·470	0·
E........	Main South Intake Airway..........	150	55	0·01	0·000	...
E........	Main South Return Airway..........	150	......	0·24	0·095	0·

This table shows that as the air passes through the mine it ste loses oxygen and gains carbon dioxide. On the average, however, the ox loss is 3·13 times the gain in carbon dioxide. It is very noticeable tha temperature increases with the diminution of oxygen from the air, Haldane and Meachem's calculations above quoted show this increase greater than could be accounted for by friction.

TABLE II.

Composition of air in mine.

(Haldane and Meachem.)

Temperature Degs. Fahr.	Deficiency of oxygen	Temperature Degs. Fahr.	Deficiency of oxygen
55	0·00	78	0·36
71	0·16	80	0·77
73	0·25	83	0·88
74	0·37	83	1·70

Two more series of tests similar to the above were made at diff times. The results checked those given above very closely except tha percentage of carbon dioxide in the samples taken on January 5 sh a marked increase over that found in previous samples. Haldane Meachem attribute this to the fact that the barometer was falling on day, and that this fall caused a flow of gas from old workings.

The absorption of oxygen by anthracite and by bituminous coals in the mine, is clearly demonstrated in a paper by G. N. Burrell.[1] The figures in Table III are for the gases in an enclosed portion of an anthracite mine. This section of the mine was sealed off because of a fire which existed in an adjoining section. The fire did not, in his opinion, affect the particular area from which these samples were obtained, because of a heavy intervening roof fall, consequently the gases represent those trapped and given off normally in a stagnant section, except that one stopping was leaking and some air was entering from the ventilating current. The stopping was tightened and rapid absorption of the available oxygen by the coal ensued, as shown by the third analysis. Four days later the oxygen had dropped to 3 per cent, even though some air was still finding access to the enclosed area.

TABLE III.

Composition of gases from an enclosed area in an anthracite mine.
(*Burrell*)

Sample No.	Date	Percentages.				
		CO_2	CO	O_2	CH_4	N_2
....1........	Oct. 31st.......	2·2	0·0	15·0	14·0	68·8
....2........	Nov. 1st.......	2·3	0·0	14·6	18·1	65·0
....3........	Nov. 2nd......	2·6	0·0	6·2	24·2	67·0
....4........	Nov. 2nd......	2·9	0·0	5·7	29·3	62·1
....5........	Nov. 3rd.	2·8	0·0	4·1	34·9	58·2
....6........	Nov. 6th.......	2·6	0·0	3·0	53·0	41·4

The composition of gas from an enclosed area in a bituminous coal mine is shown by Burrell by means of the following analyses, but the conditions as set forth in the following quotations leave one in doubt as to the complete exclusion of the gases from the burning section. The large amount of CH_4 is, however, an indication that Burrell's assumption is correct.

TABLE IV.

Composition of gases from an enclosed area of a bituminous coal mine.
(*Burrell*)

Sample No.	Percentages.				
	CO_2	CO	O_2	CH_4	N_2
........1........	1·50	0·00	0·30	5·29	92·91
........2........	1·20	0·00	0·30	5·37	93·13

"A mine fire had once existed in the area and these samples were collected by men with breathing helmets, nine months after the fire had originated and prior to the reopening of the mine. The mine is classed as non-gaseous."

[1] Coal Age, Vol. III, 1913, pp. 104, 110, 143, 147, 194, 311.

This matter of underground weathering is ordinarily of but little importance, so far as the commercial value of the coal is concerned, it is however of immense importance in mining, as a certain amount of broken coal and coal dust is unavoidably left in the workings and abandoned there, and this material and the carbonaceous and pyritic shales often found just over the coal frequently give great trouble by heating and starting underground fires. In some seams spontaneous gob fires are of so common occurrence that special methods of mining have to be employed, and in still other cases the only safe way of operating is to laboriously remove all fine coal and all fallen shale.[1, 2]

The subject of gob fires is exceptionally interesting, but it belongs properly to Coal Mining and its further consideration would be out of place in the present work.

WEATHERING LOSSES IN TRANSIT.

Parr and Wheeler sampled some coal at the mine and again a week or so later after transit in cars, and they found deterioration in the order of 100 B.Th.U. for the coals taken, whose value when mined was about 14,600 B.Th.U. It is probable that part of the above loss of calorific power was due to the escape of hydro-carbon gases, but the observers are no doubt right in ignoring this as a factor of importance.[3]

The chief loss, in transit, however, must be due to breakage caused by handling, and, although with the modern equipment now in use by large companies, breakage is greatly reduced, these breakage losses are quite considerable.

In the majority of cases of shipment by rail, the coal does not remain long enough in the cars to suffer any great change, except that of breakage just referred to, but when shipment is made by vessels, and the distances are great, the case is different. As has already been stated in the introduction, the subject of weathering was first brought before the public in connexion with the all too numerous cases of fires in sailing ships carrying cargoes of coal from England to distant ports.[4] Such ships frequently spend months on a single voyage and much of that time is often in the tropics, and unless the coal is an anthracite, or very exceptional precautions are taken, spontaneous fires are almost certain to occur. It is not necessary, however, to deal at length in the present work with this very special subject of coal cargoes, as the causes of heating will be sufficiently considered in the general discussion of weathering, oxidation and storage, while the technical problems of loading and discharging colliers, and of preventing and fighting fires on ship-board, have already been reported on at length by the several Royal Commissions appointed for the purpose.

[1] Lamprecht. Recovery work after Pit fires. 1901—p. 32 and 48.
[2] Morris. T. I. M. E. Vol. XLVII, 1914, p. 195.
[3] White, Bulletin 29, U.S. Bureau of Mines, 1911, pp. 69-70—thinks that lignites and many sub-bituminous coals lose say 200 calories in transit. His figures show losses ranging from $\frac{3}{4}$ to $3\frac{1}{4}$ % of total calorific value.
[4] Probably the most detailed and interesting non-official paper on this subject is by Bunning—"The Prevention of Spontaneous Combustion of Coal at Sea."—Trans. North of Eng. Inst. Min. & Mech. Eng'rs., Vol. XXV, 1876, pp. 107-140.

WEATHERING LOSSES IN STORAGE.

From the work of many experimenters we know that if fresh coal of almost any character be stored in a pile, the temperature of the mass will at first rise. Many kinds of coal never go further than this, in ordinary storage, but gradually cool off again and remain without further marked change for any length of time.

A great variety of coals on the other hand continue to heat, and if nothing be done to ventilate them or otherwise artificially cool them, they ultimately catch fire, and the main purpose of the present report is to discuss the causes of this destructive action and the various methods which have been proposed for its prevention or cure.

In our study of the subject of weathering in greater detail it will be unnecessary to attempt to distinguish any further between action taking place in the mine, in transit, or in storage. In fact it would be impossible to do so satisfactorily as in some cases the character of the coal seam and the method of mining make it possible to get out the coal very promptly, and to place it in the consumers' storage pile while it is still giving off hydro-carbon gases, and has scarcely had time to begin to oxidize. In other cases much of the coal remains in underground pillars for a very long time and even the mined coal is handled slowly and suffers considerable change before it reaches the consumer. It is, therefore, best from the practical point of view to consider the question of weathering as a whole in our further discussion of the subject.

CHAPTER III.

DISCUSSION OF THE CAUSES OF WEATHERING IN GENERAL.

In the following d'scussion it will be assumed in a general way that the coal has been mined and prepared for the market under ordinary conditions. All weathering which may take place under these circumstances will be included, but as the chief part of the avoidable action occurs in storage the discussion will, to a great extent, be on the storage of coal.

It is impossible to draw any hard and fast line between mere weathering and serious heating even to the point of spontaneous combustion. Both of these phenomena are due to the absorption of oxygen, and as a matter of fact all oxidation whether resulting in little or great rise of temperature, may really be considered spontaneous combustion in an absolute sense.

The most important conditions which influence the weathering of coal in transit and storage are named below, and in so far as is practicable the subject will be discussed under the separate headings in the order given, but the causes of weathering are so numerous and so interdependent that a really systematic and logical treatment of the subject is impossible, and the author craves the indulgence of readers in regard to his presentation of this part of the subject.

Classification of the Causes of Weathering.

1. The kind of coal (without reference to its inorganic impurities).
2. The time of previous exposure.
3. The presence of moisture.
4. The presence of pyrite and the mechanical condition of the same.
5. The size of the coal.
6 The size, shape, etc., of the storage piles.
7. The initial temperature of storage.

˝ THE KIND OF COAL.

It is generally believed that anthracite[1] is not liable to spontaneous combustion and this belief is correct in that anthracite will not ignite spontaneously under ordinary conditions. Fayol,[2] however, states and probably with truth, "que toutes les houilles sont susceptibles de s'echauffer lorsequ'elles sont exposèe à l'air dans certaines conditions." The tendency

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[1] The name anthracite is ordinarily used in eastern Canada and the United States for the hard Pennsylvania anthracite only, but other and less stable coals are also entitled to the name. Technically anthracite is a coal having a fuel ratio of over 12.

[2] Études sur l'Altération de la houille exposée à l'air. M. Fayol (1879).

of different coals to catch fire is, however, very different. Fayol exposed different kinds of coal to hot air and found that the order of inflammability in air was lignite, bituminous gas coal, bituminous coking coal, and anthracite. This is the same order of inflammability as he found for coals in contact with a flame. He made further experiments using three kinds of coal each one in three different kinds of vessels, namely: a porcelain crucible containing 50 grammes of coal; a rectangular box 12 cms. by 12 cms. by 3 cms; and a cubical box of 12 cms. side.

When exposed to air at 400° C. the samples of all the coals caught fire, the lignite easily, and the anthracite after thirty to forty minutes. At 200° the bituminous coals did not catch fire except the sample in the large vessel, and the anthracite only when powdered. At 150° only the powdered lignite caught fire in all three vessels. At 100° only the dust of the lignites and the impalpable powder of the bituminous coal caught fire. At 75° none of the coals ignited. (See pp. 53 and 108 for further details).

Fayol's experiment which has been fully confirmed in a general way by numerous observers, proves conclusively that liability to weathering is least in anthracites and greatest in lignites with bituminous coals in an intermediate position, and in a practical sense we may take it that hard anthracite is not appreciably affected by exposure. On the other hand the true lignites suffer so greatly not merely by spontaneous heating, but by dehydration and disintegration, that their storage on a large scale is unlikely to become an important problem for some time in Canada at least. The real practical problem is, therefore, to be found in a study of bituminous and semi-bituminous coals, and the remainder of this paper will deal almost exclusively with coals of this character.

Bituminous coal—ranging as it does from semi-lignite to semi-anthracite —falls itself within Fayol's conclusions, and there is a very evident decrease in liability to serious weathering as we go up in the scale toward the anthracites, but we find very great individual variations in coals of substantially the same grade. These variations are due largely to differences in friability, but are also due in part to the presence or absence of small quantities of very easily oxidized substances such as the resins. The amount and character of mineral impurities also play a part.

It should be noted that the term "anthracite" is used to describe a considerable range of coals and that some so-called "anthracites" are sufficiently close to bituminous coals to be liable to weathering and even to considerable heating if stored under particularly unfavourable conditions; for instance certain very valuable Welsh smokeless coals often spoken of as anthracites, have been found unsuitable for shipment in large quantities to or through the tropics; these cases, however, are somewhat aside from the scope of the present investigation.

The purity of a coal, that is to say its relative freedom from inorganic matter, is no longer generally considered to be an indication of its comparative immunity from weathering, except that one particular impurity—

pyrite—is still believed by many to be one of the main causes of trouble. With the exception of pyrite, which will be specifically dealt with later, it is now believed by many observers[1] that the presence of considerable amounts of ordinary ash-forming impurities is likely to lessen the rate of weathering of the coal, although this must depend to a large extent on the character of the impurities themselves. The fact that the impure coals are often less liable to spontaneous combustion is no doubt due to the fact that the mineral matter often occurs in the form of thin plates in the cleavage planes, thus coating and protecting a considerable part of the surface of the coal proper when it is broken. It is also probable that pure are, generally speaking, softer than impure coals, and therefore more easily reduced to dust.

The differences in the rate of weathering of coals of substantially the same class are shown by Porter and Ovitz who experimented with coals in a current of 50% oxygen at 140° to 160° C. The results of their experiments are shown in the appended figure (Fig. 2), and admirably illustrate the individuality of these coals.

TIME OF PREVIOUS EXPOSURE.

In many cases coal is subjected to a more or less extended storage in piles at the mines and in coal-cars in transit, and is then stored in considerable quantities by the distributing agents or consumers. In such a case there is usually less likelihood of heating in the final storage, as the only surfaces which will be attacked by oxygen with any marked energy are those new faces caused by breakage in handling. As an example of this we have the case of very large quantities of coal which are mined and stored in eastern Canada during the winter, then shipped during the summer season of navigation to Montreal for storage until the following winter. Such coal, although piled the second time in hot weather, is much less likely to heat than freshly mined coal stored under similar conditions.

Parr and Wheeler[2] find the loss of a coal during the second year of storage to be only one-half that occurring during the first year.

An experiment made by Porter and Ovitz[3] shows the effect of previous exposure upon absorption of oxygen. Fine coal was used and the exposure was but short, yet the results may be taken as an indication on a small scale of what happens more slowly in a large pile. (Curve C, Fig. 13).

THE EFFECT OF THE PRESENCE OF MOISTURE.

From the Reports of the Royal Commissions on Coal Cargos in England (1876) and in New South Wales (1897) one might conclude that coal containing much moisture would be likely to heat badly; yet out of 26 persons

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[1] Dennstedt and Bünz found that coals which were most free from mineral matter were on the whole more readily oxidized than impure coals and increased in temperature more rapidly when exposed to air. See Zeitschrift fur Ang. Chemie. Vol. XXXV, 1908, p. 1825.
[2] Univ. of Illinois Eng. Exp. Sta. Bull. 38, 1909.
[3] U. S. Bur. of Mines Tec. paper No. 16, 1912.
    Int. Cong. of Appl. Chem. Vol. 10, 1912, p. 251.
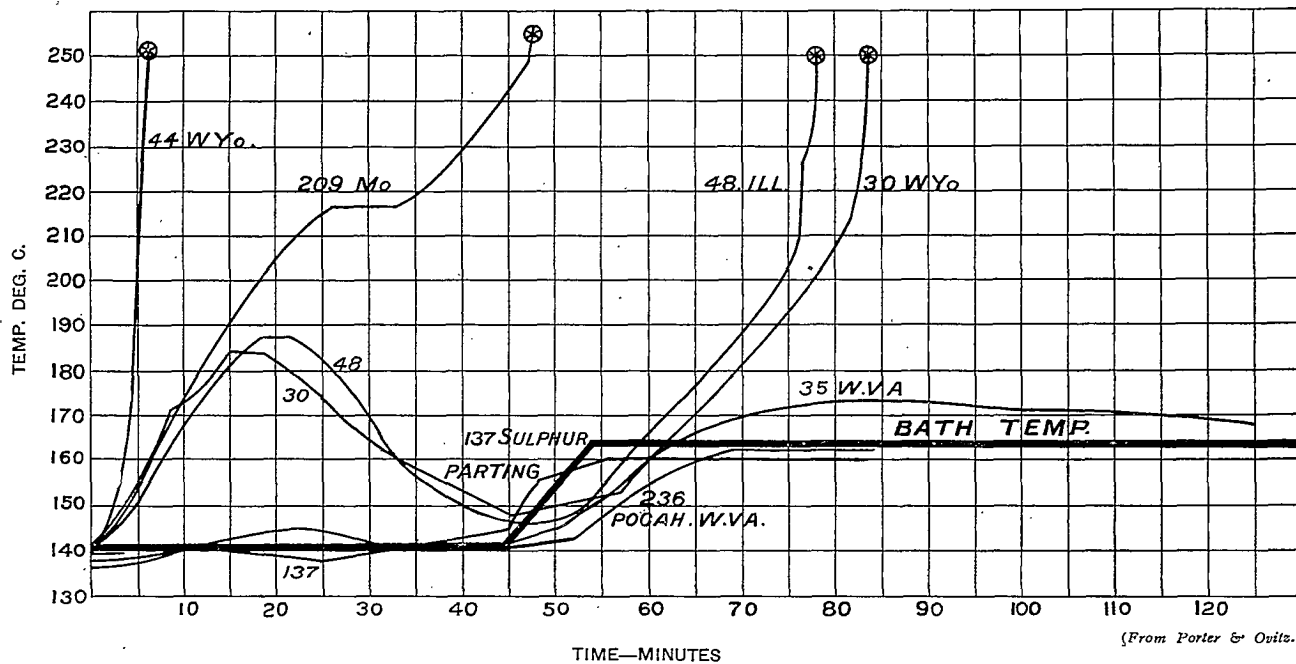
FIG. 2. Behaviour of coals in a current of 50 per cent oxygen at 140° and 160°C. Rate of flow of oxygen—4 litres per hour.

who in 1876, testified to the injurious effects of moisture, 25 admitted on cross-examination that they were simply repeating hearsay, and the other remaining witness was not available for cross-examination; furthermore, although the bulk of the testimony in 1897 was apparently to the same effect, the conclusions of the Commission did not give it much weight.

One would naturally expect that a coal containing moisture would be retarded in its heating because, until all the moisture has been evaporated, the temperature cannot give rise above 100°C. Yet, on the other hand, the steam percolating through the surrounding mass, and condensing in the cooler parts, will heat as well as moisten them, and may thus tend to hasten oxidation in those parts.

Richters[1], one of the ablest of the early students of coal weathering, who worked from 1867 to 1870, made some experiments to determine whether moisture aided or retarded the absorption of oxygen by coal. He took two tubes and placed air-dried coal in one and moist coal in the other, both coals being freshly mined. The air-dried coal absorbed oxygen more quickly than the moist coal. He also found that by placing small bulbs containing fused calcium chloride alongside the dry sample of coal, so that it became gradually drier, the rate of absorption was increased. The same phenomenon was observed when coal was used which had been dried for a day over sulphuric acid, although this coal must already have absorbed a considerable amount of oxygen while drying. It would seem that these experiments definitely prove that moisture hindered the absorption of oxygen by the coal in question, but this is not in accordance with the results of recent experiments by Porter and Cameron[2] and, furthermore, there is no doubt that moisture will increase the rate of oxidation of pyrite, and whether the net results will be an increase or decrease in the final temperature must depend on the amount of pyrite present and on the amount of moisture.

Fayol[3] made a number of experiments in order to determine the effect of moisture on Commentry coal. The coal was tested in three different conditions:—

1. Freshly won fines.

2. The same coal previously dried in ovens at a temperature not exceeding 40°.

3. The same coal not dried, but sprinkled to make it damp, but not wet.

A sufficient number of piles of each material were made to last the winter. These piles contained from 2 to 12 cubic metres each and were built, some on the surface under open sheds, and the remainder in dry levels, underground. Temperature observations were made every day in each pile for several months, and the behaviour of the different piles of the same

[1] Dinglers Poly. Jour. Vol. 190, 1868, p. 398.
    Dinglers Poly. Jour. Vol. 193, 1869, pp. 54 and 264.
    Dinglers Poly. Jour. Vol. 195, 1870, pp. 315 and 449.
[2] See page 144 et seq.
[3] Études sur l'altération de la houille exposée à l'air. M. Fayol, 1879, p. 155.

level, both wet and dry, was almost identical. In no case did any one of the piles rise to a temperature above 50°.

Parr and Kressmann[1] conducted some experiments with both dry and thoroughly wet coal, which they studied at elevated temperatures—40°, 60°, 80°, and 115°C.—and their work at first sight appears to contradict that of Fayol described above.

They say that without exception in all of their series of tests "wetting the coal increased the activity as shown by the ultimate temperature." Their statement is of course correct as applied to their tests, but it must be remembered that their samples were "stored" for a total of 12 days at elevated temperatures, which were raised in stages by external heat from 40°C. to 60°, and 80° and finally to 115°C. irrespective of any additional heating due to their own oxidation. A study of their results would seem to show that the wet coals did not heat on their own account as much as the dry ones until this externally applied heat raised them above 80°C. a temperature which is fatal to many coals. They also note that the coals tested, while typical of their district, are of very unusual composition, being high in sulphur and exceptionally high in moisture[2]. The hand picked lump coal tested had $1 \cdot 29\%$ sulphur and $4 \cdot 62\%$ moisture, and the run-of-mine a great deal more of these constituents.

Porter and Ovitz[3] in a brief, but very valuable report to the United States Government, conclude that:—

"In not one of the many cases of spontaneous combustion found by the authors, could it be proved that moisture had been a factor. Still the physical effects of moisture on fine coal, such as close packing together of dust or small pieces, may in many cases aid spontaneous heating."

Cox[4] quotes Doane as saying that moisture is an indication of the liability of coal to heat; he then points out that combined water is an indication of the grade of a coal, and as upon the grade of coal depends liability to heat, so moisture in the sense of combined water "does increase the heating." The use of the term moisture in this sense is, however, unusual and misleading and there is little evidence that moisture in the true sense has any effect in the majority of cases.

In conclusion it may be said that in all probability the temperatures of ordinary coals under ordinary conditions of storage are not raised to any appreciable extent by moisture. The question naturally arises, what was the basis of the once prevalent belief that moisture was an important factor in spontaneous heating?

This belief is, no doubt, chiefly due to the confusion of cause and effect on the part of persons who have discovered fires in coal storage. It is commonly observed that fires or hot spots in the pile are discovered shortly after rain storms, and that nearly always a hot spot is surrounded by damp or wet coal even if the main part of the pile is dry. The first case is easily

[1] For fuller description of Parr and Kressmann's work see pp. 37-40, 42, 109-110.
[2] In this connexion see Cox, just below and on p. 58.
[3] Tech. Paper, No. 16, U. S. Bureau of Mines, 1912.
[4] Internat. Cong. App. Chem. Vol. X, 1912, p. 109.

explained by the fact that dry coal is so poor a conductor that the surface of a pile may show no indication of a hot spot or even an incipient fire in the interior. A rain storm would however provide moisture enough to soak into the pile, and this moisture on approaching the hot spot would be turned into steam which would work its way back to the surface and be observed, thus attracting attention to the hitherto unsuspected heating. The second explanation is equally simple. Air dry coal always contains some moisture, and in lignitic coals there is also a very considerable amount of combined water. In the case of a hot spot in the interior of a pile this moisture is driven off, either escaping at the surface as steam, or condensing on the cooler coal in the neighbourhood. Added to this there is of course an actua formation of water when the hydrogen constituents of coal are oxidized.

As an illustration of the second case it may be noted that during the experiments of the author at Outremont and Glace Bay (see pp. 154-164) vapour or condensed moisture was always noticed in the observation tubes in the neighbourhood of hot spots even when the temperature was far below the boiling point.

PRESENCE OF PYRITE.

The presence of pyrite may affect the weathering of coal in two[1] ways:—

(a) By disintegration of the coal due to the slow oxidation of pyrite.

(b) By actual generation of enough heat when oxidized to warm up the coal surrounding it to a dangerous extent.

Disintegration Due to Weathering of Pyrite.

That pyrite causes disintegration of coal on weathering is well known, and the fine coal thus produced, undoubtedly increases the tendency of the mass to heat, but it is difficult to get any very definite measure of the effect, as other causes also result in disintegration. The action in brief is that pyrite in the presence of moisture and oxygen is more or less completely converted into oxide and sulphate of iron with the simultaneous production of appreciable quantities of sulphuric acid. This acid in time attacks the carbonates of lime and magnesia which are usually present in the cleavage and joint planes of the coal, converting them into sulphates.[2] These chemical reactions all involve increase in bulk followed often by shrinkage due to the solution of the soluble sulphates produced. Thus the coal on the whole suffers a much greater degree of disintegration than might at first be expected from the small amount of pyrite oxidized, which in ordinary cases does not exceed from 10 to 25% of the total pyritic matter in the coal, i.e., a small fraction of 1% of the total.

[1] In addition to the two very important effects of pyrites noted above, it is quite possible that it may contribute to weathering in still other, although less important ways, such as catalytic action, etc. Dennestedt and Bünz—Zeit fr. Ang. Chemie. Vol XXXV, 1908, p. 1825, discuss the possibility of catalytic action being a factor in weathering and ultimately dismiss it as likely to be of little or no effect.
[2] This was probably first noted by J. P. Kimball. Trans. Am. Inst. Min. Engrs. Vol. VIII, 1879, p. 207.

The most valuable information available bearing on the extent of the disintegration of coal due to weathering is the result of some experiments by **S. W. Parr** and **W. F. Wheeler**. The coals tested are the same as those used for their main experiments, described at length on pp. 69-86.

Tables V and VI, copied from Parr and Wheeler, show that the proportion of small sizes in the nut coal increased considerably due to the action of weathering, and that the average diameter decreased proportionately.

The disintegration was no doubt largely due to the oxidation and swelling up of the pyrite as already stated, but it was also due partly to the action of frost, both of these causes acting in conjunction with the oxidation of the coal proper and the disintegration produced thereby. In the case of the Vermilion county nut coal the amount of coal that would pass through a half-inch hole was nearly doubled. The figures for the nut coal from Williamson and Sangamon counties show that there was seven times as much coal below half-inch diameter after one and one-half year's storage as was originally present. The average diameter of the pieces of coal in all these lots was about three-fourths as great after storage as before, the average weight being only about 40% as great.

The changes in the screenings were not so great as in the nut coal, but they were probably of as much, or more importance in the matter of affecting the economic value of the coal and its liability to give trouble.

TABLE V.

Sizing Test Showing Disintegration of Nut Coal.

(Parr and Wheeler)

Vermilion County, Illinois.

Round hole screen		Original sizes		Exposed bins 1½ years		Covered bins 1½ years	
Through. Inches	Over. Inches	Per cent	Cumulative per cent	Per cent	Cumulative per cent	Per cent	Cumulative per cent
3	1	66·2	....	42·5	....	44·2	....
1	¾	5·0	71·2	8·0	50·5	7·6	51·8
¾	½	7·2	78·4	11·8	62·3	11·7	63·5
½	⅜	4·0	82·4	6·9	69·2	6·7	70·2
⅜	¼	4·0	86·4	6·8	76·0	· 7·1	77·3
¼	⅛	5·0	91·4	10·9	·86·9	10·4	87·7
⅛	0	8·6	100·0	13·1	100·0	12·3	100·0
Total......	..	100·0	....	100·0	....	100·0	....
Average diameter...........1·458 inches				1·074 inches		1·102 inches	

Williamson County, Illinois.

3	1	94·0	....	70·2	....	68·5	....
1	¾	1·6	95·6	5·7	75·9	5·7	74·2
¾	½	1·8	97·4	6·6	82·5	7·1	81·3
½	⅜	0·7	98·1	3·1	85·6	4·1	85·4
⅜	¼	0·5	98·6	3·2	88·8	3·6	89·0
¼	⅛	0·5	99·1	4·6	93·4	4·9	93·9
⅛	0	0·9	100·0	6·6	100·0	6·1	100·0
Total......	.....	100·0	....	100·0	....	100·0	....
Average diameter............1·910 inches				1·532 inches		1·506 inches	

Sangamon County, Illinois.

3	1	89·4	....	64·3	....	52·0	....
1	¾	4·1	93·5	6·9	71·2	9·3	61·3
¾	½	3·5	97·0	8·4	79·6	10·8	72·1
½	⅜	1·2	98·2	3·2	82·8	5·7	77·8
⅜	¼	0·6	98·8	4·0	86·8	5·8	83·6
¼	⅛	0·6	99·4	7·4	94·2	8·1	91·7
⅛	0	0·6	100·0	5·8	100·0	8·3	100·0
Total......	....	100·0	....	100·0	....	100·0	·....
Average diameter...........1·854 inches				1·442 inches		1·252 inches	

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TABLE VI.

Sizing Test Showing Disintegration of Screenings.

(Parr and Wheeler)

Vermilion County, Illinois.

Round hole screen		Original sizes		Exposed bins 1½ yrs.		Covered bins 1½ yrs.	
Through. Inches	Over. Inches	Per cent	Cumulative per cent	Per cent	Cumulative per cent	Per cent	Cumulative per eept
$1\frac{3}{4}$	1	19·0	....	11·3	..	11·6	....
1	$\frac{3}{4}$	8·9	27·9	6·3	17·6	6·3	17·9
$\frac{3}{4}$	$\frac{1}{2}$	14·8	42·7	12·9	30·5	12·2	30·1
$\frac{1}{2}$	$\frac{3}{8}$	8·5	51·2	9·3	39·8	9·3	39·4
$\frac{3}{8}$	$\frac{1}{4}$	11·1	62·3	11·8	51·6	11·8	50·2
$\frac{1}{4}$	$\frac{1}{8}$	16·4	78·7	21·0	72·6	21·0	71·2
$\frac{1}{8}$	0	21·3	100·0	27·4	100·0	27·8	100·0
Total......	....	100·0	....	100·0	....	100·0	....
Average diameter.............0·548 in.				0·425 in.		0·425 in.	

Williamson County, Illinois.

$1-\frac{3}{4}$	1	18·9	....	19·0	....	14·2	....
1	$\frac{3}{4}$	9·0	27·9	9·2	28·2	7·0	21·2
$\frac{3}{4}$	$\frac{1}{2}$	14·4	42·3	15·4	43·6	13·0	34·2
$\frac{1}{2}$	$\frac{3}{8}$	8·5	50·8	9·5	53·1	9·0	43·2
$\frac{3}{8}$	$\frac{1}{4}$	10·4	61·2	10·6	63·7	11·4	54·6
$\frac{1}{4}$	$\frac{1}{8}$	15·4	76·6	17·0	80·7	20·2	74·8
$\frac{1}{8}$	0	23·4	100·0	19·3	100·0	25·2	100·0
Total......	....	100·0	....	100·0	....	100·0	....
Average diameter.............0·542 in.				0·557 in.		0·466 in.	

Sangamon County, Illinois.

$1-\frac{3}{4}$	1	38·8	....	15·1	....	15·6	....
1	$\frac{3}{4}$	7·9	46·7	9·3	24·4	9·1	24·7
$\frac{3}{4}$	$\frac{1}{2}$	13·2	59·9	15·6	40·0	15·6	40·3
$\frac{1}{2}$	$\frac{3}{8}$	6·6	66·5	7·7	47·7	9·7	50·0
$\frac{3}{8}$	$\frac{1}{4}$	7·2	73·7	9·4	57·1	11·5	61·5
$\frac{1}{4}$	$\frac{1}{8}$	11·2	84·9	17·2	74·3	19·6	81·1
$\frac{1}{8}$	0	15·1	100·0	25·7	100·0	18·9	100·0
Total......	....	100·0	....	100·0	....	100·0	....
Average diameter.............0·768 in.				0·498 in.		0·518 in.	

Heating due to Oxidation of Pyrite.

The fact that pyrite evolves heat on oxidation is universally acknowledged, but the extent to which this affects a large storage pile is a matter upon which there is great difference of opinion.   It has been stated by some authorities that the heat generated by the oxidation of pyrite is the primary cause of spontaneous combustion. · Thus, although the first authoritative report[1] on the subject had concluded that the presence of pyrite in the coal was of secondary importance, and Blackwell[2] and others had supported this view, yet the English Royal Commission[3] (1875) appointed to investigate the carriage of coal on board ships, gave the causes of spontaneous combustion in order of importance as follows:—

1. The oxidation of pyrite which the coal contains.
2. The absorption of gas and notably of oxygen by the coal dust.
3. The oxidation of carbon and of certain compounds which are present in the coal.

M. Haton de la Goupilliere[4], in a report of the French Firedamp Commission, states that oxidation of pyrite, or of certain organic substances in coal is often the primary cause of spontaneous combustion. This and many other opinions expressed in that report seem, however, to be offered without very firm convictions.

In **Fayol's**[5] experiments which are referred to on pp. 25, 52, and 108, it was found that the amount of oxygen absorbed was not proportional to the amount of pyrite in the coal, hence some of the oxygen must have been absorbed by the coal.   Fayol found in fact that the pyrite in the Commentry coal does not oxidize as quickly as the coal itself; in dry air the pyrite is not oxidized at all, and in moist air only slowly.

Many observations of actual facts tend to show that the oxidation of pyrite is not the primary cause of spontaneous heating.   Thus Dr. Percy[6] notes that no coal in Great Britain is so liable to spontaneous combustion as the ten yard or thick coal of South Staffordshire, which only contains a small amount of pyrites, usually equivalent to not more than $0 \cdot 5$ per cent of sulphur.   Percy had already expressed this opinion in his lectures at the Royal School of Mines, and in a paper in 1864 in Chemical News.

Richters[7] calculated the heat which could be evolved by a coal containing $1 \cdot 01$ per cent of pyrite.   He showed, by reference to Dulong's experiments on heats of combustion, that in this case, under the most favourable assumptions regarding pyritic combustion, the temperature of the coal could not possibly be raised more than $72°C$.   He assumed in this calculation that the heat of oxidation of pyrite is the same as would

[1] De la Beche and Playfair—"Steam Coal for the Royal Navy," London, 1846 (1848-51).
[2] Trans. North Eng. Inst. Min. & Mech. Eng., Vol. X, 1861, pp. 161-7, 192-3.
[3] Report of Eng. Royal Commission on "Spontaneous combustion of Coal in Ships," 1876.
[4] Rapport de la Comm. d'étude des Moyens propre a prévenir les Explosions de Gison, 1878.
[5] Etude sur l'Altération de la houille exposeé à l'air, 1879.
[6] Metallurgy, Percy, Vol. Fuel, 1875, pp. 289-298.
   Dinglers Poly. Journ. Vols. 190, 193, 195,—1868-9-70.

be produced by the combustion of the iron and of the sulphur separately. This, as he no doubt well knew, is a vastly excessive assumption. He further assumed that the combustion takes place instantaneously, and that all of the heat produced is used in raising the temperature of the coal. In actual fact, the oxidation of the pyrite requires a long period for its completion. On the other hand he assumed the pyrite to be uniformly distributed through the coal, whereas it occurs in lumps which might be conceived to become local centres of combustion. Richters thus arrived at the conclusion that the pyrites ordinarily present in coal could not be more than a secondary factor in its spontaneous combustion.

Richters also experimented with a mixture of pyrites and quartz sand, which he submitted to the action of oxygen. His results do not strengthen the theory that pyrite is the cause of spontaneous heating, because it was found to absorb very little oxygen. For a description of his experiment see pp. 59-62, and 103-108.

Kimball[1] points out the importance of distinguishing between pyrite and marcasite, owing to the greater ease with which the latter weathers; if much of the so-called pyrites in coal is really marcasite, then sulphides in coal may have a greater influence on heating. This observation although made many years ago has apparently been overlooked by most experimenters, who apply the term pyrite to both pyrite proper and marcasite without distinction. Almost the only recent reference to the matter is in a paper by Lamplough,

Lewes[2] does not believe that pyrite, scattered through a mass of coal, and undergoing slow oxidation, can raise the temperature of the coal to the ignition point. He points out, however, that pyrite may increase the liability to ignition, when present in large quantities, by liberating sulphur. The ignition point of sulphur is 250° C, over 100° C below the ignition point of coal.

Sulphur in coal is mainly present as either pyrite or marcasite. Some coals contain large nodules of pyrite, while others contain the pyrite very finely disseminated along planes of weakness in the coal; it may also be disseminated finely throughout the whole mass.

Experimenters appear to be universally agreed upon the fact that particles of pyrite expand on weathering, thus breaking up the enclosing coal into smaller sizes, and exposing new surfaces to the air. The main point about which opinions seem to differ widely, is the importance of the heat set free due to the oxidation of pyrite.

"Sulphur balls" are known to find their way frequently into coal piles, but the surface of such a ball of pyrite would soon become oxidized, after which there would be very little reaction. To generate sufficient heat to materially affect the surrounding coal, one would imagine that finely disseminated particles, having large area in comparison with their size, would

[1] Trans. Am. Inst. Min. Engrs. Vol. VIII, 1879, pp. 204-225.
[2] T. I. Naval Architects. Vol. 31, 1890, pp. 204-228.
    Abstract Journ. Soc. Chem. Ind. Vol. IX, 1890, pp. 483-5.

be necessary, and coals containing considerable quantities of fine pyritic matter do in fact often fire spontaneously underground.

Haldane and Meachem[1] made an approximate calculation of the heat which might be generated underground in a colliery, assuming, for the sake of argument, that the total shortage of oxygen in the upcast air is all due to the oxidation of the pyrite. As no data were available for the heat of combustion of iron pyrite they followed Richters, and took the heats of combustion of the sulphur and iron separately, thus:—

$$\text{``}2Fe + 4S + 15O = Fe_2O_3 + 4SO_3 + 761,700 \text{ Cals.''}$$
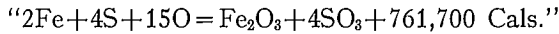
That is for every 15×16 lbs. of oxygen used enough heat is generated to raise the temperature of 761,700 lbs. of water 1° centigrade. Hence, 5,700 B.Th.U. are formed per 1b. of oxygen absorbed. In the north side of the mine 295 cubic feet of oxygen were consumed per minute and, therefore, since 1 cubic foot of oxygen at the pit bottom weighs 0·09 lb., the total heat production per minute on the above assumption, would have been $295 \times 0·09 \times 5,700$ or about 150,000 B.Th.U. By calculation it was found that the air current from the north side carried away about 48,000 B. Th. U. per minute. The surplus, about 100,000 B.Th.U. per minute, went partly into the surrounding strata and partly into the coal.

The above calculation gives the benefit of every doubt to the pyrites, but it shows that in a large mine a very considerable amount of heat may conceivably be generated by the oxidation of pyrites. It must be remembered, however, that this heat is distributed over an immense surface, and that by far the greater part of it is conducted away into the mass of virgin coal, and the rock strata above and below the seam. As a matter of fact it is extremely improbable that all, or even the main part of the oxygen absorbed in a coal mine, goes into combination with pyrites. Most of it probably combines with the carbonaceous matter of the coal itself. This does not better matters so far as heating is concerned as carbon has a higher calorific power than sulphur and iron, but it relieves the pyrites of a large share of the responsibility.

The effect of pyrite has recently been studied by **Parr and Kressmann.**[2] They made numerous experiments on coal from Williamson county, Illinois. Lumps were selected, crushed and screened into three sizes:— $0-\frac{1}{8}$ inch, $\frac{1}{8}-\frac{1}{4}$ inch, $\frac{1}{4}-\frac{3}{4}$ inch. A portion of the finest size was further pulverized in a ball mill until it went through an 80- mesh screen and 75% of it through 120- mesh screen; thus four groups were made, which in the following discussion will be called size 0, size $0-\frac{1}{8}$, size $\frac{1}{8}-\frac{1}{4}$, size $\frac{1}{4}-\frac{3}{4}$.

The sized samples were analysed and portions set aside for experiment as they stood. Other portions had pyrite added to them in known quantities, thus giving lots of each size which were identical in all respects but pyritic contents.

[1] T. I. M. E. Vol. 16, 1898, p. 457.
[2] Univ. of Illinois. Eng. Expt. Station, Bull. No. 46, 1910.

The tests were conducted in four constant temperature ovens maintained at 40°, 60°, 80°, and 115° centigrade, respectively. The coal was first placed in the 40° oven, and after a period of three days was moved to the 60° oven where it was left for three days and so on. Thus each sample remained three days in each oven. Each sample was contained in a five gallon stone jar, whose bottom was perforated with ½-inch holes. A jar of this size held thirty-five or forty pounds of coal. Air at the temperature of the oven was allowed to circulate freely around the jar. The temperature of the samples was observed periodically by means of thermometers fixed in the coal and projecting out through the cover of the oven, and the difference between this observed temperature and that of the oven at the end of each three day period was tabulated and plotted.

The composition of the coal used in the experiments is indicated by proximate analyses as follows:—

TABLE VII.

Composition of Williamson Co., Illinois, Coal used by Parr & Kressman.

(Parr and Kressman)

	Size 0 and 0-⅛	Size ⅛-¼
Moisture	4·16%	4·62%
Volatile matter	33·48 „	33·37 „
Fixed carbon	50·86 „	50·88 „
Ash	11·50 „	11·13 „
Total	100·00 „	100·00 „
(Sulphur)	1·26 „	1·29 „

Calculated to Dry Coal.

	Size 0 and 0-⅛	Size ⅛-¼
Volatile matter	34·92%	34·78%
Fixed carbon	53·08 „	53·58 „
Ash	12·00 „	11·64 „
Total	100·00 „	100·00 „
(Sulphur)	1·32 „	1·35 „

The pyritic iron was determined by calculation from the difference between the total iron in the coal and the iron soluble in dilute hydrochloric acid. The results for the above two samples are as follows:—

TABLE VIII.

Composition of Williamson Co., Illinois, Coal used by Parr & Kressman

(Parr and Kressman)

	Size 0-⅛	Size ⅛-¼
Total iron	1·91%	1·73%
Soluble iron	0·73 „	0·67 „
Pyritic iron	1·18 „	1·06 „
Calculated pyrite content	1·76 „	1·60 „

Inasmuch as more of the larger size was used than of the fine, the average pyrite content of the coal was taken as $1 \cdot 65$ per cent.

The pyritic content of the samples was increased as follows. Large lumps of pyrite were taken just as they occurred in the coal measures of Vermilion county. These lumps were ground to pass through a 20-mesh sieve. The purity was determined to be $87 \cdot 62$ per cent by calculation from the sulphur content which was $46 \cdot 73$ per cent.

The experiments were made as follows: four jars were filled with the coal using one of the four different sizes in each jar. These were placed one in each oven in the same increasing ratio of size of coal to temperature of oven. Thus size 0 and size $0\text{-}\frac{1}{8}$ were put in the $40°$ oven, size $\frac{1}{8}\text{-}\frac{1}{4}$ in the $60°$ oven, size $\frac{1}{4}\text{-}\frac{3}{8}$ in the $80°$ oven, and size $\frac{3}{8}\text{-}\frac{3}{4}$ in the $115°$ oven. Each jar was left in the oven for three days and then moved to the next hotter oven. This method of procedure saved a considerable amount of time and was carried out after it was found that the larger sizes were not appreciably oxidized at the lower temperatures.

Parr and Kressman give an elaborate series of tables and curves showing the results of their numerous tests, and from these they draw conclusions from which we may summarize the following:—

a. Oxidation is greatly accelerated and in certain phases is directly dependent upon an increase of temperature.

b. Coal in a fine state of division heats much more rapidly than coarser sizes of the same material, and this oxidation is in the beginning largely due to the absorption of oxygen by "unsaturated compounds, the products being humic acids or other fixed constituents of the coal texture." This oxidation "does not result in the formation of carbonic acid."

c. The presence of pyrite in the coal is a "positive source of heat" due to oxidation of the sulphur; "this may be considered the second stage in the process of oxidation." But in coals of the Illinois type "with their high per cent of sulphur" the pyritic oxidation is of greater importance than the oxidation of the coal matter proper, particularly as these coals carry much duff or dust, which is largely pyritic.

d. Moisture is essential to pyritic oxidation, and under the circumstances of their tests it was found that in all cases "wetting the coal increased the activity as shown by the ultimate temperature."[1]

e. The oxidation of carbon and hydrogen takes place at temperatures in excess of $120°$, and may be considered a third stage.

The above very condensed statement of Parr and Kressman's work does not by any means cover the whole of the ground of which they treat, and the author has therefore prepared the following six curves from their data with a view to presenting in a summary form the results of their experiments on the effect of pyrite.

As fine coal proved much more susceptible to oxidation these redrawn curves only include the three smallest sizes.

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[1] This conclusion will receive consideration in its proper connexion.

Parr and Kressman's work is undoubtedly of great value, but, as has already been noted, and as they point out in their paper, the Illinois coal on which they worked is very different from ordinary bituminous coal in that it is exceptionally high in sulphur and contains from two to four times as much combined water. Their conclusions therefore should not be too freely applied to ordinary coal.

Fig. 3, A, B, and C show the effect of pyrite on the three sizes of coal. In Fig. 3 A the final temperature of the coal with 3% pyrite is given, but, as a matter of fact, this very fine coal had heated to a maximum of 75° in 30 hours and then cooled again to 46° before the end of the 3 day period. If the mean of its maximum and final temperatures be taken there is a gradual increase in the heat developed as the pyrite content of the coal increases. Fig. 3 B shows an increase in temperature rise as the percentage of pyrite in the coal increases. Fig. 3 C shows the same results, but less definitely. Figures 3 D and 4 A and 4 B show the results of a similar series of tests with wet coal. Fig. 3 D shows that for very fine coal the pyrite has a marked effect. Coal with 1·6 per cent of pyrite did not catch fire, whereas the coals with 3% and 5% of pyrite, respectively, ignited in the 115° oven. Neither Fig. 4 A nor 4 B shows any very different increase in rise of temperature due to the pyritic content of the coal. It is possible, however, that this may be due to the difficulty of keeping each sample thoroughly wet with the same amount of moisture and to the fact that any heat generated, while the coal is still damp, is used up in drying the coal instead of in raising its temperature. Figures 4 C and 4 D show tests with unscreened coal, Fig. 4 C with dry coal, and Fig. 4 D with wet coal. These curves show very definitely that an increase of the pyrite content from 1·4% to 3% produces a marked increase in rise of temperature. A further increase of the pyrite to 5%, however, does not seem to produce much effect.

Porter and Ovitz[1] separated a coal containing 3·34% sulphur into a lighter portion containing 2·64% sulphur, and a heavier portion containing 5·33%. "The heavier portion showed no greater tendency to develop heat in the oxidation test." It must be noted, however, that this test was made upon dried coal and that the oxidation of sulphides of iron at the temperature used probably does not take place at all except in the presence of moisture. Their figure, illustrating this experiment, is appended as Fig. 5.

Lamplough and Hill[2] experimenting quite recently with a number of English (Barnsley) coals find that in the case of certain "soft" i.e. powdery Barnsley coals which contain much finely divided "pyrites", the oxidation of this material "might possibly be the predominant factor in the spontaneous combustion of such coal dust". Their experiments and conclusions are summarized in some detail on pp. 111-114, and are very interesting, but so far as pyrite is concerned they are not very conclusive. They particularly call attention to the fact that they used the word "pyrites" to designate sulphide of iron, FeS_2, without prejudice as to its nature, but that an exami-

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[1] International Congress of Applied Chemistry, 1912. Vol. X, pp. 251-267.
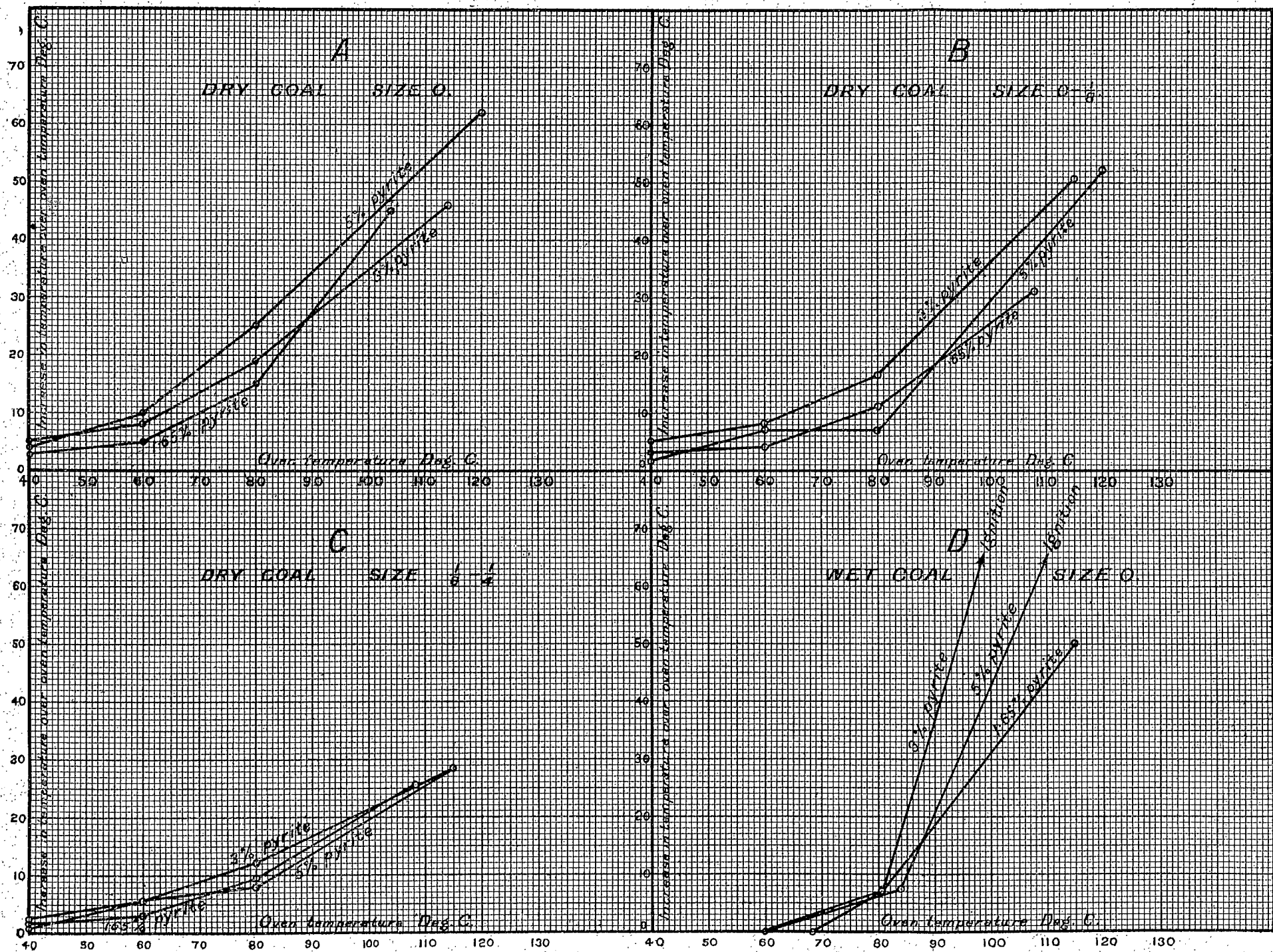[2] Trans. Inst. Min. Engrs. Vol. XLV, 1913, pp. 629-657.

Fig. 3. Effect of pyrite on rate of oxidation.
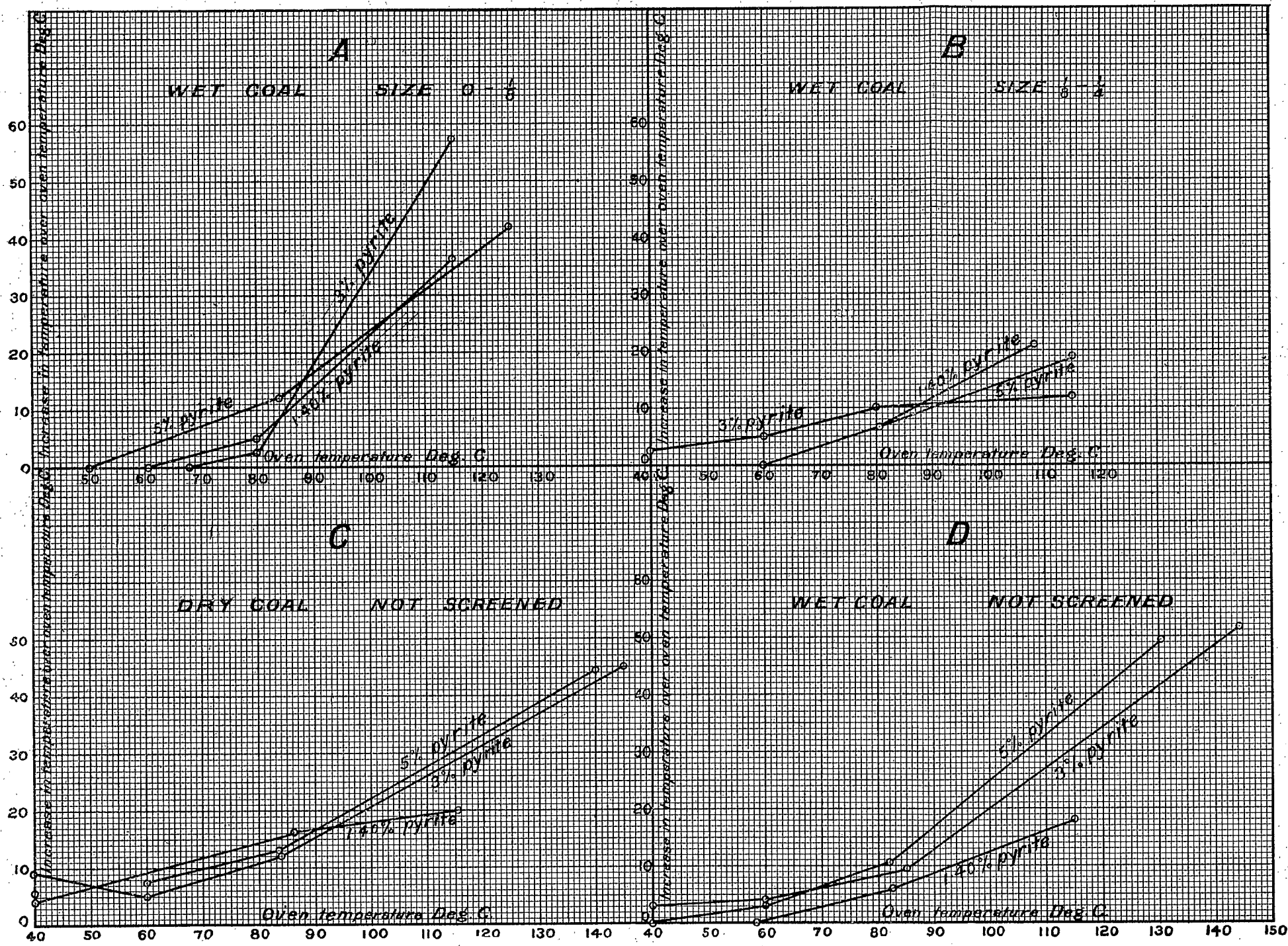
(Redrawn from Parr and Kressman.)

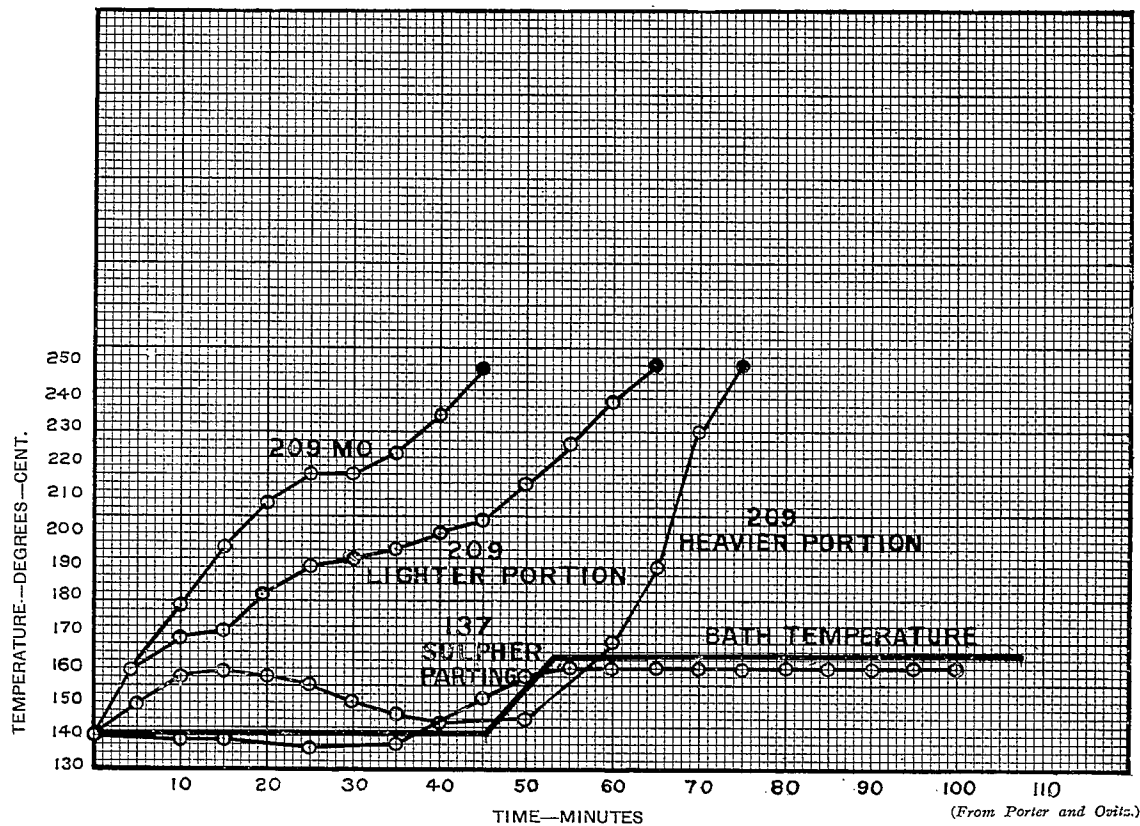FIG. 4. Effect of pyrite on rate of oxidation.

(Redrawn from Parr and Kressman)

FIG. 5.   Behaviour of coals in current of 50 per cent oxygen at 140 °and 160° Cent.   Effect of sulphur in coal
Lighter portion 2·64% sulphur, heavier portion 5·33% sulphur.
● = ignition

nation of the material showed that "some of it was pyrite". This statement implies that a large part of the "pyrites" in the coals they tested was really marcasite.

Porter and Ovitz[1] state that it was found that a particular coal containing 4-5% of pyrite gave a great deal of trouble; yet on analysis only 10% of the available sulphur had been affected. They made a laboratory test on a coal, taking it almost to a point of ignition, and on cooling and submitting a sample to analysis, the sulphur content was found to be almost unchanged: they point out, however, that the pyrites might possibly occur as pockets of fine particles, in which case, if neither too much nor too little moisture were present the temperature would rise to a considerable extent.

In connexion with this last observation of Porter and Ovitz the author has noticed the fact that coal piles are sometimes found to suffer from local heating in the immediate neighbourhood of lumps of pyrite or pyritic shale. This is not really a conclusive argument proving that the pyrites started the trouble, and it is very probable that the first heating was due chiefly to the organic matter of the coal, but we can see how the oxidation of the coal once having begun, would proceed with especial rapidity in the immediate vicinity of a mass of pyritic shale, a substance which every miner knows to be particularly prone to disintegrate.

Porter and Ovitz[2] quote Somermeier, Journal American Chem. Soc. 1904, p. 764 to the effect that

"Several samples of high sulphur coals, after standing one and a half years at ordinary temperature in the moist condition as received from the mines, showed a maximum of only 0·47% oxidized sulphur when kept in closed bottles, and 0·37% when kept in an open sack."

The exact amount of total sulphur in the samples is not stated, but it is estimated that one-tenth of it only was oxidized. They further state that a

"number of samples of weathered coal collected by them from out-door coal piles after six months to one year's storage, and in some cases after spontaneous heating had occurred in the coal, showed on analysis not over one-tenth of the total sulphur to be in the oxidized condition."

Parr and Kressmann,[3] whose experiments have been previously referred to on pages 37-40, calculated the heat rise which might be produced by the amount of pyrites which they found, at the close of an experiment, to have oxidized. The result showed a possible rise of about 74° C for dry bituminous coal. This looks imposing, but when account is taken of the fact that their coal was wet at the beginning of the experiment, it becomes clear that a much greater amount of heat must have been used up in the evaporation of moisture than would be necessary to raise dry coal to that temperature. The figure thus becomes more or less insignificant beside

[1] U. S. Bur. o {Mines Tec. paper No. 16, 1912.
[2] 8th International Cong. Appl. Chem. Vol. X, pp. 251-267.
[3] Univ. Ill. Exp. Sta. Bull. 46, 1910.

the one which should be quoted for heat generated by oxidation of the coal substance itself.

Parr and Kressmann also experimented by adding pyrite to coal in varying quantities and then subjecting it to oxidation. They report that no matter how much pyrites was added to the coal the ratio of oxidized pyrites to total pyrites present remained constant. This would seem to be analagous to the matter of cyanide extraction of gold, in that a film of a constant thickness on the outside of each grain was probably attacked. The same size of pyrite was used throughout the experiments so that additional quantities would not affect the ratio of oxidized to unoxidized, or of oxidized to total pyrite present. It would have been very interesting had the pyrite for one experiment been so treated either by screening or by further crushing as to alter the ratio of exposed surface to quantity.

Conclusions.

From the above review of the various and apparently contrary opinions held by the numerous experimenters who have studied the oxidation of pyrite in coal, it seems reasonable to conclude that the divergence of opinion is very largely due to differences in the coals studied; and that in an average bituminous coal the actual heat generated by oxidation of the pyrite is, in itself, not usually very important. Taken, however, in connexion with the fact that any small increase in temperature of the coal will greatly increase the rate of absorption of oxygen and consequent heat production, the heat produced by the weathering of pyrite may become a very important factor. Whether it will do so or not will depend on whether the coal under consideration can generate heat sufficiently fast by its absorption of, or chemical combination with oxygen, to raise its temperature to the danger point without assistance from the heat due to the oxidation of the pyrite. The effect of pyrite in liberating free sulphur and thus lowering the ignition point is unimportant since the point at which autogenous oxidation begins will have been passed before the ignition point of sulphur is reached.

The calorific value of a carbon hydrogen compound is so much greater than that of pyrites that a much smaller quantity of the former would yield any given amount of heat, and this fact taken in conjunction with the relative simplicity and accuracy of the chemical determination of sulphur makes it probable that heating has in many cases been ascribed to the alteration of the pyrite, when in reality it has been due to an oxidation of organic matter that has not been detected by the chemist.

There are, however, some coals in which the pyrite or marcasite is excessive in quantity or, like the "Barnsley softs" or the Williamson county, Illinois, "New Ohio," in which it is peculiarly susceptible to oxidation, and in such coals, it is probable that pyritic oxidation is an important, and perhaps the primary cause of heating. Such coals are, however, comparatively rare and, owing to their softness and excessive sulphur they

are of lower commercial value than normal coals. The problem of storing such coals for industrial use, although of great local interest is of relatively minor importance, but unfortunately, even when such soft shaly pyritic coals are worthless, they are bound to prove troublesome as they cause gob fires if left in the waste underground and yet are usually of little or no value if brought to the surface.

SIZE OF COAL.

Whether it be the pyrites in the coal which first oxidizes or the coaly matter itself, it is clear that the action is largely superficial, or in other words, the rate of weathering in any coal is approximately proportional to the surface exposed to oxidation. This surface is of course inversely proportional to the diameter of the particles, or in other words a ton of coal in one-inch lumps has only half the surface of a ton of half-inch lump, or one one-hundredth the surface of $\frac{1}{100}$-inch lump, which may be taken roughly as the average size of coal dust, although really fine dust is of course much finer than this, and therefore has very much more surface.

Other things being equal, therefore, we may say that the rate of weathering increases directly with the reduction in size and is immensely more rapid with fine coal than coarse, but this is only true within limits, for in order that weathering may take place it is of course necessary for air to come into contact with the surface, and excessively finely divided coal packs so close that it is virtually impermeable to air and thus after the included air gives up its oxygen no more can gain access. Coal must, however, be exceedingly fine and suitably graded to be impermeable, and ordinarily we find that "fine" coal consists in a mixture of grains of all sizes from impalpable powder up. Such material is by no means impermeable and affords immense surface to oxidation as compared with coarse coal.

If we consider the effect of size alone on the rate of weathering we see from the above considerations that it acts in three ways:—

1. The rate of absorption of oxygen varies as the surface area of the coal, that is to say inversely as the diameter of the grains.
2. The rate of absorption will decrease as the supply of oxygen to the coal decreases, i.e. as the percentage of fines increases.
3. The circulation of air being better for lump coal more heat is lost by dissipation.

A pile of fine coal is more impervious to air than a pile of lump coal and hence fineness increases the absorption in two ways, but diminishes in another. The maximum of these three effects is attained in a mixture of very fine coal with coarse, but not very coarse, material, the exact sizes and proportions no doubt differing with coals of different character and composition.

The aim of every colliery is always to produce as large a proportion of lump coal as possible, not primarily because of anticipated difficulties due to weathering, but because lump coal burns better in ordinary use and
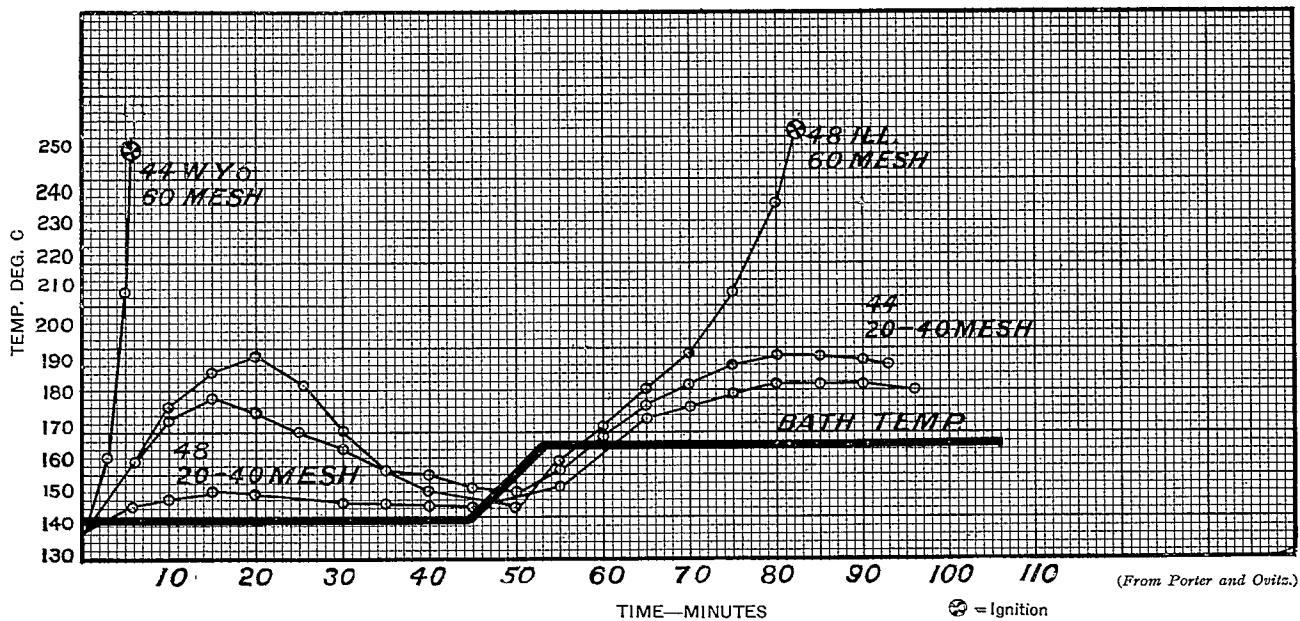
FIG. 6. Effect of size of coal on oxidation in current of 50 per cent oxygen at 140° and 160° C.

therefore, commands a better price; but the operations of mining unavoidably produce a considerable percentage of fines even from the hardest coals,- and many otherwise very good coals are so friable that "slack" constitutes the chief product of the colliery.

In all cases the amount of fines increases as the coal is handled and shipped and thus by the time the coal reaches storage it contains a very large proportion of exceedingly fine material unless it is deliberately screened and the fines removed.[1]

In addition to the mechanical production of fine above referred to, further fines are produced as the coal weathers. Pyrite is largely responsible for this action as has already been pointed out,[2] the result being due in part to the actual bursting of the coal owing to the swelling of the pyrite on oxidation, and in part to the solvent action of the sulphuric acid produced on minerals such as calcite, etc., contained in the cleavage planes of the coal itself.

Pyrite is, however, not the only mineral constituent which breaks up coal by weathering, and Roth[3] names 30 other minerals which are liable to occur in coal, all affected by weathering, and some even soluble in water; these by dissolving or swelling tend to disintegrate the coal which contains them.

Fayol remarks that washed coal heats a little less than raw; this observation, which is not true of all coals, is probably due to the fact that washing removed a large proportion of the dust and fines from the coal, and as we see from Parr and Kressmann, the larger the coal the less it heats.

Porter and Ovitz draw attention to the fact that friability is a quality which should be noted for any coal, in that as size decreases, area and consequent oxidation increase.

Parr and Wheeler quote figures to show that the smaller the coal the greater is its loss in value per year.

Bement[4], see Fig. 10, found that a good deal of disintegration took place in exposed storage; he recommends the storage of "egg" coal, as it shows the least tendency to disintegrate to smaller sizes, and it is free from marked spontaneous heating if undisturbed.

The experience of the Calumet and Hecla Mining Company may well be quoted here; they at one time stored all their coal in the form of "run-of-mine," and experienced much trouble from heating; upon changing their methods so that only oversize from a bar-screen was stored, and the undersize used as soon as possible, all trouble with heating of piles ceased.

The influence of size upon the action of two American coals exposed to oxygen is well shown in Fig. 6 taken from the work of Porter and Ovitz.[5]

[1] This was pointed out by De la Beche, Blackwell and Bunning, who were among the very early writers on the subject and all three held the view that fines were more dangerous than pyrite.
[2] See page 31 et seq.
[3] Chem. Geol. p. 69 et. seq.
[4] This writer's experiments on storing certain Illinois coals are interesting and valuable. See "The Loss in Coal due to storage." Am. Inst. Chem. Eng. Vol. III, 1910, p. 281.
  Int. Cong. App. Chem., 1912. Vol. X, pp. 251-267.

When dealing with very small quantities of coal as in laboratory experiments, the effects of fines in reducing the loss of heat by radiation and in decreasing the supply of oxygen are negligible, and hence it is possible to get the direct effect of increased surface area by experiment. This has been done by Parr and Kressman[1], and the results are shown in curves of which three sets are reproduced from their paper, (see Figs. 7, 8, and 9).

(*From Parr and Kressman.*)

OVEN TEMPERATURE DEG. C.

1·65 % Pyrite—Dry Coal.
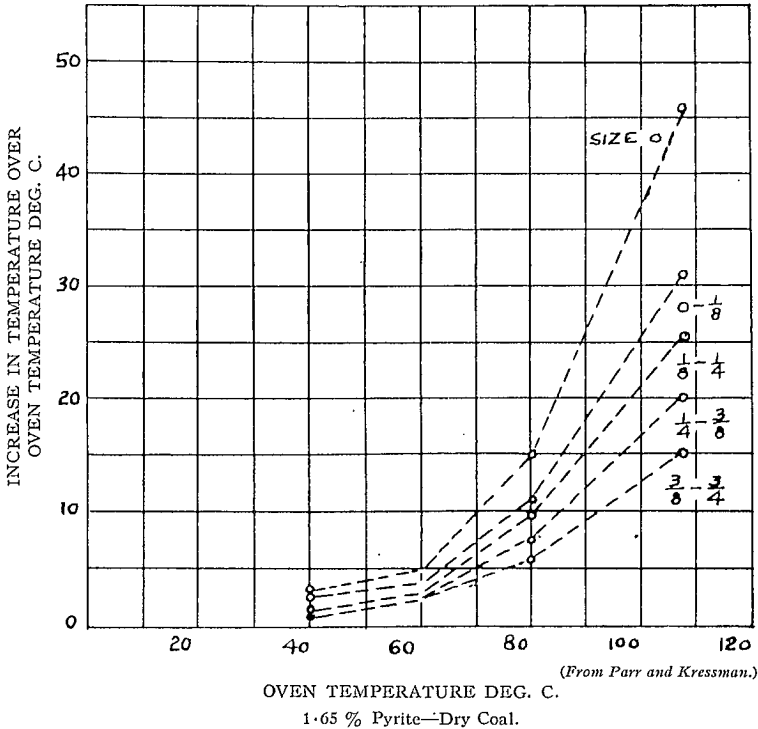
FIG. 7. Effect of size on rate of oxidation at elevated temperatures.

THE SIZE, SHAPE, ETC., OF THE STORAGE PILE.

When coal is kept in a storage pile for a considerable length of time it is a comparatively simple matter to study its condition by keeping a record of temperatures in a sufficient number of places in the pile. We can thus readily follow the variation in temperature of the mass, as all the reactions are exothermic.

Any heating of the interior of the pile, whether it be small or great, must be primarily due to oxidation, and the source of oxygen is the air which filled the voids in the broken coal during the piling, and other air which thereafter works its way into and through the interstices during the whole existence of the pile. Some of the heat evolved is lost by radiation and convection, but a considerable part of the loss is due to the cooling effect

[1] Bull. 46, Univ. of Ill. Exp. Sta., 1910.

of the interstitial circulation above referred to. It is thus clear that the physical condition of a storage pile, that is to say its bulk, porosity, etc., has a very important influence on its rate of heating. A thin or porous pile may oxidize rapidly, but it will be kept cool by radiation and excessive ventilation. A very high and compact pile will get too little air to support any serious oxidation in the interior and its deeper parts will, therefore,

FIG. 8. Effect of size on rate of oxidation at elevated temperatures.

(From Parr and Kressman.)

OVEN TEMPERATURE DEG. C
1·65 % Pyrite—Wet Coal.
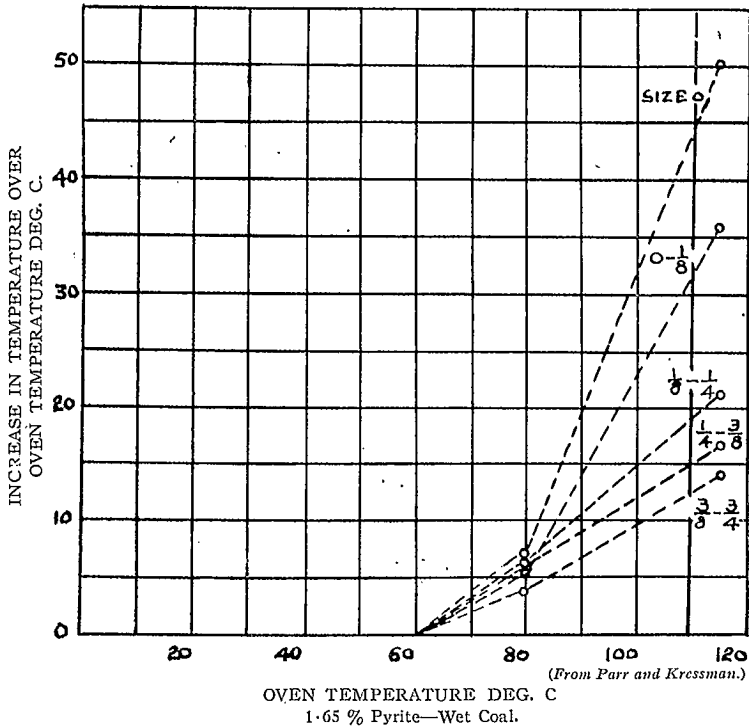
heat very little. A pile of intermediate porosity or a particular zone in a large pile will get enough air to cause heating and not enough to carry the heat away and will thus give a maximum of trouble.

This matter of porosity is of greater importance than might at first be imagined as the interstitial spaces in a pile of broken mineral range from 15 per cent to nearly 50 per cent of the total bulk, but in addition to this the initial temperature of piling also has a considerable effect. Oxidation proceeds, other things being equal, more rapidly as the temperature rises, and the rate of ventilation also increases both for evil and good as the coal gets hotter and the difference between the internal and the atmospheric temperature rises.

The inseparable way in which the phenomena of this subject are bound together is further shown when we consider that coal ordinarily contains pyrites or marcasite, and these constituents under the influence of moisture

cause disintegration which, while increasing the oxidizing surfaces, reduces the interstitial spaces in the heap; while upon surface exposed and circulation of air depend the rate of oxidation and consequent heating, and also the subsequent cooling of the pile upon excess of air to the mass. It is clear therefore that a great deal may be learned by observing the behaviour of storage piles, if an attempt is made at the same time to obtain full information as

3% Pyrite—Dry Coal
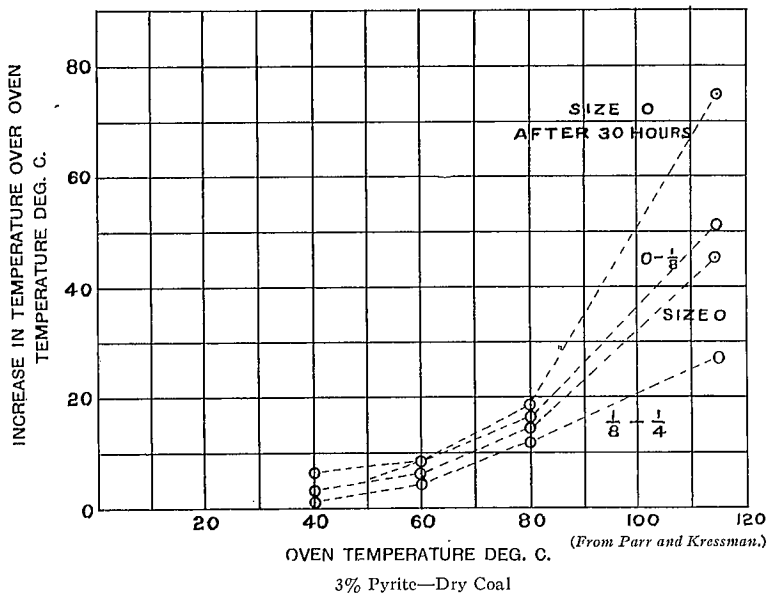
Fig. 9.   Effect of size on rate of oxidation at elevated temperatures.

to all of the various factors which enter into the matter; but as a full consideration of these factors would open up the whole subject of weathering we shall content ourselves for the present with noting a few observations, particularly concerned with the size and temperature of storage piles.

Fayol experimented with respect to the limit of depth by constructing a pile much higher at one end than the other, and placed thermometers at intervals in the mass as shown in Fig. 11, and it will be noted that heating took place in the deepest part of the pile about a foot from the ground. Fayol concludes that Commentry coal will heat dangerously if stacked in heaps exceeding two metres in depth.

Another of Fayol's experiments was with a pile in which he regulated the rise and fall of temperature by opening and closing holes in a tight fitting cover. This gave a very interesting demonstration of the effect of air supply. (Fig. 12).

Porter and Ovitz experimented in the laboratory on the rate of heating under varying rates of air supply and set forth their observations in a curve which is reproduced at page 54 (Fig. 13). They say that "The ideal conditions for heating are supplied by a large pile of run of mine coal con-

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taining a large percentage of dust, piled in such a manner that the air may enter." Presumably the large lumps of coal in this case would serve merely to protect spaces large enough for air to attack the fine dust.

Porter and Brunton studying storage piles of Sydney coal in Montreal (see p. 159), obtained apparently contrary results from those of Fayol referred to above, but the explanation is perfectly simple. In Fayol's
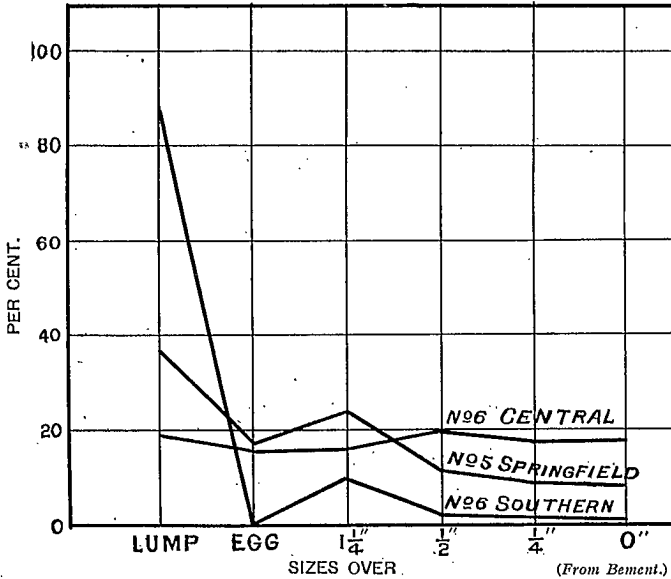
FIG. 10. Tendency of coal to disintegrate. Original samples 100 per cent lump, which in one year's outdoor storage broke down to sizes as shown.

experiments the pile was a small one provided with an impervious cover and when the air supply was totally shut off oxidation had to stop and the pile lost heat by radiation. In the case of the very large pile observed by Porter and Brunton there was no impervious cover, and on the other hand the pile in its normal state had ventilation holes 16 inches apart throughout its mass. These holes permitted access of so much air that the pile was kept cool in spite of its slow oxidation, but when the holes were closed this cooling effect ceased, and the pile heated somewhat rapidly. As a matter of fact the Porter and Brunton pile when closed was substantially in the same condition as the Fayol pile when open, and under this condition both piles heated. The two sets of observation therefore confirm one another.

Porter and Brunton also found that although a pile may be covered with snow at the surface yet three feet below the surface of the coal the temperature may be quite high, thus incidentally confirming, although in a negative way, the observations of the New South Wales Commission referred to on p. 55.

Porter and de Hart working with experimental piles at Glace Bay, N.S, found that under the conditions of their trials fresh coal quickly piled heated
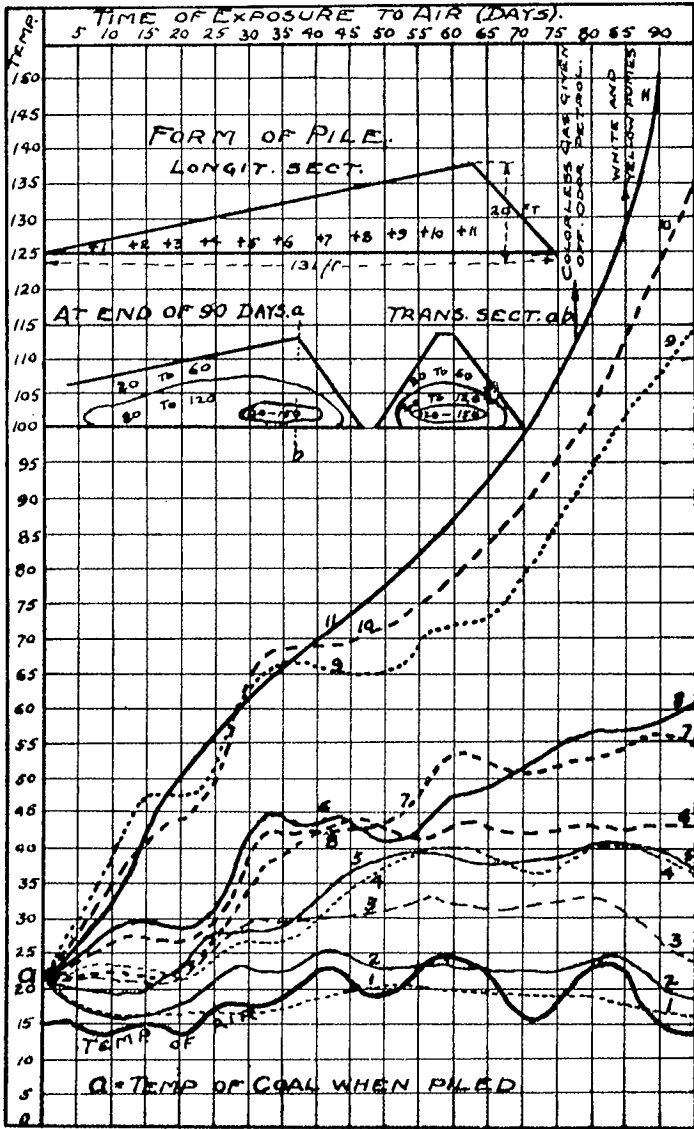
(Redrawn from Fayol.)

FIG. 11.   Form and temperature of coal piles.

more rapidly than the same coal slowly piled, or than stale coal repiled. Their results are given in some detail on pages 154-159.

THE INITIAL TEMPERATURE OF STORAGE.

Fayol, who first dealt scientifically with the subject of the initial temperature of a storage pile, found that Commentry slack if raised to a tem-
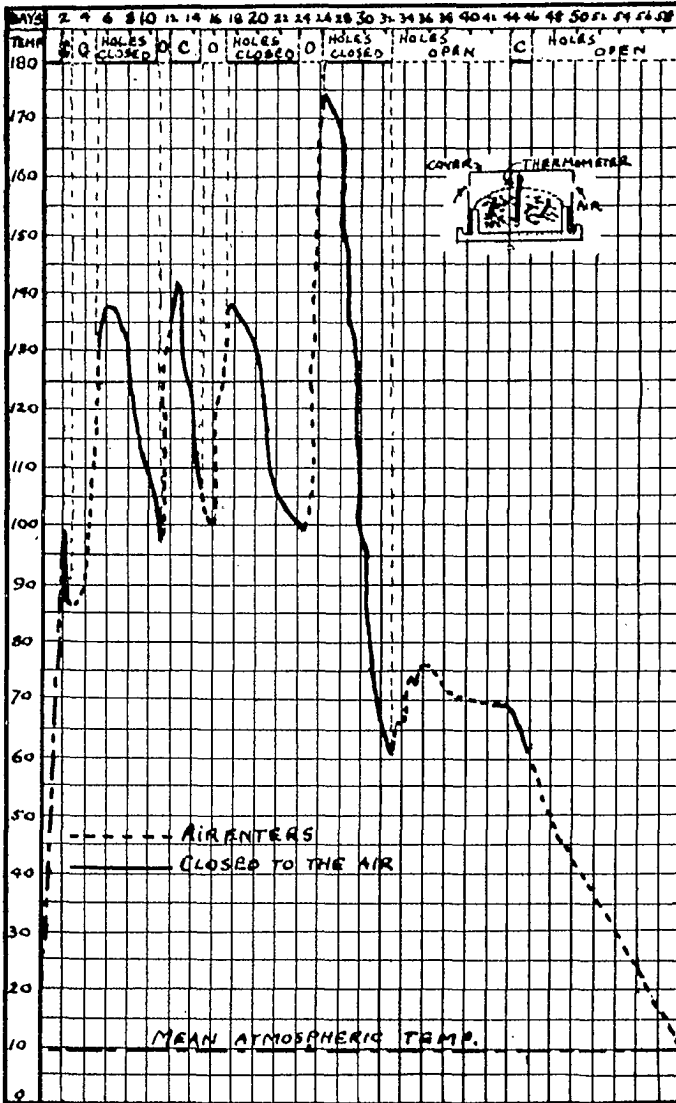
(Redrawn from Fayol.)

FIG. 12.   Form and temperature of coal piles.

perature of between 60° and 70°, would continue to generate heat of itself, but that if the temperature of a heap did not rise to 60° then it would gradually cool off again.   It may be noted that this coal is peculiarly susceptible

to atmospheric influences, and has in fact a lower point of so called "autos genous oxidation" than almost any other important coal with which the writer is familiar.

Fayol also made a series of experiments exposing small lots of variou- other coals to elevated temperatures in ovens. These experiments are also referred to in another connexion on pages 26 and 108-9. Some of the results obtained are shown in the following table which demonstrates the effect of the external heating on the ignition point. The coal in each case was contained in a box 12 centimetres square by 3 cms high. The sign +indicates that the coal caught fire, and — indicates no ignition. The small figures show the time which elapsed before ignition took place. From these experiments Fayol concluded that the temperature at which coal is piled will have a large effect on its rate of heating and its ultimate tempera- ture. Any external heat as from the sun or from steam pipes would of course have a similar influence.

TABLE IX.

Time Required to Ignite Coals Heated to Different Temperatures.

Coal	Temperatures of stoves			
	100°	150°	200°	400°
	Impalpable Powder			
Anthracite (Marais)............	—	—	—	7 mins. +
Bituminous coal (Trevil)........	—	2h. 20 mins. +	1h. 10 mins. +	5 mins. +
Gas coal (Commentry).........	5h. +	2h. 50 mins. +	50 mins. +	1 min. +
Lignite (Vosges)...............	7h. 50 mins. +	1h. 20 mins. +	40 mins. +	5 secs. +
	Dust through ½ mm. screen.			
Anthracite (Marais)............		—	—	35 mins. +
Bituminous coal (Trevil)........		—	—	25 mins. +
Gas coal (Commentry).........		6h +	1h. 30 mins. +	10 mins. +
Lignite (Dordogne)............		5h. 20 mins. +	1h. 40 mins. +	1 min. +
	10 mm. grains			
Anthracite (Marais)............		—	—	50 mins. +
Bituminous coal (Trevil)........		—	—	20 mins. +
Gas coal (Commentry).........		—	—	20 mins. +
Lignite (Dordogne)............		—	—	3 mins. +

Parr and Wheeler give an example in which coal kept in an oven at 110° C. has risen to 200°C. of itself.

Parr and Kressmann whose experiments with various sizes of coal stored at elevated temperatures have been described at some length on pages 37-40 and 42-43, give 200°C. to 275°C. as the temperature of autogenous oxidation in air, while they say that firing or actual kindling does not take place until a temperature beyond 350° C. is attained.

Their estimate is no doubt correct for the coal with which they experimented, but their figure is much too high for general acceptance, and unfortunately many of the most important coals of eastern Canada and the United States cannot rise to nearly so high a temperature without risk, and in general there is grave danger when a coal pile of its own accord heats above 100° C in temperature, as such a temperature indicates that the heat given off by the coal is more than counterbalancing the cooling due both to radiation and the evaporation of the moisture present, and as soon as all the moisture has been driven off a rapid rise in temperature is liable to ensue.

That temperature has very great influence upon oxidation, is shown in a curve drawn by Porter and Ovitz, (Fig. 13A) which approximates to the form of a parabola. The temperature at which autogenous oxidation begins appears to vary with different coals, as might be expected.

General Discussion and Conclusions.

The term "autogenous oxidation" has been so widely used that it is retained in the present volume, but the word autogenous is not always correctly employed, and here as elsewhere it is liable to give rise to misapprehension. There is undoubtedly for each particular case some particular temperature below which oxidation will generate heat no more rapidly than radiation and convection can dissipate it; and coal stored below this temperature will not rise above this critical point, and will, therefore, be safe; whereas the same coal stored at a higher temperature, or heated by any means to such a temperature, will have its rate of oxidation accelerated, and will thus generate heat more rapidly than it dissipates it, and, therefore, grow hotter and hotter until it ignites. This critical temperature is, however, dependent not merely on the particular coal used, but on the size and shape of the pile, the size of the fragments of coal itself, the degree of moisture, and to a certain extent on the external temperature, the character of ground under the coal pile, etc., etc. The changes in the critical temperature due to variations in these numerous factors are so great that any statement of the temperature of autogenous oxidation of a coal is useless and often mischievous unless accompanied by a statement of the determining conditions. It is, however, quite possible for persons experienced in the storage of particular coals to arrive experimentally at the approximate critical temperature below which their coal in their standard storage pile may be permitted to heat without anxiety to those in charge; while if the

A

B

Cu. Cm. Oxygen absorbed per gm. coal 80-100 mesh size, 2 litres air

Temperature Deg. C.

Litres air per hr. over 5 gms. coal (30 min. test.)

Cu. Cm. absorbed per gm. at 140° C.

C

Fresh coal.   Coal 1 hr. exposed.   Coal 2 hrs. exposed.

(From Porter and Ovits)
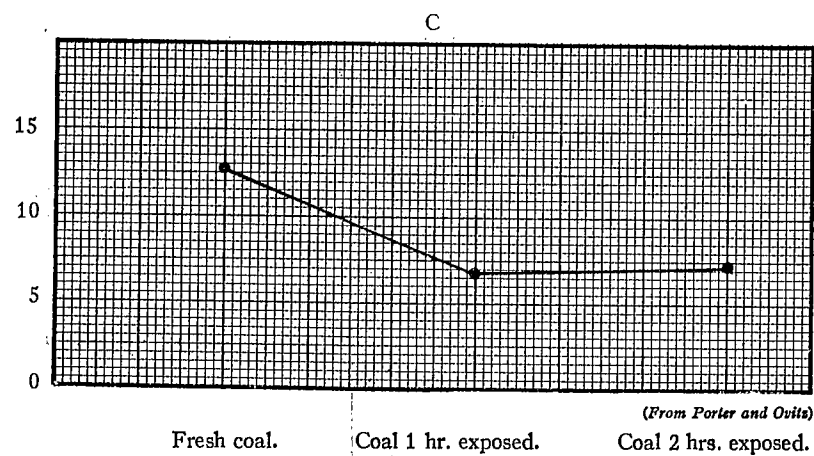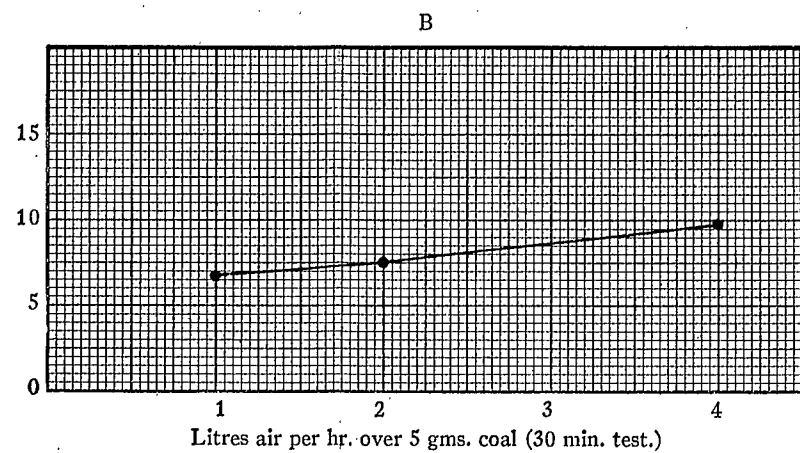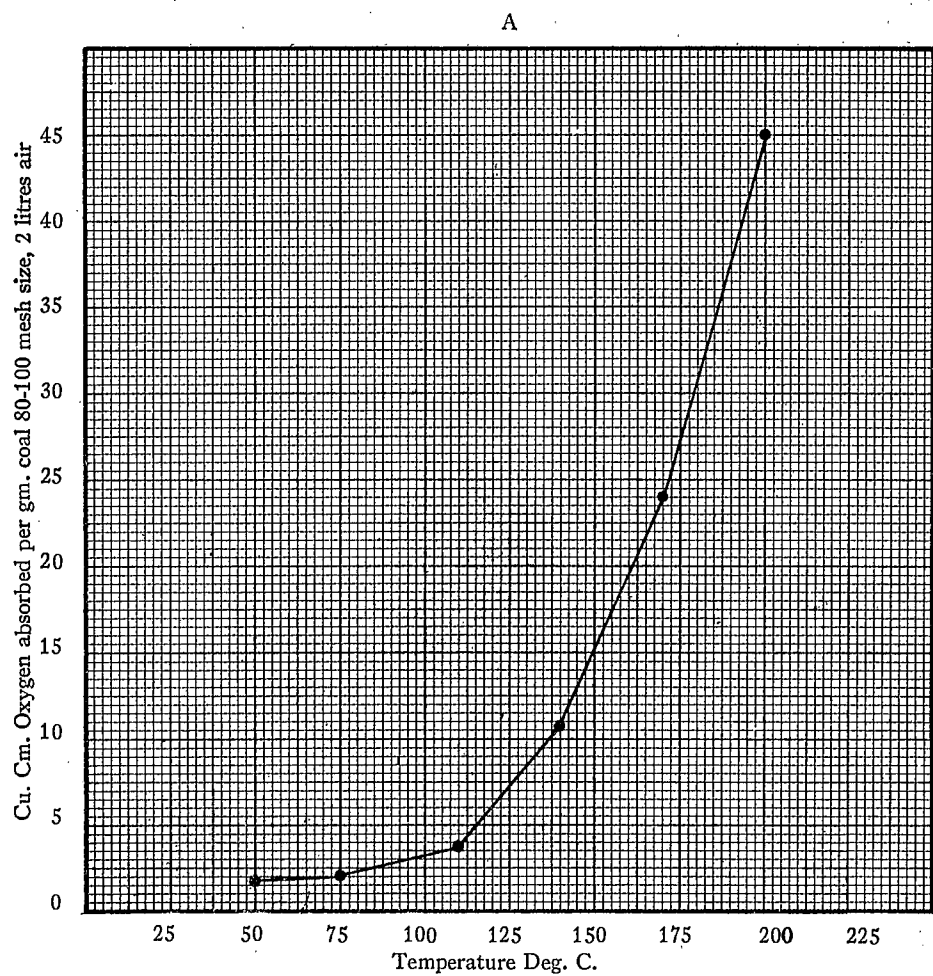
Fig. 13 A—Effect of temperature on rate of oxidation of dry coal.
B—Effect of rate of air supply on rate of oxidation of dry coal.
C—Effect of previous exposure on rate of oxidation of 200-mesh coal at 140° C.

heat in any spot rises above this temperature the coal requires prompt ventilation, careful watching, and possibly digging out.

From what has been said above it is obvious that the initial temperature of storage is of very great practical importance. Attention was directed to the matter in 1898 by the New South Wales Commission which recommended strongly that when coal was put into storage in any shape or form, the handling should be carried out as much as possible during the coolest part of the day. The commission was considering the case of loading ships in a subtropical climate, and its advice appears very necessary in that if the coal is being loaded while the sun is shining it becomes greatly heated and these hot layers get covered over and so retain their heat as the superincumbent coal is a poor conductor. As a matter of fact the Commission's advice is good even for temperate climates, and piles made in summer are often quite hot to start with and liable to give trouble. Of course the converse is also true and piles made in winter rarely give trouble; in fact it is said that ice and snow are sometimes found as late as midsummer in coal piles made at Glace Bay in midwinter.

Every precaution should also be taken to ensure that coal after being stored is not heated even locally from some external source. Coal piled near boilers, and particularly over or around hot pipes or flues is quite liable to develop violent spontaneous combustion. The action of the sun on a finished pile is on the other hand not likely to do harm as it is superficial and the heat gained in the day is usually lost in the night.

Porter and Ovitz cite a case in which a pile of cinders was observed to take fire due to the influence of heat radiated to them from a furnace. The cinders contained in one case 33%, and in another 40% of carbon.

CHAPTER IV.

THE OXIDATION OF COAL.

In the preceding discussion an attempt has been made to study each of the different factors in the weathering of coal by itself, or as nearly by itself as is possible, in order that the part played by each of these factors should be understood. It is, however, difficult and often impossible to portion out the results correctly among the several causes, and in the three next chapters we shall deal with the matter of weathering in a broader way, first discussing oxidation of the coal as a whole, and then the practical problem of how best to prevent or minimize the weathering of stored coal.

We have already seen that all coals except the hardest anthracite absorb more or less oxygen on exposure to the air. This action may be considered under three heads: occlusion, oxidation proper at low temperatures, and oxidation at elevated temperatures.

In occlusion the action is virtually the concentration of oxygen on the surface of the carbonaceous matter; this surface being enormously large in the case of powdered or porous material. No actual chemical combination takes place, but a considerable amount of oxygen is extracted from the air and retained by the coal, and a certain amount of heat is developed. The same phenomenon is even more markedly shown by charcoal which if freshly burned will on exposure occlude eighteen[1] times its bulk of oxygen; in fact some kinds of charcoal occlude far more than this, and animal charcoal takes up so much oxygen that it is liable to be so heated that actual oxidation and combustion take place.

Occlusion, which is a property of many solids with relation to many gases, is theoretically quite distinct from reaction, such as oxidation. The gas is merely condensed on the surface of the solid in a film of almost infinite thinness and no chemical combination between the two need take place, but when the gas is oxygen and the solid is a readily oxidized material such as coal, the condensation of oxygen on the surface and the consequent rise in temperature naturally lead to oxidation, and in practice it is virtually impossible to distinguish sharply between the two. Similarly, although oxidation begins at low temperatures it develops heat often more rapidly than it can be dissipated, and in such cases the temperature of the mass rises at an ever increasing rate until ignition takes place and actual combustion occurs.

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[1] Hunter, Phil. Mag. (4) Vol. 25, 1863, p. 364.
Dewar, Ann. Chim. Phys. (8) Vol. III, 1904, pp. 5-12.

OCCLUSION AND OXIDATION AT ORDINARY TEMPERATURES.

As has just been explained it is very difficult in practice to distinguish between the occlusion of oxygen by coal and the earlier stages of actual oxidation. The two will, therefore, be considered together, although the cases in which occlusion is probably important will be dealt with first.

Percy[1] states that one part of the oxygen absorbed combines with part of the carbon and hydrogen of the coal forming carbon dioxide and water vapour; while another portion enters into an unknown state of combination with the organic substance of the coal, and the remainder is consumed in oxidizing the iron pyrites invariably present in the coal.

Lewes[2] is of opinion that the absorption of oxygen is, at any rate at first, purely mechanical. He states that the absorption is at first very rapid, but the rate, which is very much influenced by temperature, decreases. This mechanical absorption causes a rise in temperature, which tends to increase the rate of the action which is going on, but which is rarely sufficient to bring about spontaneous combustion. Lewes states that air dried coal absorbs oxygen more quickly than wet coal. The gas which has been thus mechanically absorbed becomes chemically very active and soon commences to combine with the carbon and hydrogen of the bituminous portion of the coal converting them into carbon dioxide and water vapour.

Fayol[3] is of opinion that the oxygen combines chemically with the coal. His arguments in favour of this hypothesis are:—

1. That the absorption of oxygen by coal is helped by an increase of temperature whereas the occlusion of gas by charcoal is impeded by rise of temperature.

2. That charcoal returns to its original state when gas, which has been occluded, is driven off by heating, but that coal is permanently altered by the absorption of oxygen.

3. That if the absorption were mechanical it would be equal all through a lump which had been exposed to hot air, but such a lump of coal shows an alteration which is entirely superficial in character.

4. The analogy which exists between coals naturally rich in oxygen and coals which have absorbed it.

Cox[4] found that at first more oxygen was absorbed by coal than would account for the carbon dioxide evolved, but that after some months' exposure the evolution of carbon dioxide was in excess of the quantity of oxygen absorbed. In such cases part of the oxygen no doubt is occluded or condensed on the surface of the coal at the start, and while in this condition, it is better able to attack the coal-substance.

Stansfield[5] in a short discussion of the subject, remarks to the following effect upon the heat evolved by occlusion or condensation of gases, and the part that this might play in the heating of coal.

[1] Metallurgy-Fuel 1875, pp. 289-298.
[2] T. I. Naval Architects. Vol. 31, 1890, pp. 204-228.
[3] Études sur l'altération de la houille exposeé à l'air. M. Fayol, 1879.
[4] Internat. Cong., Appl. Chem. Vol. X, 1912, pp. 109-28.
[5] The Coals of Canada. Vol. VI, 1912, p. 95-120.

There can be no doubt that coal absorbs oxygen. This absorption may be mechanical, or chemical, or both. The heat evolved would be very different if the absorption were chemical from what it would be if it were mechanical, but if mechanical absorption merely preceded chemical combination the total heat evolved would be the same as if there were only chemical combination. The above statements are true whether the oxygen combines with carbon, sulphur, or any other constituent of the coal.

When a gas is absorbed by charcoal, it is rendered very chemically active, though not sufficiently so to combine, to any appreciable extent, with the pure carbon of the charcoal. If oxygen were absorbed by coal in a similar manner there would be every reason to believe that it was thereby rendered very chemically active. The experiments of Richters show that some of the carbonaceous matter of coal is more easily oxidized than the rest. It is quite conceivable that the absorbed oxygen would combine with the relatively easily oxidized compounds of carbon, oxygen, and hydrogen present in the coal. These reactions would give out heat and thereby increase the chemical activity of the oxygen and might be conceived as heating the mass sufficiently to allow the oxygen to combine with the more difficultly oxidizable carbon. This chemical action, in which only oxygen which has already been mechanically absorbed is involved, would not prevent the mechanical absorption from being proportional to the partial pressure of the oxygen.

There is one other theory as regards the absorption of oxygen: namely, that suggested by **Haldane** and **Meachem** to the effect that the oxygen absorbed is all used up in oxidizing the pyrite present in the coal. This theory, however, is contrary to the fact that the absorption of oxygen by coal is not proportional to the amount of pyrite present, but as has already been stated in another chapter it is probable that pyritic oxidation does play some part in nearly all cases of coal weathering.

In 1870, **Richters**[1] showed by rough calculations based on experiments, that coal frequently absorbed so much oxygen that if it all combined with the carbonaceous matter of the coal, and the resultant heat were not dissipated, the temperature of the coal might be raised above the ignition point. He first made experiments to find the amount of oxygen absorbed by 20 grammes of different coals in twelve days. The coals used were dried in the air, but were not heated to drive off hydroscopic water. The results are as follows:—

Sample	1	2	3	4	5
Moisture	5·15%	5·20%	5·25%	2·54%	3·10%
Oxygen absorbed	45·8c.c.	50·1c.c.	50·0c.c.	18·2c.c.	39·9c.c.

The calculation proceeds as follows:—

"Since 20 grammes of air free coal occupy a volume of about 15 cc. it follows that samples 1, 2 and 3 absorbed, in twelve days, more than three times their own volume of oxygen.

[1] This extended quotation from Richters is offered because neither the original papers in Dinglers Polytechniches'Journal nor the translations in the Report of the N. S. W. Royal Commissions are to be found in any but the largest libraries. His work is exceedingly valuable and interesting and is more thorough and trustworthy than that of any other of the early students of the subject with the one exception of Fayol.

Sample 5 absorbed two and half times its volume and sample 4 over one and a quarter times its volume."

"According to Sassure one volume of boxwood charcoal absorbs 9·25 volumes of oxygen. Since the weight of a cubic centimetre of the charcoal examined by Sassure was 0·6 grammes we see that 20 grammes would absorb 308 cc. of oxygen or about six times more than was absorbed by coal (samples 2 and 3) in twelve days. Now it is known that this absorption of oxygen is sufficient to raise the temperature of the charcoal to its firing point, which, according to Viollette, lies between 400° and 600° C, say 500° C as a mean.

Let us assume that the quantity of oxygen absorbed is diminished in the ratio of one to one-sixth, the heat which is liberated will also be diminished in the same ratio. Assuming that the same amount of heat is liberated by coal as by charcoal when the quantity of oxygen absorbed is the same in both cases, and also that the mean firing temperature of charcoal is 500° C it appears that coal, (samples 2 and 3) would, during twelve days, rise in temperature to an extent represented by $\frac{500}{6}$, that is through 83°. This, of course, is on the assumption that the specific heat of the coal is the same as that of the charcoal, which is only approximately the case, and that no heat is lost in any way". In practice some of the heat generated is lost by radiation, but Richters believes that this is more than compensated for by the increased absorption which goes on as the temperature rises. He says, "In a former communicat on I have shown that three different kinds of coal which were exposed to a temperature of about 70°—80°C. lost 3·6 per cent of their heating power."

"Let us calculate theoretically the quantity of heat liberated by the coal during fourteen days oxidation while it was losing the 3·6 per cent of its heating power."

1·76% carbon oxidized to carbon dioxide yield.................. 140 calories.
0·16% hydrogen oxidised to water yield........................ 55 calories.
2·12% oxygen absorbed forming water remaining in the coal...... 91 calories.
_____
Total... 286 calories.

"This table shows that for 1 lb. of coal 286 units of heat are liberated. If this heat were solely employed in raising the temperature of the coal, that temperature would amount to 1,100°C, or, more correctly, the coal would quickly be raised above its firing temperature, and would then burst into flame. It appears, therefore, that the heat, which is liberated is quite sufficient to raise coal to its firing temperature".

"Whether this temperature will be reached or not in any specific case depends (1) upon whether the coal can obtain a sufficiency of oxygen and (2) whether the heat developed at such temperature can or cannot pass off as quickly as it is generated."

Richters' calculation is based on a number of assumptions. Most of them are no doubt substantially true, but a considerable part of the heat generated always necessarily passes off by radiation and convection and as a matter of fact few if any coals catch fire spontaneously unless exposed to the air for much longer periods,[1] except when they have been previously heated.

Richters' observations have been confirmed by Parr and Francis[2], who were able to experimentally note in coal indications of a type of combustion or heat generation accompanied by evolution of gases at a temperature far below the ignition point.

Taffanel says that oxidation has two main forms, absorption of oxygen by the coal, and removal of carbon as carbon dioxide; there is probably a third form in the removal of hydrogen as water, but this has not been deter-

[1] Journ. N. of Eng. Inst. Min. & Mech. Eng. Vol. 35, 1876, p. 107.
[2] Bul. Univ. Ill. Eng. Expt. Sta. No. 24, 1908.

mined with any degree of accuracy, although determinations of hydrogen have shown sensible variations in the proportions of this substance.

The rate of fixation of oxygen varies with the nature of the coal, and it appears, in general, greater for coals rich in volatile matter than for those poor in it. The rate varies with time, being comparatively rapid at the beginning of exposure, but slow towards the end.

Richters himself at a later date and several other experimenters have confirmed and extended the above observations, and certain of their observations may be noted here.

Richters[1] experimented with two forms of apparatus. One consisted of a glass tube open at one end and capable of being closed at the other by means of a tap. The other was an apparatus devised by Dietrich for gas analysis, and more particularly for the determination of carbon dioxide, modified in that the lead condensing worm was replaced by a glass tube. A weighed quantity of coal was introduced into the glass tube of the first apparatus and packed tight with a small asbestos stopper. The open end of the tube was dipped below mercury and the tap at the upper end allowed equilibrium to be established between the external and internal pressure. After standing for one hour during which the temperature of the room had been kept constant, the tap was closed and the volume, temperature and height of the barometer were noted. When using the Dietrich apparatus the flask intended for an evolution of gas was employed as a receptacle for the coal.

The first experiment was made with the Dietrich apparatus. Fifty grammes of powdered coal, from the Jacob level of the Theresien shaft were used, which had been lying in a loosely stopped bottle exposed to the air in the laboratory for two months. Readings were taken every twelve hours and reduced to normal temperatures and pressure. In 168 hours, 16 cubic centimetres of air were absorbed. To determine whether the absorbed gas was oxygen or not, the oxygen left after the experiment was absorbed by an alkaline solution of pyrogallol. Taking air as containing $20 \cdot 8\%$ of oxygen by volume, there were originally present $40 \cdot 5$ cubic centimetres of oxygen. Thus if all the gas absorbed by the coal was oxygen, there should have been $24 \cdot 5$ cubic centimetres of oxygen left, but only $23 \cdot 1$ cubic centimetres were absorbed by the pyrogallol solution. Richters did not claim any great degree of accuracy for this experiment; but it clearly showed that oxygen is absorbed by coal.

The second experiment was made in the calibrated glass tube with 20 grammes of coal. After nine days $6 \cdot 6$ cubic centimetres of oxygen, i. e., 95% of that originally present, had been absorbed and after this there was no more absorption. Powdered coal was used from the Robert level of the Theresien shaft. The sample was dried in a desiccator until its weight became constant and then immediately removed to the slightly warm tube through which a gentle stream of dried air was passed until the tube became cold.

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[1] Report of N. S. W. Commission on Ships carrying Coal. 1898.

A third experiment was made with the same apparatus and 20 grammes of coal powder from the Carl level of the Theresien shaft. The air was saturated with moisture during the whole experiment. In 10 days 7·2 cubic centimetres of oxygen were absorbed. The air originally contained 11 cubic centimetres so that the absorption must have ceased after it had reached about 65·4% of the oxygen originally present.

In order to show that the oxygen was not absorbed by the pyrite in the coal, Dr. Richters calculated the possible maximum amounts of pyrite in the three seams by assuming the ash to be wholly ferrous sulphide. This gave Carl seam 0·31%, Robert seam 0·42%, and Jacob seam 0·36%, all the coals being very low in pyrite. Quartz sand was then mixed with pyrite so that the mixture had the same pyrite contents as the coals and the experiments were repeated on this mixture instead of the coals. In the first case when dry air was used no oxygen was absorbed, and in the second, using moist air, only a very small quantity even when the mixture was left in contact with air for a very long time.

Haldane and Meachem, who seem to lean to the opinion that the absorption is largely mechanical at first, studied the action of air on coal, by a series of laboratory experiments. In the first instance coal was crushed in a mortar and placed in a thick walled flask closed by a rubber cork soaked in paraffin through which there was a bent glass tube to form a manometer. The limbs of this tube were half filled with mercury. The flask was immersed in a water bath so that its temperature was known, and the manometer, barometer and thermometer recorded for a long period of time. It will be sufficient to quote one of the experiments made with this apparatus. (Tables X and XI.)

The coal used was from "Bough's bolt hole", Hamstead colliery, sent up three months previously and allowed to lie in lumps in the laboratory since that time. The coal was crushed in a mortar and left spread out in a thin layer for two hours before it was placed in the flask and sealed. The pressures given are corrected for atmospheric temperature and pressure.

TABLE X.

Absorption of Oxygen by Coal in a Closed Vessel.

(Haldane and Meachem)

Time since closing flask	Negative pressure of mercury	Time since closing flask	Negative pressure of mercury
Hours	Inches	Days	Inches
1	0·15	4	5·05
5	0·65	5	5·45
12	1·25	6	5·75
24	2·00	7	6·00
36	2·80	9	6·10
48	3·40	11	6·10
56	3·85	24	6·00
72	4·30	6 months	5·85

A sample of gas was then withdrawn and analysed. The results of this analysis were:—

<div align="center">TABLE XI.</div>

<div align="center">**Composition of Residual Gases in Vessel.**</div>

<div align="center">(*Haldane and Meachem*)</div>

Oxygen	0·066%
Carbon dioxide	1·286%
Firedamp	0·651%
Carbon monoxide	0·042%
Nitrogen	97·957%
Total	100·002%

Assuming that only oxygen is absorbed by the coal and that no nitrogen is evolved this analysis would indicate a diminution of pressure of 19·3 per cent. When the flask was closed the barometer was at 29·75 inches and the diminution in pressure was 5·85 inches, or 19·6 per cent of 25·95 inches. An even closer check was obtained in another experiment made with similar coal under similar conditions.

Some experiments were then made to obtain quantitative data on the rate of oxidation of coal and the effect of variation of temperature on the rate of oxidation. The apparatus used consisted of a vessel with two tightly fitted perforated corks, one at each end. Through the lower cork a current of pure air was introduced. The bottom of the vessel was covered with pumice stone and the coal was placed in a thick layer on top of this with a view to securing an even stream of air through the coal.

The air, on leaving the vessel, passed through a smaller vessel which could be disconnected at any time and its contents analysed. The air then passed through a small meter and thence to an aspirator. The vessels were both fully immersed in the water bath and the temperature was kept constant for at least one hour before any sample of air was taken for analysis. The results of two experiments are shown in Tables XII and XIII.

TABLE XII.

ABSORPTION OF OXYGEN.

Experiment I with 0·92 pounds of finely crushed coal sent from the pit 4 days previously and crushed just before the experiment.

(*Haldane and Meachem*)

Temper-ature of bath	Time since coal was crushed	Rate of ventilation per hour	Deficiency of oxygen	Carbonic acid increased	Fire damp and carbonic oxide	Oxygen absorbed per ton of coal and per hour
Degs. C.	Hours	Cubic feet	Per cent	Per cent	Per cent	Cubic feet
15	2	0·091	1·10	0·07	0·290	2·45
15	5	0·131	0·72	0·02	—	2·30
15	8	0·080	1·00	0·05	—	1·95
16	20	0·114	0·46	0·04	—	1·26*
38	25	0·114	1·29	0·05	0·075	3·58
42	29	0·114	1·48	0·12	0·100	4·11
52	32	0·103	2·18	0·10	0·110	5·59

*Ventilation left on for 12 hours since last determination.

TABLE XIII.

ABSORPTION OF OXYGEN.

Experiment II with 2·7 pounds of crushed coal (same sample as used in last experiment) sent from pit 3 months previously and fragments crushed a few hours before the experiment.

(*Haldane and Meachem*)

Temper-ture of bath	Rate of ventilation per hour	Deficiency of oxygen	Carbonic acid increased	Fire damp	Carbonic oxide	Oxygen absorbed per ton of coal and per hour
Degs. C	Cubic feet	Per cent	Per cent	Per cent	Per cent	Cubic feet
15	0·078	0·40	0·09	0·00	0·00	0·26
71	0·084	5·31	0·67	0·07	0·14	3·70

These experiments show clearly that the coal continuously absorbs oxygen from the air, but that this absorption is at a decreasing rate as time passes, so long as the temperature is constant. The rate increases, however, very considerably as the temperature rises.

It should also be noted in passing that the evolution of carbonic acid while continuous is somewhat erratic, and is in all cases very small as compared with the amount of oxygen absorbed.

Table XIV shows the result of an experiment by Haldane and Meachem to determine the effect of sealing off a sample of coal with a limited quantity of air. The rate of absorption of oxygen was comparatively rapid at the start, but decreased steadily and with considerable uniformity. This decrease is ascribed by them to the decrease in the pressure of the remaining oxygen in the flask, and no doubt it is partly due to this, but the first four lines of Table XII show that a similar decrease in rate occurs with time, even when the oxygen supply is constant. The calculations which Haldane and Meachem make as to the probable rate of absorption under various conditions would, therefore, seem to lose a part of their value.

TABLE XIV.

Absorption of Oxygen at Reduced Pressures.

(Haldane and Meachem)

Period	Mean partial pressure of oxygen in percentage of 1· Atmospheres. Pressure.	Oxygen absorbed	
		Observed	Calculated
		Per cent	Per cent
First 24 hours..................	17·6	6·7	6·7
Second 24 hours...............	11·9	4·7	4·5
Third 24 hours................	7·9	3·1	3·1
Fourth 24 hours...............	5·2	2·5	2·1
Fifth 24 hours................	3·2	1·3	1·3
Sixth 24 hours................	2·1	1·0	0·8

Porter and Ovitz[1] believe that the absorption of oxygen by coal is chemical rather than mechanical. This opinion is largely based on an experiment with Benton, Illinois coal (No. 49):—

"After being supplied with oxygen for five months, during which time it combined with oxygen equal in volume to nearly seven times its own volume, a sample of the coal was placed in a flask in boiling water. The gases evolved during 15 minutes boiling, showed no excess of oxygen over that contained in the air".

The experiment outlined above shows that the oxygen absorbed was not merely occluded at the end of its five months' contact with the coal, but it does not prove that occlusion was not the first step in the process. It should also be noted as Stansfield[2] has already pointed out,

"that when the coal is heated to drive out any oxygen occluded, the experiment becomes unreliable, as, at the higher temperatures the occluded oxygen would react so readily with the coal that there would be little chance of its being evolved".

The series of experiments is, however, so interesting that a summary description of them is appended.

[1] Technical paper II. U. S. Bureau of Mines, 1911. "The escape of gas from coal."
[2] The Coals of Canada. Vol. VI, 1912, p. 109.

The method of procedure adopted was as follows:—

"A sample of about 10 kilogrammes of coal was taken from a clean fresh face of the seam in the manner prescribed, by the U. S. Bureau of Mines[1]; for mine sampling. This sample was crushed so as to pass a ½-inch screen, and placed in a 5-gallon crated glass bottle, which was then stoppered as quickly as possible—usually within 50 to 80 minutes after beginning the cut. A tight fitting rubber stopper was wired in. Through the stopper passed a 20 cm.length of glass tubing of 2 mm. bore, its outer end being sealed by a piece of heavy rubber tubing and a solid glass plug. The crushed coal consisted largely of small lumps between one-tenth and one-half inch in size, but contained 10 to 20 per cent of material under one-tenth inch in size. The bottle was shipped forthwith to the laboratory at Pittsburg. As soon as it arrived there the rubber stopper connections were painted with shellac to avoid all risk of leakage, and a gas sample was at once withdrawn for analysis. The bottles were then allowed to stand in the laboratory for several months at a temperature varying from 12° to 32°.

Four coals, No. 37 (Pocahontas, Va.) No. 39 (Harrisburg, Ill.), No. 43 (Sheridan, Wyo.) and No. 49 (Benton, Ill.), were subjected to further investigation as follows. "The bottle of Pocahontas coal was connected through the glass tube in the stopper to a reservoir of oxygen, so that oxygen flowed into the bottle as fast as it was absorbed by the coal. From time to time the gas that accumulated in the bottle was drawn out in order to relieve the pressure and permit the inflow of oxygen. The bottles containing coals No. 39 and 43 were connected to a supply of air instead of oxygen and the inlet tube extended to the centre of the coal in each bottle. There also was attached to each of these two bottles a collecting reservoir for the escaping gas, the connecting tube for this purpose passing from the top of the bottle to the reservoir. The bottle of Benton, Ill. coal (No. 49) was connected with both an oxygen supply and a gas collecting reservoir, but oxygen not air was admitted to the bottle and was admitted at the top, the gas being withdrawn from underneath the coal".

A number of other coals were tested in a somewhat similar manner, occasional samples of gas being taken from the bottles, but without drawing off the accumulated gas into collecting reservoirs or admitting a supply of oxygen.

The results of these tests are shown in Tables XV, XVI and XVII.

TABLE XV.

Descriptive list of coals tested.

(Porter and Ovilz)

Coal No.	Kind of coal	State	County	Place	Name of coal bed	Mine
29	Bituminous....	Wyo.	Sweetwater..	Rock Springs	Rock Springs	No. 1.
30	"	Do.	Carbon......	Hanna.......	Lower.......	No. 2.
33	" cannel	Ky. ...	Johnson.....	Paintsville...	....	Flambeau.
35	"	W. Va.	Marion......	Monongah ..	Pittsburg....	No. 6.
37	Semi-bitumin-ous.........	Va....	Tazewell.....	Pocahontas..	No. 3	Baby.
39	Bituminous....	Ill....	Saline.......	Harrisburg...	No. 5........	No. 9.
41	Bituminous....	Pa.....	Fayette......	Connellsville.	Pittsburg....	Leisenring No. 1
43	Semi-bitumin-ous.........	Wyo.	Sheridan.....	Sheridan.....	No. 9........	Dietz No. 2
49	Bituminous.....	Ill.....	Franklin.....	Benton......	No. 7........	Hart-Williams.

[1] Technical Paper I. U. S. Bureau of Mines, 1911. "The Sampling of Coal in the Mine."

TABLE XVI.

Absorption of Oxygen by Coal.

(Porter and Ovitz)

Coal	Weight of coal	Period of time	Oxygen removed	Oxygen admitted	Vol. of Oxygen absorbed ÷ Vol. of coal (a) (c)
Pocahontas, Va.... (No. 37)	Kilos 13·4	First 31 days.........	c.c. 37·	c.c. 1,830	0·174
		Next 28 days.........	7	4,010	0·390
		Next 31 days.........	9	7,275	0·705
		Next 183 days........	44	24,510	2·375
		Next 31 days.........	5	4,860	0·471
		10 months	102	42,485	4·115
Harrisburg, Ill..... (No. 39).	14·6	First 4 days..........	24	1,660	0·145
		Next 24 days.........	0	0	0·000
		Next 31 days.........	456	7,320	0·610
		Next 30 days.........	102	2,744	0·235
		Next 153 days........	363	17,460	0·520
		Next 31 days.........	181	4,040	0·343
		9 months	1,126	33,224	2·853
Sheridan, Wyo.... (No. 43).	8·1	First 7 days..........	0	2,520	0·403
		Next 23 days.........	52	1,550	0·240
		Next 31 days.........	61	3,110	0·488
		Next 30 days.........	54	2,940	0·462
		Next 92 days.........	282	13,760	2·157
		Next 31 days.........	166	3,990	0·612
		7 months	615	27,870	4·362
Benton, Ill........ (No. 49)	12·2	First 15 days.........	0	2,040	0·220
		Next 15 days.........	34	4,610	0·494
		Next 62 days.........	844	33,700	3·532
		Next 30 days.........	603	10,970	1·113
		Next 31 days.........	872	15,520	1·576
		Next 365 days........	....	....	....
		17 months	2,353	66,840	6·935 (b)

(a) Relative volumes of gas are computed on the basis of the apparent specific gravity of the coal (taken as 1·3), this value being the average of a large number of determinations of small lump size (1–inch) coals. The volume occupied by 10 kilogrammes of coal is therefore taken as 10/1·3 = 7·7 litres. The volume of the pores in small lump coal, assuming an average absolute specific gravity of 1·45 may be computed as one-tenth of the volume of the lumps, that is (1·45 − 1·30) ÷ 1·45 = 0·103.

(b) Total for five months only.

(c) Oxygen from air in case of Nos. 39 and 43. Oxygen 95% pure, in case of Nos. 37 and 49. The great irregularities in the rate of absorption of oxygen are due to the irregular admission of oxygen.

TABLE XVII.

Absorption of Oxygen by the above coals in closed vessels.

(Porter and Ovitz)

Coal No.	Period of time	Oxygen absorbed	Vol. of oxygen absorbed ÷ Volume of coal
		c.c.	
29.........	First 22 days...............	2,500	0·313
	Next 9 days................	0	......
30.........	First 10 days...............	2,500	0·313
	Next 21 days...............	0	......
33.........	First 24 days...............	2,500	0·313
	Next 249 days..............	......	......
35.........	First 4 days................	2,300	0·288
	Next 26 days...............	......	......
41.........	First day..................	1,080	0·135
	Next 10 days...............	1,220	0·153
	Next 415 days..............	......	......

The figures in Table XVI do not permit of any trustworthy estimate of the rate at which coal absorbs oxygen, due to the fact that it was found, late in the course of the experiment, that the degree of concentration of the oxygen had a great influence on the rate of absorption. Ordinary air had been used in some of the tests and 95% pure oxygen in others. In all cases, however, a rapid and long-continued absorption is shown, and there was little or no evolution of carbon dioxide.

The volume of air enclosed with the coal in the 5 gallon bottles used to contain the samples was a little over 11 litres. Thus there were originally present about 2,500 cubic centimetres of oxygen in each with about three times this volume of coal. Samples of the air from some of these bottles were withdrawn from time to time and analysed and the results, which are given in Table XVII, show that virtually all of the oxygen was absorbed quite soon, for example, coal No. 41 absorbed slightly more than half of the amount in one day; at the same time it evolved little more than one-tenth as much carbon dioxide as would have been formed if all the oxygen absorbed had combined with carbon to form carbon dioxide.

Parr and Barker[1] experimenting with Illinois coals obtained results showing a large absorption of oxygen. Their tests may be summarized as follows: coal drillings were sealed for twelve months in jars with volumes of air equal to from six to ten times the volume of the coal. After one year the air was withdrawn and analysed. The coals used were:—

1. Springfield, Sangamon Mine, Sangamon Coal Co.
2. Springfield, Sangamon Mine, Sangamon Coal Co.
3. Eldorado, Mine No. 8, O'Gara Coal Co.
4. Marion, Chicago and Big Muddy Coal Co.

[1] Univ. of Illinois Eng. Expt. Station Bulletin No. 32, 1909.

5. Herrin, Squirrel Ridge Mine, Chicago and Cartierville Coal Co.
6. Du Quoin, Greenwood, Davis Coal Co.
7. Belleville, Suburban Coal Mining Co.
8. O'Fallon, Mine No. 2, Louis and O'Fallon Coal Co.

TABLE XVIII.

Absorption of Oxygen by Illinois Coals.

(Parr and Barker)

Sample	I	II	III	IV	V	VI	VII	VIII
Wt. of coal (grms.)............	109	139	180	183	146	134	138	153
Total volume of gas enclosed in c.c....................	873	849	816	814	843	853	850	837
Oxygen %.................	0·16	0·13	0·00	0·00	0·25	0·00	0·00	1·45
Nitrogen %...............	99·36	98·93	93·04	98·13	97·33	98·77	98·99	96·93

Parr and Wheeler[1] have done very valuable work on the losses in calorific value of Illinois coals due to oxidation, which they conclude to range from 1·3% to 3·4% over a period of ten months. In view of the importance of their work no apology is necessary for the following some-what extended abstract of their published report now out of print.

The coals used for the principal series of tests were from Sangamon, Williamson and Vermilion counties. Car load lots both of nut coal and screenings were procured and one-half of each was piled out of doors to a depth of 3½ feet in rough bins with earth floors. The other half-carloads were put in covered wooden bins with board floors raised about eighteen inches above the ground. The coal in these bins was partly exposed on two sides. Other portions of these coals were placed in large earthenware jars holding one hundred pounds each, and after being covered with water were stored in a cellar having a temperature of about 70 degrees Fahrenheit.

In addition to the above coals, samples were obtained from piles 3-7 feet deep containing not over 500 tons of screenings from Christian and Fulton counties; these piles had been entirely exposed for six months: and from large piles of Williamson and Franklin county coals belonging to the Common-wealth Edison Co., one containing 25,000 tons of egg coal between 3 and 6 in. diameter, another 3,500 tons of nut, and a third 4,500 tons of washed No. 1. Samples were also obtained from a fifteen ton lot of Vermilion county coal which had been piled on the ground for two and a half years and analysed from time to time, and finally some mine pillars over 25 years old, and a natural outcrop[2] in Peoria county, were accurately sampled.

Since it is impossible to sample any lot of coal exactly as regards ash and sulphur, all B.Th.U. determinations were referred to the actual coal

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[1] Univ. of Ill. Eng. Exp. Sta. Bull. 38, 1909.
[2] See page 169, this volume.

basis for the sake of comparison.   In order to do this the following formula was used.

$$\frac{\text{B.Th.U. as determined} - 5000 \times \text{Weight of Sulphur.}}{1 \cdot 00 - (\text{Moisture} + 1 \cdot 08 \times \text{ash} + (22 \cdot \div 40) \times \text{Sulphur})}$$

"In explanation of the terms of this formula it may be stated that "5000 × Weight of Sulphur" in pounds per pound of coal represents the heating value of the sulphur in B. Th. U.   This is deducted from the heating

VERMILION COUNTY, ILLINOIS

Nut Coal·
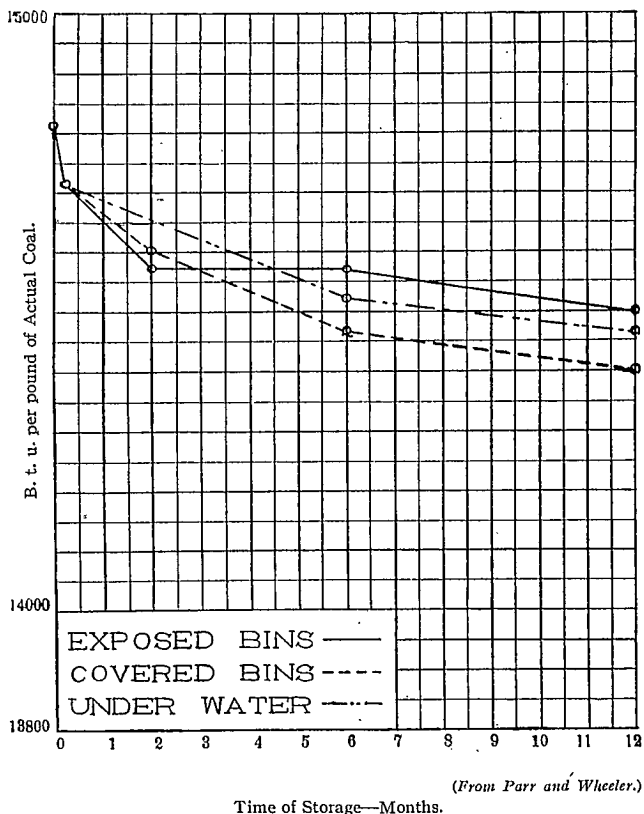

(*From Parr and Wheeler.*)

Fig. 14.   Calorific power stored coal.

value of the coal given by the calorimeter in order to overcome any variation in the amount of sulphur present in the several samples.   The term "1·08 × ash" represents the mineral matter of the coal that remains after burning completely and also an additional eight per cent for the water and carbon dioxide that were not part of the coal, but which combined with the mineral matter of the ash and thus took the place of an equal

TABLE XIX.

Calorific Losses in Storage, Vermilion County, Illinois, Nut Coal.

(Parr and Wheeler)

Sample taken	Dry coal			B.Th.U. referred to actual or unit coal	Decrease	
	Ash	Sulphur	B.Th.U.		B.Th.U.	Per cent

STORED IN EXPOSED BINS.

Sample taken	Ash	Sulphur	B.Th.U.	B.Th.U.	B.Th.U.	Per cent
Same day as mined	10·55	4·25	12,991	14,814	—	—
7 days after mining	13·98	2·65	12,412	14,716	98	0·66
2 months after mining	14·21	2·47	12,265	14,577	237	1·60
6 months after mining	13·53	2·10	12,396	14,575	239	1·61
12 months after mining	13·62	2·82	12,282	14,498	316	2·13

STORED IN COVERED BINS.

Sample taken	Ash	Sulphur	B.Th.U.	B.Th.U.	B.Th.U.	Per cent
Same day as mined	10·55	4·25	12,991	14,814	—	—
7 days after mining	13·98	2·65	12,412	14,716	98	0·66
2 months after mining	13·08	2·13	12,475	14,604	210	1·42
6 months after mining	11·76	2·14	12,571	14,472	342	2·31
12 months after mining	13·52	2·72	12,220	14,403	411	2·77

STORED UNDER WATER.

Sample taken	Ash	Sulphur	B.Th.U.	B.Th.U.	B.Th.U.	Per cent
Same day as mined	10·55	4·25	12,891	14,814	—	—
Same day as submerged	13·98	2·65	12,412	14,716	98	0·66
6 months after mining	15·37	3·34	12,013	14,526	290	1·96
12 months after mining	13·85	3·81	12,231	14,517	297	2·00

weight of actual coal. The last term "$(22 \div 40) \times$ Sulphur" represents the sulphur corrected for the oxygen that replaces it in the ash. When the coal is burned, any sulphur that was combined with iron as pyrite is replaced by oxygen leaving $Fe_2 O_3$ in the ash. This exchange results in a loss of weight of only five-eighths of the amount of sulphur burned; since, however, part of the sulphur is not in the form of pyrite, but in a non-combustible form which may remain in the ash, the fraction $22 \div 40$ is used instead of $\frac{5}{8}$. The denominator, therefore, in the above formula, is the weight of actual coal in a unit weight of coal as analysed."

WILLIAMSON COUNTY, ILLINOIS

NUT COAL
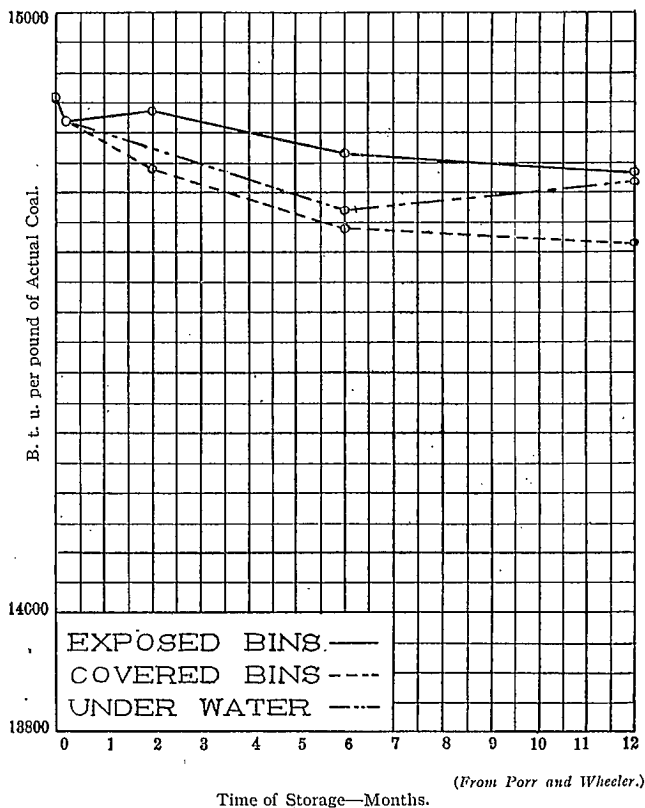

(*From Porr and Wheeler.*)

Time of Storage—Months.

FIG. 15. Calorific power stored coal.

Tables XIX to XXVIII show the results obtained from these tests. The calorific values from the tables have been plotted (Figs 14 to 21) and the curves show very clearly the loss of calorific value due to weathering. In nearly all cases the screenings show a greater loss of calorific value than the nut coal. None of the coals used for these experiments, however, show a loss of calorific value which would warrant the storage of the coal under water; nevertheless the tests show very clearly that this method of storage decreases the weathering losses.

TABLE XX.

Calorific losses in Storage, Williamson County Nut Coal.

(Parr and Wheeler)

Sample taken.	Dry coal.			B.Th.U. referred to actual or unit coal.	Decrease.	
	Ash.	Sulphur.	B.Th.U.		B.Th.U.	Per cent.

STORED IN EXPOSED BINS.

Same day as mined............	13·98	3·73	12,499	14,859	—	—
7 days after mining............	14·90	3·02	12,341	14,821	38	0·26
2 months after mining.........	14·32	4·12	12,409	14,835	24	0·16
6 months after mining.........	13·81	3·43	12,455	14,765	95	0·64
12 months after mining.........	11·88	2·73	12,759	14,734	125	0·84

STORED IN COVERED BINS.

Same day as mined.............	13·98	3·73	12,499	14,859	—	—
7 days after mining............	14·90	3·02	12,341	14,821	38	0·26
2 months after mining.........	14·08	3·84	12,378	14,739	120	0·81
6 months after mining.........	13·06	3·60	12,469	14,644	215	1·45
12 months after mining.........	13·24	3·20	12,428	14,616	243	1·64

STORED UNDER WATER.

Same day as mined............	13·98	3·73	12,499	14,859	—	—
Same day as submerged........	14·90	3·02	12,341	14,821	38	0·26
6 months after mining..........	15·65	3·12	12,097	14,673	186	1·25
12 months after mining.........	14·87	3·42	12,251	14,721	138	0·93

SANGAMON COUNTY, ILLINOIS
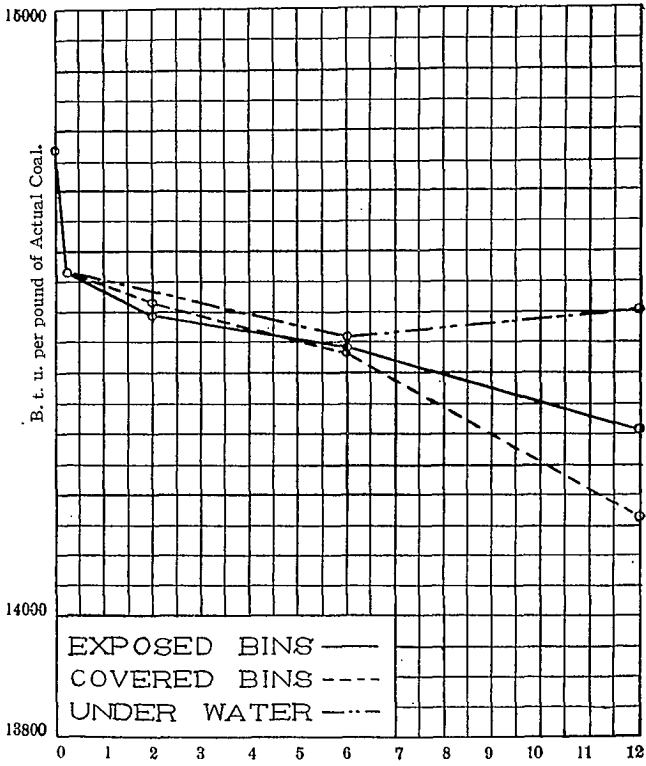
, Nut Coal

(From Parr and Wheeler.)

Time of Storage—Months.

Fig. 16.   Calorific power stored coal.

TABLE XXI.

Calorific losses in Storage, Sangamon County, Illinois, Nut Coal.

(Parr and Wheeler)

Sample taken.	Dry coal.			B.Th.U. referred to actual or unit coal.	Decrease.	
	Ash.	Sulphur.	B.Th.U.		B.Th.U.	Per cent.
STORED IN EXPOSED BINS.						
Same day as mined............	17·87	5·75	11,741	14,773	—	—
7 days after mining............	16·63	5·10	11,800	14,571	202	1·37
2 months after mining..........	17·45	4·66	11,626	14,497	276	1·87
6 months after mining..........	16·03	4·91	11,798	14,444	329	2·23
12 months after mining.........	14·97	4·68	11,860	14,307	466	3·15
STORED IN COVERED BINS.						
Same day as mined............	17·87	5·75	11,741	14,773	—	—
7 days after mining............	16·63	5·10	11,800	14,571	202	1·37
2 months after mining (sample a)..	16·08	5·03	11,912	14,600	173	1·17
2 months after mining (sample b) .	ʌ 17·57	5·01	11,626	14,535	238	1·61
6 months after mining..........	16·30	4·52	11,682	14,336	437	2·96
12 months after mining.........	15·99	4·65	11,589	14,165	608	4·12
STORED UNDER WATER.						
Same day as mined............	17·87	5·75	11,741	14,773	—	—
Same day as submerged........	16·63	5·10	11,800	14,571	202	1·37
6 months after mining..........	15·90	4.21	11,854	14,461	322	2·18
12 months after mining.........	15·95	5.11	11,851	14,503	270	1·83

VERMILION COUNTY, ILLINOIS

SCREENINGS

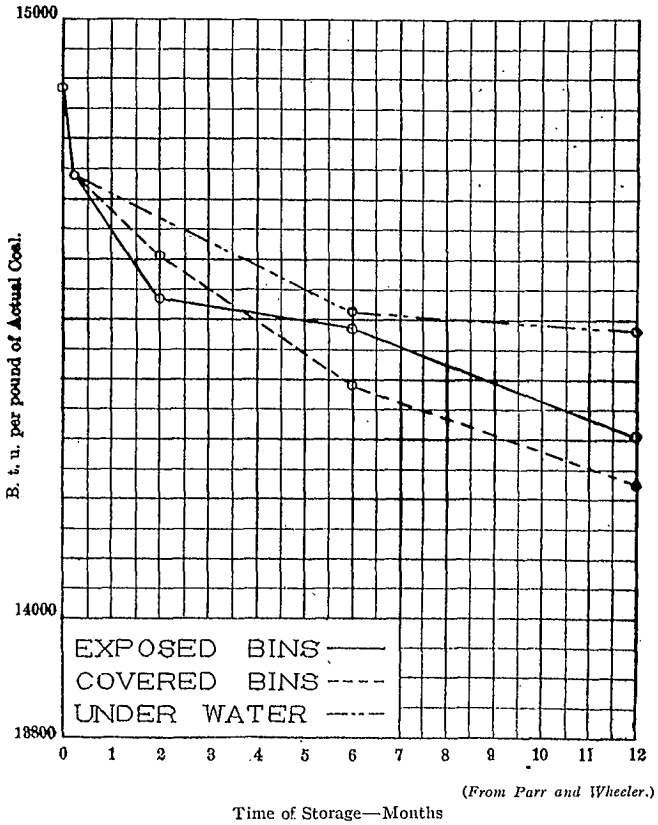*(From Parr and Wheeler.)*

Time of Storage—Months

FIG. 17.   Calorific power stored coal.

TABLE XXII.

Calorific losses in Storage, Vermilion County, Illinois, Screenings.

(Parr and Wheeler)

Sample taken.	Dry coal			B.Th.U. referred to actual or unit coal.	Decrease.	
	Ash.	Sulphur.	B.Th.U.		B.Th.U.	Per cent.

STORED IN EXPOSED BINS.

Same day as mined............	17·88	2·35	11,937	14,888	—	—
7 days after mining (sample a)....	13·98	2·87	12,414	14,726	162	1·09
7 days after mining (sample b)....	13·69	2·29	12,507	14,759	129	0·87
2 months after mining (sample a).	15·73	2·53	11,958	14,497	391	2·63
2 months after mining (sample b)..	14·69	2·90	12,178	14,578	310	2·08
6 months after mining..........	15·63	2·44	11,969	14,487	401	2·69
12 months after mining.........	14·46	2·24	12,006	14,304	584	3·92

STORED IN COVERED BINS.

Same day as mined............	17·88	2·35	11,937	14,888	—	—
7 days after mining (sample a)....	13·98	2·87	12,414	14,726	162	1·09
7 days after mining (sample b)....	13·69	2·29	12,507	14,769	129	0·87
2 months after mining..........	15·26	2.51	12,124	14,608	280	1·88
6 months after mining..........	14·51	2·25	12,071	14,391	497	3·34
12 months after mining.........	15·36	2·42	11,797	14,225	663	4·46

STORED UNDER WATER.

Same day as mined..........	17·88	2·35	11,937	14,888	—	—
Same day as submerged (sample a)	13·98	2·87	12,414	14,726	162	1·09
Same day as submerged (sample b)	13·69	2·29	12,507	14,759	129	1·87
6 months after mining........	13·87	2·32	12,270	14,514	374	2·51
12 months after mining.......	13·55	2·71	12,283	14,488	405	2·72

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WILLIAMSON COUNTY, ILLINOIS

SCREENINGS

(From Parr and Wheeler.)
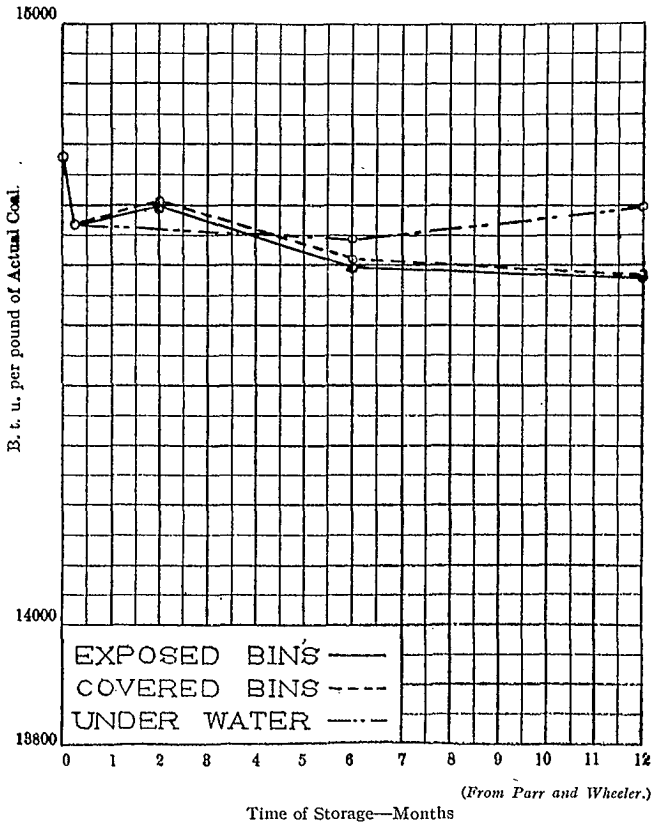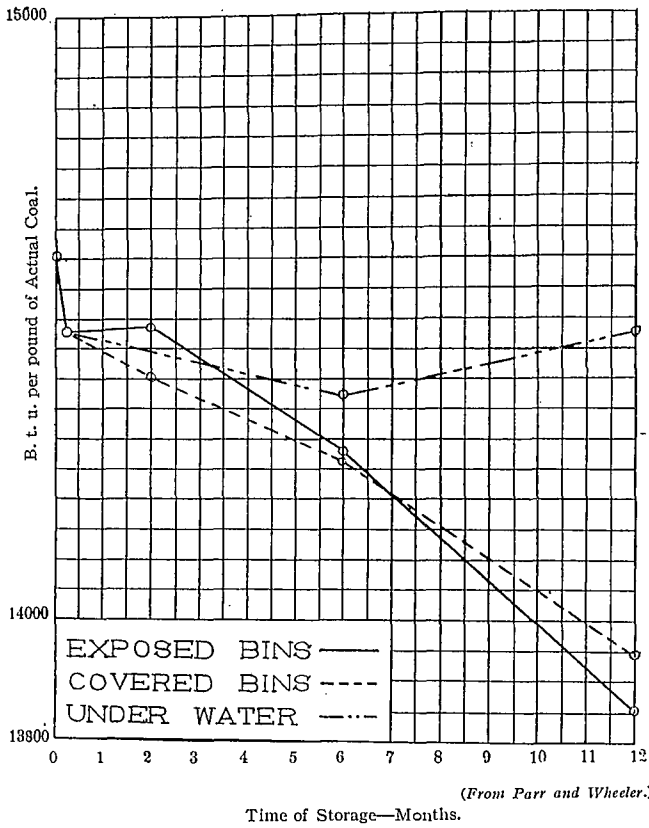
Time of Storage—Months

FIG. 18. Calorific power stored coal.

TABLE XXIII.

Calorific losses in Storage, Williamson County, Illinois, Screenings.

(*Parr and Wheeler*)

Sample taken.	Dry coal.			B.Th.U. referred to actual or unit coal.	Decrease.	
	Ash.	Sulphur.	B.Th.U.		B.Th.U.	Per cent.

STORED IN EXPOSED BINS.

Same day as mined............	14·13	3·17	12,426	14,782	—	—
7 days after mining............	14·37	3·34	12,287	14,666	116	0·78
2 months after mining..........	15·66	2·67	12,133	14,701	81	0·55
6 months after mining..........	13·76	2·84	12,342	14,597	185	1·25
12 months after mining.........	13·77	2·75	12,328	14,579	203	1·37

STORED IN COVERED BINS.

Same day as mined............	14·13	3·17	12,426	14,782	—	—
7 days after mining............	14·37	3·34	12,287	14,666	116	0·78
2 months after mining..........	12·62	2.98	12,608	14,705	77	0·52
6 months after mining..........	13·60	3·03	12,372	14,610	172	1·16
12 months after mining.........	13·43	2·72	12,385	14,582	200	1·35

STORED UNDER WATER.

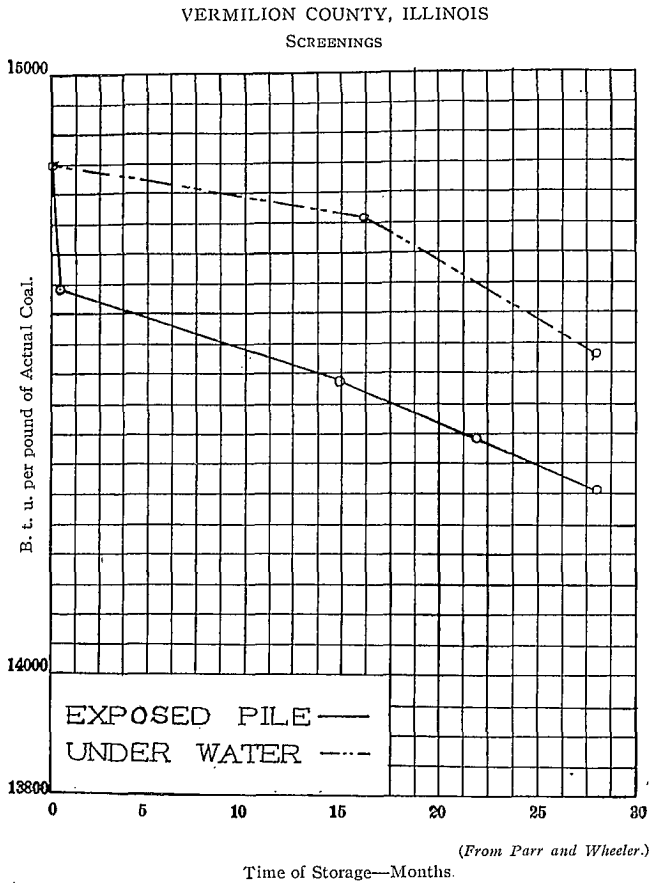|						
Same day as mined............	14·13	3·17	12,426	14,782	—	—
Same day as submerged	14·37	3·34	12,287	14,666	116	0·78
6 months after mining..........	14·38	3·54	12,262	14,645	137	0·93
12 months after mining.........	13·60	2.97	12,447	14,698	84	0·57

FIG. 19.   Calorific power stored coal.

TABLE XXIV.

Calorific losses in Storage, Sangamon County, Illinois, Screenings.

(Parr and Wheeler)

Sample taken.	Dry coal.			B.Th.U. referred to actual or unit coal.	Decrease.	
	Ash.	Sulphur.	B.Th.U.		B.Th.U.	Per cent.

STORED IN EXPOSED BINS.

Sample taken.	Ash.	Sulphur.	B.Th.U.	unit coal.	B.Th.U.	Per cent.
Same day as mined............	17·13	4·92	11,752	14,604	—	—
7 days after mining............	17·04	4·47	11,684	14,481	123	0·84
2 months after mining.........	17·22	5·00	11,645	14,488	116	0·79
6 months after mining..........	17·02	4·54	11,526	14,281	323	2·21
12 months after mining.........	17·25	4·54	11,153	13,853	751	5·14

STORED IN COVERED BINS.

Sample taken.	Ash.	Sulphur.	B.Th.U.	unit coal.	B.Th.U.	Per cent.
Same day as mined............	17·13	4·92	11,752	14,604	—	—
7 days after mining............	17·04	4·47	11,684	14,481	123	0·84
2 months after mining.........	18·33	4·70	11,414	14,404	200	1·37
6 months after mining.........	17·30	4·67	11,466	14,263	341	2·33
12 months after mining........	17·06	4·73	11,248	13,944	660	4·52

STORED UNDER WATER.

Sample taken.	Ash.	Sulphur.	B.Th.U.	unit coal.	B.Th.U.	Per cent.
Same day as mined............	17·13	4·92	11,752	14,604	—	—
Same day as submerged........	17·04	4·47	11,684	14,481	123	0·84
6 months after mining..........	19·86	5·60	11,127	14,372	232	1·59
12 months after mining.........	18·27	4·81	11,479	14,478	126	0·86

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AVERAGE VALUES FROM THE SIX PRECEDING FIGURES.

(*From Parr and Wheeler.*)

Time of Storage—Months.
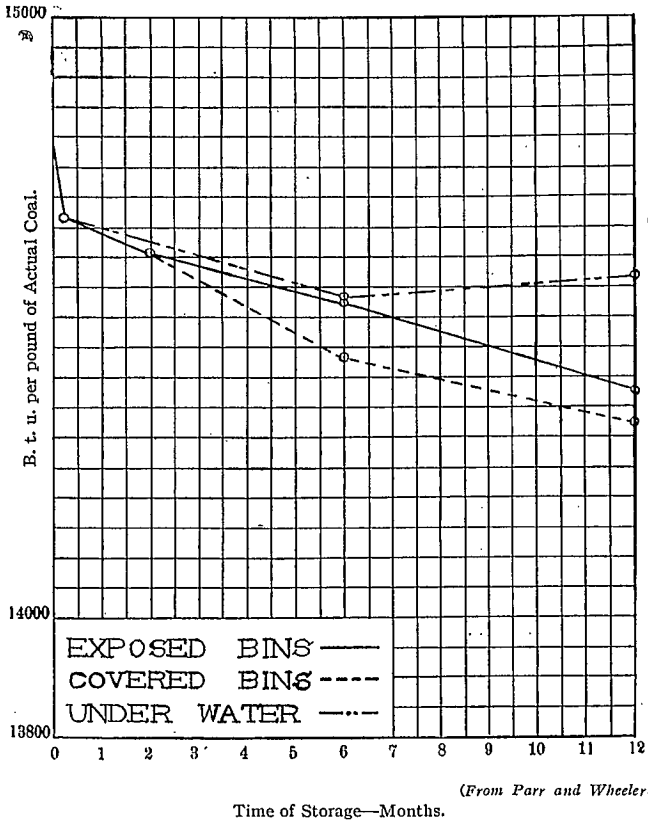
FIG. 20. Calorific power stored coal.

TABLE XXV.

Calorific losses in Storage, average values from six preceding tables.

(Parr and Wheeler)

Sample taken.	Dry coal.			B.Th.U. referred to actual or unit coal.	Decrease.	
	Ash.	Sulphur.	B.Th.U.		B.Th.U.	Per cent.

STORED IN EXPOSED BINS.

Same day as mined............	15·26	4·03	12,224	14,787	—	—
7 days after mining............	15·13	3·53	12,164	14,666	121	0·82
2 months after mining.........	15·68	3·61	12,024	14,606	181	1·22
6 months after mining.........	14·96	3·36	12,081	14,525	262	1·77
12 months after mining........	14·33	3·29	12,065	14,379	408	2·76

STORED IN COVERED BINS.

Same day as mined............	15·26	4·03	12,224	14,787	—	—
7 days after mining............	15·13	3·53	12,164	14,666	121	0·82
2 months after mining.........	15·07	3·53	12,128	14,605	182	1·22
6 months after mining.........	14·42	3·37	12,105	14,453	334	2·26
12 months after mining........	14·77	3·57	11,945	14,323	464	3·14

STORED UNDER WATER.

Same day as mined............	15·26	4·03	12,224	14,787	—	—
Same day as submerged........	15·13	3·53	12,164	14,666	121	0·82
6 months after mining.........	15·84	3·69	11,937	14,532	255	1·73
12 months after mining........	15·02	3·81	12,090	14,567	220	1·44

TABLE XXVI.

Calorific losses in Storage, Christian County, Illinois, Screenings.

(Parr and Wheeler)

Sample taken.	Dry coal.			B.Th.U. referred to actual or unit coal.	Decrease.	
	Ash.	Sulphur.	B.Th.U.		B.Th.U.	Per cent.
When stored. (About 2 weeks after mining)	19·20	5·04	11,325	14,475	—	—
5 months in exposed pile of about 500 tons (Had heated badly)	16·68	4·43	11,425	14,083	392	2·71

TABLE XXVII.

Calorific losses in Storage, Fulton County, Illinois, Screenings.

(Parr and Wheeler)

Sample taken.	Dry coal.			B.Th.U. referred to actual or unit coal.	Decrease.	
	Ash.	Sulphur.	B.Th.U.		B.Th.U.	Per cent.
2 weeks after mining.	20·97	3·42	11,114	14,500	—	—
6 months in exposed pile 3 feet deep.	21·12	3·17	11,021	14,398	102	0·70

VERMILION COUNTY, ILLINOIS

SCREENINGS

(*From Parr and Wheeler.*)

Time of Storage—Months.

FIG. 21.   Calorific power stored coal.

TABLE XXVIII.

Calorific Losses in Storage, Vermilion County, Illinois, Screenings.

(*Parr and Wheeler*)

Sample taken.	Dry coal.			B.Th.U. referred to actual or unit coal.	Decrease.	
	Ash.	Sulphur.	B.Th.U.		B.Th.U.	Per cent.
STORED IN EXPOSED PILE.						
When mined..............	—	—	—	14,850*	—	—
About 2 weeks after mining......	19·11	1·96	11,561	14,644	206	1·39
15 months after mining.........	19·54	2·20	11,368	14,491	359	2·42
22 months after mining.........	20·61	1·88	11,134	14,392	458	3·08
28 months after mining.........	21·70	1·83	10,901	14,307	543	3·66
STORED UNDER WATER.						
When mined..............	—	—	—	14,850	—	—
15 months after submerging.....	15·90	2·29	12,154	14,761	89	0·60
28 months after submerging.....	17·75	1·97	11,686	14,531	319	2·15

*Calorific value taken from other analyses of fresh coal from same mine and neighbouring mine.

A valuable paper on oxidation by **Winmill**[1] has appeared as this volume is being prepared for the press, and the following extracts are included as they have a decided bearing on the subject under discussion. The paper describes the first[2] of a series of investigations undertaken by the Doncaster Coal-owners Association in England, who have undertaken a systematic study of their coal seams. In this first paper the results of four sets of experiments are set forth:—

(a) On the relative rates of oxidation of various parts of the Barnsley seam.

(b) On the effect of reducing the oxygen content of the intake air on the rate of oxidation.

(c) On the effect of the size of coal dust particles on the rate of oxidation.

(d) On the effect of temperature on the rate of oxidation.

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[1] "The Absorption of Oxygen by Coal," by T. F. Winmill. T. I. M. E. Vol. XLVI, 1914, pp. 559-591.
[2] Further reports have just appeared but it has been impossible to make use of them in the present work without delaying its publication. They are (a) "The Absorption of Oxygen by Coal "(Parts 2-6) by T.F.Winmill and J. Ivon Graham, Tr. Inst. Min. Engrs. Vol. XLVIII, 1915, pp. 503-49; (b) "The Absorption of Oxygen by Coal" (Part 7) by J. Ivon Graham. Tr. Inst. Min. Engrs. Vol. XLIX, 1915, pp. 35-43.

The methods used were as follows: a vessel containing coal was immersed in a bath of constant temperature and a steady stream of air passed through the coal mass, particular care being taken to ensure that the air did not find its way through definite channels. Pure air was obtained from a pipe passing through the wall of the laboratory into the outside atmosphere, and was drawn through the coal dust by a water aspirator, the rate of flow of the air being measured by the rate of flow of water from the aspirator. The air-stream issuing from the coal was analysed at intervals by means of a Haldane gas analysis apparatus. These analyses gave the percentages of oxygen, carbon dioxide, combustible gas and nitrogen in the sample; and the amount of oxygen absorbed was calculated by a method which took into account the dilution produced by the combustible gas and the carbon dioxide taken up from the coal, and allowed for all changes in the temperature and barometric pressure.

Six kinds of coal from the Barnsley seam near Doncaster[1] were tested as follows:—

Hard coal, Soft coal, Cannel coal, Jacks, Shale, and Mother-of-coal.

A portion of each was ground to pass through a 200-mesh sieve and was tested at 30°C in the apparatus above described. Further portions of the hard coal in coarser fragments were similarly tested to determine the difference in rate of absorption due to size.

Further portions of the 200-mesh "Hard" coal were similarly tested at 40°-50° and 60°C to determine the effect of elevated temperatures.

The results of the tests are set forth in Fig. 22 and Tables XXIX to XL, pp. 88-99.

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[1] The paper states that the samples "have all been taken from a mine working the Barnsley seam, which is liable to spontaneous combustion." The coal oxidized so readily that fresh coal was required for the experiments, and "the average interval from the winning of the coal to the time when it was ground and in the experimental vessel has been about two hours." The sample was always selected from a "rapidly advancing face." The name of the mine is not given, but as the laboratory was in Doncaster the above statement makes it clear that the samples came from that immediate locality.

TABLE XXIX (A).

Hard Coal, Weight 150 grammes, passing through a 200-mesh sieve; Temperature 30°.

(Winmill)

No. of sample.	Rate of flow of air per hour.	O₂	CO₂	Combust. gas.	Hours from start.	O₂ at N.T. & P. absorbed by 100 g. coal per hour.
	c.c.	Per cent.	Per cent.	Per cent.		c.c.
1..............	993	18·16	0·10	0·64	1·75	20·86
2..............	984	18·88	0·07	0·45	3·75	15·28
3..............	437	18·04	0·06	0·43	7·75	9·78
4..............	423	18·64	0·08	0·28	11·75	7·51
5..............	398	18·99	0·07	0·21	16·25	5·99
6..............	351	19·14	0·07	0·14	25·00	4·92
7..............	325	19·56	0·05	0·08	36·00	3·51
8...	290	19·47	0·09	0·10	44·00	3·35
9..............	294	19·47	0·08	0·09	47·00	3·26
10.............	276	19·51	0·08	0·05	52·25	3·08
11.............	248	19·60	0·08	0·00	64·25	2·60
12.............	554	20·40	0·05	—	71·00	2·34
13.............	236	19·84	0·05	—	87·75	2·02
14.............	234	20·00	0·07	—	112·50	1·72
15.............	286	20·22	0·06	—	139·00	1·62
16.............	286	20·25	0·07	—	161·00	1·53

TABLE XXIX (B.)

Hard Coal. Weight 136 grammes, passing through a 200-mesh sieve; Temperature, 30° C. The intake air contains 8·28 per cent of oxygen[1].

(Winmill)

No. of sample.	Rate of flow of air per hour.	O_2	CO_2	Combust. gas.	Hours from start.	O_2 at N.T. & P. absorbed by 100 g. coal per hour.
	c.c.	Per cent.	Per cent.	Per cent.		c.c.
1.............	974	6·09	0·08	1·10	1·75	14·87
2.............	882	6·96	0·05	0·35	3·75	8·62
3.............	355	6·11	0·10	0·30	7·75	5·79
4.............	351	6·52	0·09	0·12	11·75	4·65
5.............	329	6·66	0·11	0·17	16·25	4·02
6.............	311	6·84	0·13	0·12	25·0	3·35
7.............	321	7·17	0·17	—	36·0	2·69

[1] This special test was run to determine the effect of exposure to air which had already been deprived of the chief part of its oxygen.

TABLE XXX.

Soft Coal. Weight of Coal, 150 grammes, passing through a 200-mesh sieve; Temperature, 30° C.

(*Winmill.*)

No. of sample.	Rate of flow of air per hour.	.O_2	CO_2	Combust. gas.	Hours from start.	O_2 at N.T. & P. absorbed by 100 g. coal per hour.
	c.c.	Per cent.	Per cent.	Per cent.		c.c.
1.............	474	15·09	0·16	2·04	2·0	21·71
2.............	490	17·10	0·11	1·11	5·5	14·36
3.............	487	17·99	0·10	0·45	9·75	11·21
4.............	474	18·47	0·09	0·34	13·75	8·96
5.............	380	18·55	0·10	0·33	18·0	7·09
6.............	280	18·49	0·10	0·37	24·0	5·36
7.............	226	18·23	0·40	0·22	30·0	4·72
8.............	500	19·93	0·08	0·10	43·0	3·89
9.............	492	19·95	0·08	0·16	53·0	3·70
10.............	480	20·17	0·07	0·06	66·0	2·86
11.............	470	20·24	0·06	0·03	78·0	2·57
12.............	465	20·22	0·07	0·00	90·0	2·62
13.............	461	20·35	0·06	—	101·0	2.15
14.............	435	20·37	0·08	—	114·0	1·96
15.............	187	19·61	0·10	—	143·75	1·94
16.............	168	19·80	0·11	—	160·75	1·49

TABLE XXXI.

Cannel Coal. Weight of coal, 150 grammes, passing through a 200-mesh sieve; Temperature 30° C.

(Winmill)

No. of sample.	Rate of flow of air per hour.	O_2	CO_2	Combust. gas.	Hours from start.	O_2 at N.T. & P. absorbed by 100 g. coal. per hour.
	c.c.	Per cent.	Per cent.	Per cent.		c.c.
1............	925	17·96	0·14	0·98	1·25	20·34
2............	901	19·26	0·06	0·53	4·25	11·88
3............	901	19·78	0·05	0·27	8·00	7·74
4............	480	19·76	0·07	0·12	20·75	4·31
5............	476	19·73	0·06	0·12	25·25	4·35
6............	319	19·16	0·09	0·47	32·50	4·11
7............	299	19·87	0·07	0·68	45·25	2·20
8............	289	19·87	0·08	0·05	56·75	2·35
9............	300	20·09	0·05	0·00	72·00	2·02
10............	295	20·21	0·06	—	94·00	1·69
11............	274	20·29	0·05	—	117·50	1·38
12............	276	20·35	0·05	—	142·75	1·26

TABLE XXXII.

Jacks. Weight of dust, 150 grammes, passing through a 200-mesh sieve; Temperature, 30° C.

(*Winmill*)

No. of sample.	Rate of flow of air per hour.	O_2	CO_2	Combust. gas.	Hours from start.	O_2 at N.T. & P. absorbed by 100 g. coal per hour.
	c.c.	Per cent.	Per cent.	Per cent.		c.c.
1.............	487	15·85	0·14	2·15	2·00	18·44
2.............	480	18·02	0·07	0·90	5·50	10·52
3.............	474	18·97	0·05	0·48	9·75	7·16
4.............	470	19·32	0·05	0·29	13·75	5·88
5.............	470	19·56	0·06	0·25	18·00	4·67
6.............	474	19·80	0·07	0·23	24·00	4·14
7.............	355	19·63	0·06	0·20	30·00	3·61
8.............	500	20·13	0·03	0·18	43·00	3·04
9.............	488	20·24	0·04	0·14	53·00	2·59
10.............	480	20·42	0·05	0·10	66·00	1·90
11.............	475	20·49	0·05	0·01	78·00	1·63
12.............	473	20·46	0·05	0·00	90·00	1·75
13.............	471	20·46	0·06	—	101·00	1·74
14.............	706	20·67	0·04	—	114·00	1·47
15.............	212	20·06	0·05	—	143·75	1·45
16.............	188	20·27	0·04	—	160·75	0·99

TABLE XXXIII.

Shale. Weight of shale, 158 grammes, passing through a 200-mesh sieve; Temperature, 30° C.

(Winmill)

No. of sample.	Rate of flow of air per hour.	O_2	CO_2	Combust. gas.	Hours from start.	O_2 at N.T. & P. absorbed by 100 g. coal per hour.
	c.c.	Per cent.	Per cent.	Per cent.		c.c.
1.............	900	20·03	0·08	0·36	1·75	5·54
2.............	889	20·39	0·04	0·17	4·50	3·34
3.............	526	20·37	0·06	0·05	9·75	2·13
4.............	204	20·13	0·04	0·00	25·25	1·26
5.............	194	20·42	0·04	—	48·75	0·76
6.............	181	20·47	0·04	—	71·25	0·64
7.............	166	20·55	0·04	—	96·00	0·50
8.............	181	20·61	0·04	—	119·00	0·42

TABLE XXXIV.

Mother-of-Coal. Weight of mother-of-coal, 120 grammes; Temperature, 30° C.

(Winmill)

No. of sample.	Rate of flow of air per hour.	O_2	CO_2	Combust. gas.	Hours from start.	O_2 at N.T. & P. absorbed by 100 g. coal per hour.
	c.c.	Per cent.	Per cent.	Per cent.		c.c.
1.............	511	20·05	0·17	0·56	2·00	3·82
2.............	506	20·36	0·08	0·18	9·75	2·65
3.............	500	20·42	0·09	0·05	13·75	2·47
4.............	500	20·42	0·07	0·10	18·00	2·42
5.............	436	20·44	0·09	0·10	30·00	2·16
6.............	500	20·55	0·10	0·11	43·00	1·71
7.............	479	20·65	0·08	0·00	90·00	1·30
8.............	219	20·37	0·15	—	144·25	1·18
9.............	217	20·47	0·12	—	160·75	0·96

TABLE XXXV.

Hard Coal.—Weight 250 grammes; coal dust passing through 10-mesh and remaining on 30-mesh. Temperature 30°C. The column headed "R" gives the percentage ratio of the oxygen absorption for the coarse dust to that for the fine dust. The figures for the latter are taken from Table XXIX A.

(Winmill)

R[1]	No. of sample.	Rate of flow of air per hour.	O_2	CO_2	Combust. gas.	Hours from start.	O_2 at N.T. & P. absorbed by 100 g. coal per hour.
%		c.c.	Per cent.	Per cent.	Per cent.		c.c.
—	1	250	6·80	0·20	46·50	1·50	(14)
72	2	909	18·15	0·08	4·72	5·75	8·24
69	3	392	17·19	0·04	4·58	10·50	5·49
75	4	380	18·40	0·05	1·95	21·50	3·92
70	5	373	18·79	0·05	1·3)	26·25	3·33
75	6	373	19·14	0·03	1·10	32·50	2·84
74	7	227	18·51	0·07	0·86	44·25	2·44
73	8	221	18·74	0·06	0·89	53·25	2·12
70	9	207	19·10	0·05	0·54	68·50	1·65
74	10	195	19·31	0·05	0·37	93·00	1·41
72	11	165	19·29	0·06	0·32	118·75	1·23
72	12	94	18·74	0·07	0·41	164·75	0·94

[1]Mean value of R, 72 per cent.

TABLE XXXVI.

Hard Coal. Weight 200 grammes; coal dust passing through 30-mesh and remaining on 60-mesh. Temperature 30° C.

(Winmill)

R^1	No. of sample.	Rate of flow of air per hour.	O_2	CO_2	Combust. gas.	Hours from start.	O_2 at N.T. & P. absorbed by 100 g. coal per hour.
%		c.c.	Per cent.	Per cent.	Per cent.		c.c.
—	1	250	9·28	0·12	44·00	1·50	
85	2	920	18·75	0·05	2·31	5·75	9·46
83	3	500	18·54	0·04	0·85	10·50	6·62
80	4	496	19·47	0·05	0·50	21·50	4·00
80	5	496	19·82	0·02	0·27	32·50	3·02
82	6	174	18·56	0·06	0·39	53·25	2·37
80	7	174	19·02	0·06	0·39	68·50	1·89
78	8	157	19·30	0·06	0·24	92·50	1·49
79	9	153	19·44	0·09	0·14	116·00	1·31
70	10	125	19·67	0·08	0·28	165·00	0·90

[1]Mean value of R, 80 per cent.

TABLE XXXVII.

Hard Coal. (Secondary oxidation[1]). Weight of coal, 150 grammes, passing through a 200-mesh sieve. Temperature 30° C.

(Winmill)

No. of sample.	Rate of flow of air per hour.	O_2	CO_2	Combust. gas.	Hours from start.	O_2 at N.T. & P. absorbed by 100 g. coal per hour.
	c.c.	Per cent.	Per cent.	Per cent.		c.c.
1............	536	19·09	0·16	0·40	1·50	7·39
2............	536	19·53	0·11	0·33	3·00	5·65
3............	308	19·25	0·10	0·31	5·50	3·90
4............	311	19·65	0·10	0·29	9·00	2·98
5............	209	19·65	0·07	0·32	21·00	1·92
6............	207	19·97	0·06	0·20	32·00	1·50

[1] The coal used in this experiment was a portion of the sample from Table XXXV which had already oxidized as coarse dust for 165 hours. It was then crushed through 200-mesh and re-treated as shown.

TABLE XXXVIII.

Hard Coal. Weight, 121·4 grammes, passing through a 200-mesh sieve. Temperature 40° C.[1]

(Winmill)

No. of sample.	Rate of flow of air per hour.	O_2	CO_2	Combust. gas.	Hours from start.	O_2 at N.T. & P. absorbed by 100 g. coal per hour.
	c.c.	Per cent.	Per cent.	Per cent.		c.c.
1.............	1,017	16·36	0·09	1·48	1·00	43·80
2.............	1,014	17·80	0·08	0·83	2·00	29·93
3.............	1,014	19·02	0·04	0·23	4·00	18·85
4.............	990	19·59	0·03	0·12	7·00	13·00
5.............	524	19·12	0·05	0·09	12·00	9·32
6.............	280	18·35	0·05	0·16	20·00	7·07
7.............	260	18·49	0·09	0·18	24·00	6·20
8.............	261	18·56	0·10	0·21	27·50	6·02
9.............	251	18·78	0·10	0·17	32·25	5·24
10.............	250	18·95	0·05	0·15	36·00	4·82
11.............	233	19·16	0·05	0·17	47·50	4·03
12.............	214	19·24	0·08	0·16	54·00	3·50
13.............	217	19·76	0·10	0·17	70·25	3·04
14.............	204	19·74	0·03	0·10	82·25	2·38
15.............	209	19·74	0·08	0·09	94·50	2·40

[1] This and tests XXXIX and XL were in parallel to XXIX (A) but at higher temperatures.

TABLE XXXIX.

Hard Coal. Weight 150 grammes, passing through a 200-mesh sieve. Temperature 50° C.

(Winmill)

No. of sample.	Rate of flow of air per hour.	O_2	CO_2	Combust. gas.	Hours from start.	O_2 at N.T. & P. absorbed by 100 g. coal per hour.
	c.c.	Per cent.	Per cent.	Per cent.		c.c.
1.............	1,260	13·20	0·13	1·91	1·00	74·65
2.............	1,260	15·69	0·12	0·97	2·00	50·69
3.............	1,260	17·63	0·12	0·43	4·00	31·92
4.............	779	17·58	0·11	0·27	6·50	20·30
5.............	853	18·50	0·09	0·13	10·00	16·15
6.............	375	17·21	0·14	0·19	19·50	10·89
7.............	268	16·59	0·22	0·23	26·00	9·07
8.............	268	17·49	0·15	0·20	32·50	7·20
9.............	264	18·27	0·13	0·16	46·50	5·46
10.............	392	19·31	0·13	0·21	55·00	4·84
11.............	187	18·11	0·20	0·25	74·00	4·06
12.............	181	18·52	0·19	0·10	92·25	3·62
13.............	173	18·80	0·21	0·10	123·50	2·88
14.............	159	18·93	0·19	0·09	140·50	2·48

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TABLE XL.

Hard Coal. Weight 100 grammes, passing through a 200-mesh sieve; Temperature 60° C.

(*Winmill*)

No. of sample.	Rate of flow of air per hour.	O_2	CO_2	Combust. gas.	Hours from start.	O_2 at N.T. & P. absorbed by 100 g. coal per hour.
	c.c.	Per cent.	Per cent.	Per cent.		c.c.
1............	1,744	16·03	0·07	0·95	1·00	99·70
2............	1,705	17·63	0·06	0·50	2·00	66·03
3............	1,700	18·93	0·07	0·23	3·75	39·98
4............	897	18·72	0·13	0·07	8·25	22·16
5............	809	19·18	0·08	0·05	13·00	16·88
6............	302	18·34	0·18	0·10	34·00	9·29
7............	302	18·46	0·18	0·08	36·00	8·89
8............	306	18·96	0·19	0·06	50·00	7·13
9............	302	18·97	0·17	0·06	54·00	7·01
10............	300	19·25	0·16	0·05	75·00	5·97
11............	197	18·75	0·24	0·04	99·00	5·08
12............	141	18·14	0·30	0·04	123·00	4·65
13............	201	19·31	0·27	0·03	148·00	3·79
14............	217	19·65	0·19	0·00	172·00	3·24
15............	189	19·96	0·16	—	288·00	2·14

The general conclusions to be drawn from Winmill's results are as follows:—

(a) In the coals of the Barnsley seam, very rapid oxidation takes place in the first few hours in freshly got coal, and this is followed by a much slower absorption which persists for a long time. The great similarity of results for the different coals is noteworthy.

The absorption curves, Fig. 22, for the different coals are very close together for the most part and show that there is very little difference in the rate of oxidation. The amount of oxygen absorbed is roughly proportional to the content of carbonaceous matter in each case.

Winmill gives a mathematical analysis of these curves to show that each represents with a fair degree of accuracy the sum of two chemical reactions obeying definite equations. He states that his tests while not

FIG 3 INFLUENCE OF TEMPERATURE ON RATE OF OXIDATION
OF BARNSLEY HARDS.

REFERENCES TO FIG 3.
A. AT 30°C.
B. AT 40°C.
C. AT 50°C.
D. AT 60°C.

FIG 2. HARD COAL BARNSLEY BED

REFERENCES TO FIG 2.
A. FINE DUST AT 40°C.
B. FINE DUST AT 50°C.
C. COARSE DUST AT 30°C.
D. FINE DUST IN AN ATMOSPHERE
CONTAINING 9.25 PER CENT
OF OXYGEN.

FIG 1. COMPARISON OF VARIOUS
PARTS OF BARNSLEY SEAM

REFERENCES TO FIG. 1.
E SOFT COAL.
F HARD COAL.
G JACKS.
H CANNEL.
I SHALE.
J MOTHER OF COAL.

C.C. OF OXYGEN ABSORBED PER 100 GMS. COAL PER HOUR

HOURS

(Redrawn from Winmill.)

FIG. 22. Rate of oxidation of coal under various conditions.

showing that pyrite is not a contributary factor to spontaneous combustion, point to the fact that heating can occur in the absence of oxidizable pyrite.

(b) Certain combustible gases—principally methane—are given off by the coal during oxidation, the total quantities per 100 grammes of each substance being as follows:—

Hard coal.. 37 c.c.
Soft coal... 80 c.c.
Cannel coal...................................... 70 c.c.
Jacks.. 70 c.c.
Shale.. 12 c.c.
Mother-of-coal................................... 30 c.c.

These quantities are of course exclusive of those lost during the grinding, which certainly far exceed those tabulated above as can be seen from the tables for coarse dust. (Tables XXXV and XXXVI).

(c) That a reduction of the oxygen of the intake air appreciably reduces the rate of oxidation is shown by Tables XXIX, A and B, but the rate is still very considerable, and "a proposal to stop, at any rate the earlier stages of spontaneous combustion by a reduction short of almost total removal of the oxygen, would appear to have no basis in fact".

(d) From Tables XXXV, XXXVI and XXXVII it is seen that the rate of oxidation is not proportional to the size of the particles probably because the coal is porous and the oxygen is able to penetrate more or less into the interior of each particle; but it is shown that "the total absorption is the same whether the dust is ground up very slowly and oxidized at the same time or whether it is ground up rapidly and then oxidized."

(e) Conclusions are not drawn as to the effect of temperature on the rate of oxidation as the experiments have not proceeded far enough to warrant them. A series of curves are given, however, together with four tables showing the results obtained for temperatures—30°C, 40°C, 50°C and 60°C, Tables XXIX (A) and XXXVIII—XL and the curves Fig. 22. These show clearly that the rate of oxidation increases greatly with increase of temperature.

Lamplough's criticism of the experiments is perhaps worthy of note here. He says:—

The effect of fineness of dust is apparently inconsiderable when the temperature is constant, yet, in practice, with a partial retention of heat the effect would probably be of much greater importance.

He does not believe that the absorption curves can properly be interpreted as due to two chemical actions, as suggested by Winmill, for—

though many different equations could be constructed to fit a limited curve, they could not be assumed true for later periods of the reaction. The fact is that it is quite incorrect to attempt to apply velocity equations to such reactions. The laws governing the velocities of chemical actions refer only to reactions occurring in a homogeneous solution, and any attempt to apply these laws to so heterogeneous an action as the absorption of a

gas by so complex a substance as coal dust is fallaceous. This is further shown by the fact, that the experiments show that a gradual rise in temperature gradually increases the total absorption although this is contrary to the laws governing chemical actions. Moreover the rate is not proportional to nor yet independent of the fineness of dust.

A study of the various tables shows that in all the experiments the rate of flow of air has been a variable quantity, being usually of larger velocity at the beginning of the experiment than at the end. A variable rate of flow would undoubtedly affect the oxygen content of the sample taken, and as this is not shown as corrected, it would appear probable that the absorption results shown are not the results of constant and similar conditions in all samples taken during each test. Moreover it has been the experience of the author that the rate of flow of gas plays a part in the temperature rise of the coal[1] and therefore very probably also in the absorption of oxygen by the coal. In experiments of this kind too much care cannot be taken to keep all conditions constant except that one which it is desired to study.

If Winmill had kept the flow of air constant throughout each test it is extremely probable that his curves would not show such similarity, especially in the later hours of the experiment, and that this should be the case seems only right. For example, Winmill says that the amount of oxygen absorbed is roughly proportional to the content of carbonaceous matter in each substance, and quotes the soft coal with 90% carbonaceous matter absorbing 830 c.c. of oxygen, and the Jacks with 75% absorbing 560 c.c., whereas the curves in Fig. 22, show that after the 70th hour the Jacks are absorbing an average of about 2 c.c. per hour, a result that hardly seems justifiable if we assume the above statement to be substantially correct.

[1] See page 136 et seq.
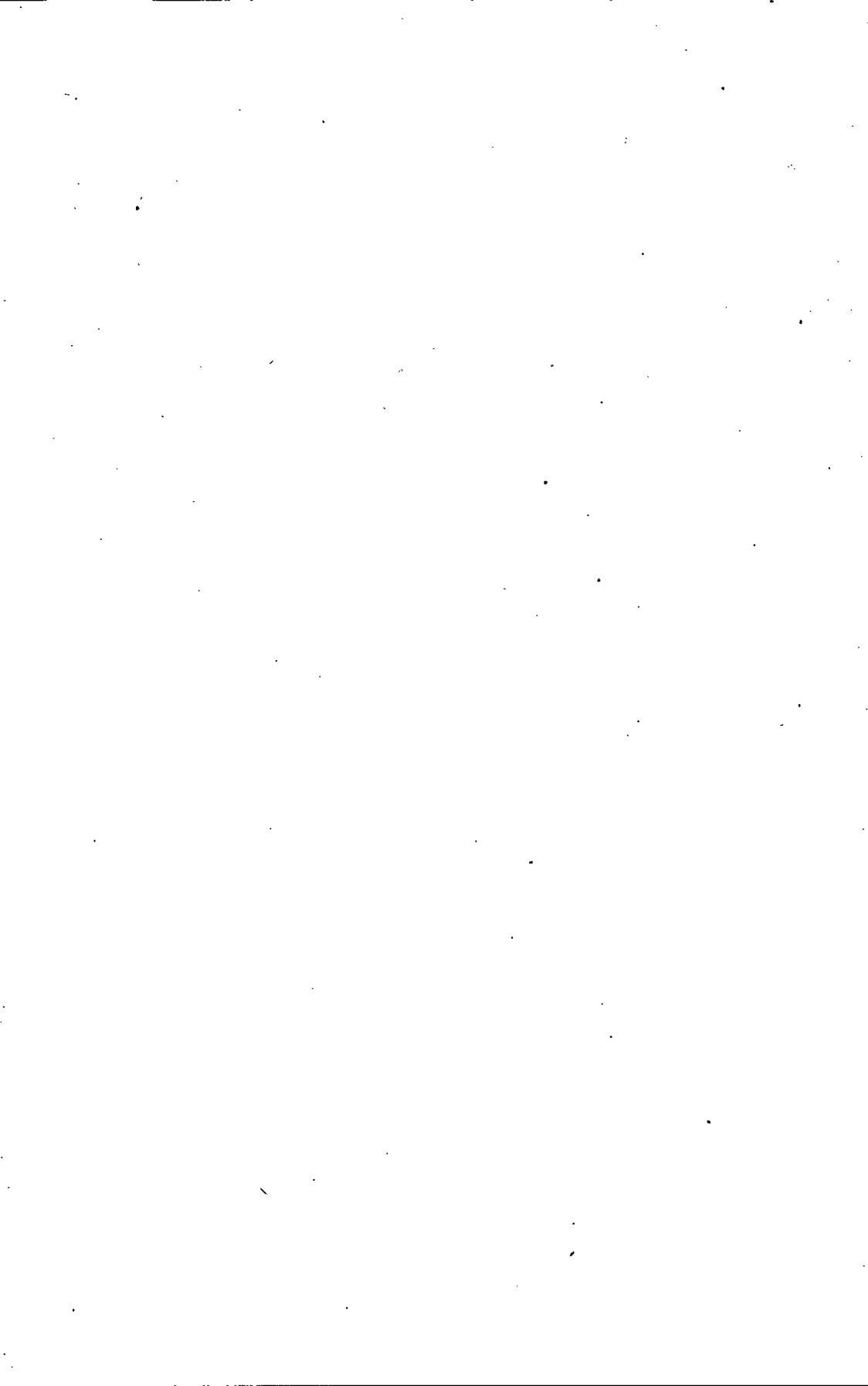
CHAPTER V.

OXIDATION AT ELEVATED TEMPERATURES.

Varrentrapp[1] is quoted by Langley as having placed a quantity of pulverized coal in a closed vessel through which a current of air could be drawn. The vessel and air were brought to a temperature of 280°F and the air, after passing through the apparatus, was caused to bubble through "certain chemical solutions which have the property of retaining and rendering visible" carbon dioxide. The solutions showed that carbon dioxide was present in the air and it is stated that the combustion was so complete even at 280°F that the whole of the carbon in the coal oxidized inside of three months. Langley evidently considered the latter part of the statement exceptional and stated that he had never known of such extreme oxidation with American coals; and Richters criticized the first part of the experiment on the ground that the carbon dioxide may have been occluded in the coal before the experiment was started.

In the light of our present knowledge of the subject it is scarcely necessary to say that Langley's criticisms are more than justified. No ordinary coal oxidizes to the extent stated, and even Langley's much more moderate estimates were over rather than under the truth. The statements are, however, interesting as showing the opinions of very early experimenters.[2]

Richters[3] work, although done half a century ago, is of interest here, and a résumé is therefore given below. His conclusions in brief are that the volume of oxygen absorbed by freshly mined coal is to a certain extent dependent upon the hygroscopicity of the coal. He also thinks it probable that there is a "definite relation between the absorption of oxygen and the content of disposable hydrogen in coal", and he was able to prove that oxygen becomes chemically combined with the coal.

The quotations which follow are taken with few corrections from the translation by Wilson and Helms in the Report of the New South Wales Commission on Coal Cargoes, pp. 80–2 (1897.)

"We know that coal always absorbs oxygen quickly at elevated temperatures and slowly at ordinary temperatures. The chemical and other changes which the combustible substance of coal undergoes under the first condition have already been established by me. On the other hand, at ordinary temperatures the absorption of oxygen is, in so far, a matter which in no way assists us in understanding the chemical changes which are consequent upon it. Whether and how far the carbon or hydrogen is the cause of the oxidizing action

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[1] See discussion of Pechin's paper, T. A. I. M. E. Vol. I, 1872, p. 285.
[2] Porter and Ovitz have recently experimented using 5 grammes of coal (80-100 mesh), in an electrically heated tube kept at definite temperatures. They passed a measured volume of dry air over the coal at a definite rate. The carbon dioxide evolved from the coal was found to be equal to only one-tenth of the volume of oxygen absorbed. (See International Congress of Appl. Chem. Vol. X,1912,p. 265, Fig. p. 253. This matter is much more fully dealt with by Porter and Ralston in "A Study of the Oxidation of Coal", Tech. Paper No. 65, U. S. Bur. of Mines, Washington, 1914.
[3] Dinglers Poly. Journal. Vol. 195, 1870, pp. 315 and 449.

of the oxygen; whether the action of the latter is not essentially confined to the formation of carbon dioxide, which is then absorbed by the coal; and whether, further, the absorption is a chemical or more or less physical process, are all questions which are of the greatest interest for a critical examination of the phenomena of the weathering of coal. * * *

"I shall offer several observations which appear to me to be of importance for throwing light upon the first of the questions propounded above. If we heat coal-dust to a temperature from 180° to 200° C., the weight at first increases rapidly in a very marked manner; carbon dioxide and water are then separated, and oxygen is taken up in greater proportion than is required for the oxidation of the carbon and hydrogen. After a certain time the oxygen absorption, and with it the alteration in weight, comes to an end. If we continue to heat the coal, at first there is a small diminution in weight, but after a while the weight, as well as the chemical composition of the coal, becomes constant, or rather, the variations which the coal undergoes are so small that in an experiment which was continued for six days a good chemical balance was unable to show any further variation. If we examine the constitution of coal which has been heated up to the point of maximum absorption of oxygen, we find that the oxygen and hydrogen are present approximately in the same proportions as in water. This interesting behaviour of coal brings to light two important phenomena. It shows firstly that the carbon of the coal is endowed with a very variable degree of oxidizability, and makes it, in the second place, probable that there is a perfectly definite relation between the absorption of oxygen and the content of disposable hydrogen in the coal, since with the vanishing of the latter the oxygen absorption comes to an end. The first circumstance agrees with the view which is generally taken by chemists that the carbon in coal exists in two different chemical forms. We may say that the coal is a mixture of pure carbon with obscure organic compounds containing carbon, hydrogen, oxygen and nitrogen. These carbon compounds are sometimes grouped together under the name of "bitumen". The rapid evolution of carbon dioxide which takes place when the coal is first heated may be attributed to the oxidation of the carbon of the bituminous constituents, while the relatively much smaller evolution of carbon dioxide which succeeds, may be attributed to the oxidation of the more difficultly oxidizable carbon."

Richters thinks this view may be supported by Saussure's observations of the similar phenomena occurring during the absorption of oxygen by wood, charcoal, etc., and by the researches of Liebig on lignite and true coal.

"On the ground of these observations we come to the following conclusions, which are of importance for our knowledge of the behaviour of coal in the presence of oxygen:—

(1) "The peculiarity of coal, when heated to 190°C., in taking up oxygen, depends almost entirely on the fact that the coal contains disposable hydrogen. This is oxidized in presence of a certain quantity of carbon. On the one hand water is formed, while on the other oxygen takes its place directly in the composition of the coal; (2) the carbon of coal when exposed to oxygen at a temperature of 190°C, behaves in a totally different manner, in that the smaller part—5 to 6 per cent only—of the whole weight combines, forming carbon dioxide. The remainder is only slightly or not at all altered by oxygen at that temperature."

"It is to be noted that both these conclusions refer exclusively to the oxidation of coal at elevated temperatures; since, however, we observed precisely the same relations existing during the oxidation of coal at ordinary temperatures, there is very strong evidence that the processes of oxidation at both high and low temperatures are essentially similar."

"During the heating of coal, as well as at ordinary temperatures, oxygen is absorbed. That, in the latter case the absorption of oxygen is related to the disposable hydrogen in the same manner as in the first case, is made clear by the behaviour of wood and its decomposition products."

"It is also clear that the content of disposable hydrogen is diminished when coal is exposed to air in a manner similar to that in which it is diminished when the coal is heated.

It may be shown with certainty that carbon dioxide is formed at ordinary temperatures in the same way as it is formed at higher temperatures, and, in both cases, when the more easily oxidized portions of the carbon come to an end, the oxygen absorption reaches its maximum.

The assumption that the more difficultly oxidizable carbon behaves with regard to oxygen at low temperatures differently to the way in which it behaves at high temperatures, would contradict all experience.

It cannot be maintained that the absorption of oxygen at ordinary temperatures is merely a physical process, still the surface action of the coal is perhaps not to be neglected.

We must distinguish between the tendency which the coal has to absorb oxygen and the intensity with which oxygen is at first actually absorbed. It appears to be not improbable that in the earlier stages the absorption of oxygen is a purely mechanical process, and that this precedes the chemical combination.

The quantity of hygroscopic water which coal actually takes up when exposed to air saturated with water vapour at 15°C. was determined for more than 100 samples by heating them to 100°C. until the weights became constant. The percentage of hygroscopic water thus liberated varied from 2 to 7·5, but the power of the coal for condensing hygroscopic moisture did not appear to be related to its structure in any determinate manner. The condensing of hygroscopic water on the surface of the coal, however, shows very clearly the condensing power possessed by coal. If we examine the quantity of oxygen which different coals absorb from the air, under similar circumstances, we find that there is a very close connection between this quantity and the power of the coal for condensing moisture. In order, however, to obtain complete and decisive experimental results in this connection it is necessary that care should be exercised in selecting coal which has been freshly obtained, and has not been lying in contact with atmospheric air.

Fresh coal, after it has been pounded, ground, and sieved, gives an apparently dry powder, although this is saturated with moisture.

* * * * * *

"The absorption of oxygen by the freshly-prepared coal begins at once and goes on rapidly. The volume of the absorbed gases, though not proportional to the surface action of the coal as indicated by its hygroscopicity, are, nevertheless, very dependent upon it. I intend to make a further communication in greater detail as to the results of this experiment, and will, therefore, confine myself in this place to the statement of the quantity of oxygen absorbed during the first twenty-four hours by 20 grammes of different samples of coal, a quantity which varies between 2 and 9 c.c. I may, however, mention certain circumstances which appear to me to strengthen my position in considering that at first the absorption of oxygen is chiefly mechanical."

(The observation on which reliance is placed appears to be that the oxygen absorption is at first very much more rapid than is the case later on.)

Richters then notes that Varrentrapp has shown that when coal is exposed at ordinary temperatures to a stream of air, carbon dioxide is formed. He suggests that carbon dioxide may have been originally condensed upon the surface of the coal, and that it is gradually removed by the stream of air, its place being taken to some extent by oxygen. In order to clear up this point certain special experiments were made which rendered it probable that the continued absorption of oxygen is not to be explained by assuming that it merely takes the place of carbon dioxide condensed upon the surface of the coal.

"Coal absorbs carbon dioxide with the greatest readiness. The volume of this gas which is taken up in a given time is often greater than three times the volume of oxygen which could be taken up. Samples of coal whose absorptive power for oxygen has almost vanished, so much so that 20 grammes will only take up about 1 cubic centimetre of oxygen, will absorb in a few hours at least their own volume of carbon dioxide. If a sample of coal saturated with carbon dioxide is brought into contact with atmospheric air, we find at first an increment of volume as if the carbon dioxide is given off. Soon, however, the volume again begins to diminish. If, at the same time, a small bulb containing caustic potash is introduced in the absorption tube, or if the sides of the latter are moistened with a solution of caustic potash, the absorption of the oxygen goes on very quickly, as does the separation of the carbon dioxide which, of course, forms a compound with the caustic potash. If we leave samples of coal saturated with carbon dioxide for thirty-six hours under the receiver of an air pump exhausted to 2 inches of quicksilver, the greater portion, but not all, of the absorbed carbon dioxide is given off. If a sample of coal which has been so treated is then saturated with moisture and again put into an absorption tube it begins to take up oxygen with the same avidity as when it was freshly prepared, and this whether any potash is present or not. If potash is present, however, we soon discover that a certain quantity of carbon dioxide has been liberated, which shows that the absorption of oxygen is at first accompanied by a separation of carbon dioxide, and that this carbon dioxide will again be taken up by the coal in the absence of any other substance capable of absorbing it."

"If coal which has been saturated with carbon dioxide is boiled for half-an-hour in water and is then air-dried, so that it remains saturated with hydroscopic moisture, it is found to have recovered its original absorptive properties."

"Coal which has been exposed for a long time to the air until it has lost its power of absorbing oxygen behaves in a completely different manner when the foregoing experiments are performed upon it. For instance, when exposed under the receiver of an air-pump it does not by any means recover its original power of absorption, though this power is still partly restored by boiling out with water. Carbon dioxide is either not absorbed at all by such coal or in only very small proportions."

The observations show that the small absorptive power of coal which has been lying for a long time in the air does not depend upon a condensation of carbon dioxide upon its surface, and other conclusions may also be drawn. Amongst these may be mentioned the following:—

"We may now explain the experiments of Varrentrapp. The coal which has lost its power of absorbing oxygen may, nevertheless, absorb large quantities of carbon dioxide, and, on the other hand, when this coal which contains carbon dioxide begins to take up oxygen the process is accompanied by a separation of carbon dioxide. Now, this process is not very noticeable when the experiment is carried out in closed tubes, but it becomes noticeable when the experiment is performed by Varrentrapp's methods."

In considering the influence of heat on the process of oxidation,

I have formerly shown that a rise of temperature is the most important determining circumstance of the process of oxidation. It is not, however, necessary to use a temperature which lies far above 100°C., though the higher the temperature the greater the acceleration of the process. In pursuance of these experiments I heated coal for fourteen days on the water bath at from 70° to 80° C. The first sample of coal increased in weight during this process by 1·01 per cent, the second sample by 0·2 per cent, and the third by 0·35 per cent. (The constitution of these three samples of coal before and after fourteen days heating is given by three tables of analyses accompanying Richters' paper). In all cases there was a diminution in the carbon and hydrogen content and an increase in the oxygen content, exactly as in ordinary weathering. The coking power of sample (1) was diminished from 1·4 to 1·1; of sample (2) from 2 to 1·6; sample (3) was a so-called "sandkohle" which does not give coke. The quantity of the coke did not appreciably change, and the specific gravity certainly did not. The heating power of sample (1) fell by 2·62 per cent; of sample (2) by 3·61 per cent; and of sample (3) by 3 per cent. * * * * * * * *

"Samples of coal employed in these researches had remained for a long time in loosely stoppered bottles, so that the absorption of oxygen at ordinary temperatures only took place very slowly. As a control, check analyses of the unheated coals were made after they had suffered fourteen days longer exposure. The fact that during this time the composition of the samples did not undergo any variation, shows clearly that the increase in oxygen and loss in carbon and hydrogen is really to be attributed to the higher temperatures to which the coals were exposed."

"There appears to be a certain contradiction between the observation that oxidation goes on more rapidly at upper temperatures, and our thesis that oxidation follows a preliminary surface condensation of oxygen. This apparent contradiction is, in my opinion, easily cleared up if we distinguish clearly between oxidation and mere absorption. The first goes on more rapidly at elevated temperatures, the latter at lower temperatures. If the coal has been saturated with oxygen at lower temperatures, the condensed gas combines only gradually with the substance of the coal, and only in proportion as the latter process advances can new quantities of gas be taken up. When, however, coal which is saturated with oxygen is heated, a portion of the gas is evaporated; but the greater part enters into chemical combination, and does so more rapidly as the temperature is higher. The surface action, however, neither undergoes any appreciable change, nor produces any result at all comparable with the chemical action."

In studying the influence of moisture on the absorption and on the oxidation of coal,

"The greater number of technicologists are of opinion that moisture has an important aiding action in the weathering of coal. (Thompson's researches are mentioned in connexion with this point). That moisture may, under certain circumstances, aid the oxidation of coal is not to be denied; but the action of moisture is very complicated, and is influenced by various circumstances, and is not so generally prejudicial as Thompson's observations would lead us to imagine. I will communicate the result of a few experiments made upon this subject."

"If we take two tubes, and into one of them introduce air-dried and into the other moist coal, both being freshly won, the first absorbs oxygen much more rapidly than the second. If, in addition, small bulbs containing fused chloride of calcium are introduced alongside of the dry sample of coal so that the coal gets gradually drier, the intensity of the absorption of oxygen becomes greater. The same is the case if the coal has been dried for a day over sulphuric acid, although during this process a very considerable quantity of oxygen must certainly have been taken up."

"If instead of fresh coal we take two samples of coal with different surface properties, both of which have been exposed to the air for a long time and which have lost their power of absorption to a great extent, and expose them to the drying action of sulphuric acid, both of them recover to some extent their absorptive power. That coal with the greater surface action recovers most completely."

"If we dry coal at 100°C., and cool it in a desiccator and place it in an absorption tube, it is found to absorb gas with extraordinary rapidity. This gas consists in part of nitrogen (from 12 to 21 per cent., from the mean of many experiments). Coal which has been dried at ordinary temperatures also takes up nitrogen, but in smaller percentages, at the same time as it absorbs oxygen."

"All these experiments indicate only a relative increment of the power of absorption by the removal of moisture, and establish in so far the view which has been taken in the former work as to the nature of surface action. They also show that a dry coal will take up a larger volume of gases than one which is merely air dried, before the absorptive power of the two samples sinks to the same level."

These researches, however, still leave unanswered the question as to how far the moisture is disadvantageous for the chemical action of the oxygen upon the coal. I had hoped to be able to give a definite answer to this question, but I have not succeeded in coming to a positive decision. * * * * * *

"These observations would seem to support the assumption that water assists the process of oxidation; but on repeating the experiment several times—that is, first wetting and then drying the coal by means of chloride of calcium—we finally reach a state at which no further increment of absorptive power is to be observed."

"We may, however, approach the question by inquiring whether the action of water on the decomposition of coal is not to be attributed to the consequences of secondary action. Many coals contain pyrites which is only oxidizable in the presence of moisture. This process is undoubtedly of importance, even if it is regarded only as indirectly introducing active material for the oxidation of the coal."

The well-known action of pyrites in breaking up the coal and exposing fresh surfaces is then described. The question as to whether ferrous oxide can act as a carrier of oxygen to the coal is discussed, and it is considered that the small quantity of this substance which is present can only account for a very small part of the action.

General average results
from all the coals tested, in dust

Time of exposure (hours)
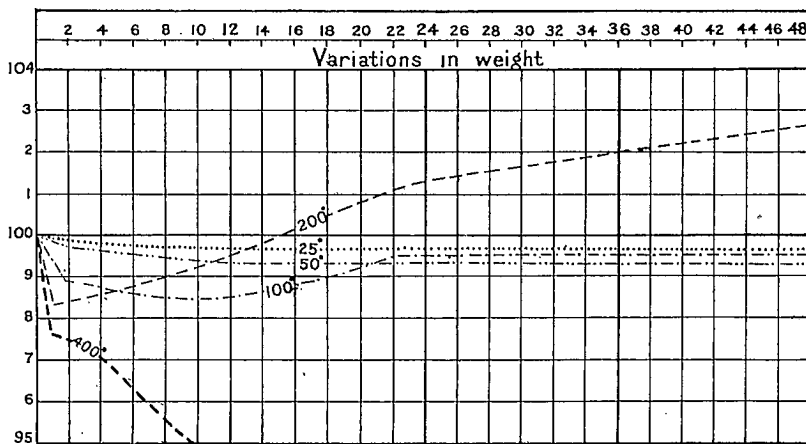
(Redrawn from Fayol.)

FIG. 23.

Fayol[1] took samples of a large number of coals, varying from anthracites to lignites, and heated them in loosely covered porcelain crucibles in ovens maintained at temperatures ranging from 25° to 430°C. Air was slowly passed through the ovens and the crucibles were weighed from time to time to determine the variations in weight. Twenty gramme samples were taken and for each coal four similar crucibles were used—two contained powdered coal and two lump. Each time the crucibles were weighed the coal was stirred with an iron spatula to allow penetration of air. The results obtained were plotted by Fayol in a series of very interesting curves

[1] Études sur l'altération de la houille exposeé à l'air, 1879.

which are too numerous for reproduction here. His two final summary curves, giving the mean results for all of the samples tested, are reproduced in Figs. 23, and 24. (See also pages 26 and 52-3.)

Parr and Kressmann[1] draw attention to the rapidity of oxidation of certain hydrocarbon compounds at temperatures in excess of 120°C. and to the extremely exothermic nature of this reaction when once started; they point out the danger of any influence existing near coal which may tend to increase the velocity of this reaction which is almost negligible at ordinary temperatures.

General average results
from all the coals tested, in dust
Time of exposure (days)
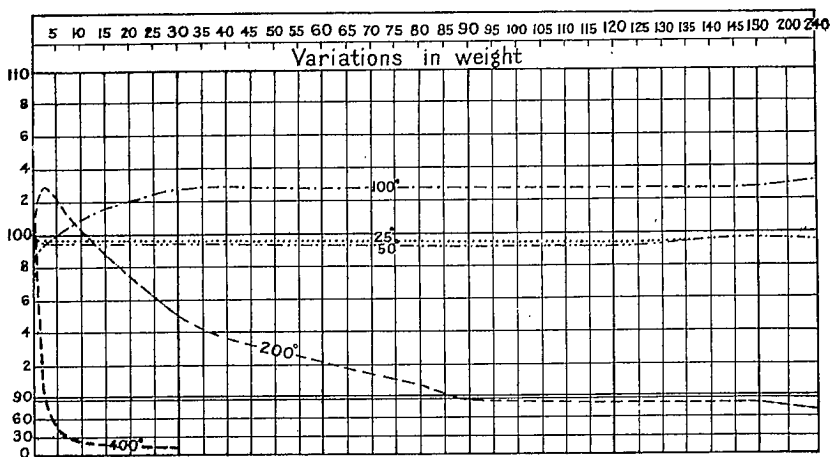
FIG. 24.

(Redrawn from Fayol.)

The following are among the conclusions arrived at by Parr and Kressmann[1] after making a number of experiments on spontaneous combustion of coal.

1. "A number of oxidation processes are involved, which are more or less distinct in character, some being relatively slow and moderate in form, while others are rapid and vigorous in their action."

2. "In general it may be said that for a given coal a point exists, as indicated by the temperature, below which oxidation is not ultimately destructive. The continuance of this point is dependent upon certain accessory conditions; if these conditions are withdrawn, the oxidation ceases. On the other hand above this critical point, which is best indicated by temperature, oxidation is ultimately destructive and is characterized by the fact that it does not depend for its continuance upon external conditions, but is self-propelling or autogenous."

3. "The point of autogenous oxidation, while varying for different conditions may be indicated by temperatures of the mass ranging from 140° to 160°C in an atmosphere of

[1] Univ. of Illinois, Eng. Expt. Station. Bulletin No. 46, 1910.

oxygen or approximately between 200° to 275°C in oxygen diluted with nitrogen, as in air, depending to a great extent upon the fineness of division. The phenomenon of fire or actual kindling does not occur until a much higher temperature is reached, usually beyond 350°C."

4. "The temperature at which autogenous oxidation begins is the sum of numerous temperature components, each one of which either because of its own contribution to the total heat quantity or because of its function as a stimulus for chemical activities, must be looked upon as a dangerous factor, tending directly to the ultimate result of active combustion throughout the mass."

An enumeration of the more important factors in oxidation is then given together with a short discussion of each. These are, in brief:—

a. External sources of heat.—Oxidation, especially of the lower form is greatly accelerated by, and in some cases dependent upon, external or physical sources of heat such as climatic or seasonal temperature, the heat of the sun, etc., contact with steam pipes, and heat of impact or pressure due to depth of piling or method of loading or unloading.

b. Fineness of division.—Coal in a state of fine division exposes a relatively very large surface area to oxidation. It especially facilitates the initial form of oxidation described under c.

c. Easily oxidizable compounds.—A first or initial stage of oxidation exists in bituminous coals which does not result in the formation of carbon dioxide. There are present in coals of this type, unsaturated compounds, which have a marked avidity for oxygen at ordinary temperatures, the products being humic acid or other fixed constitutents of the coal texture.

d and e. Pyrites and moisture.—These have already been dealt with. The oxidation of pyrite may be considered the second stage in the oxidation of coal.

f. The oxidation of Carbon and Hydrogen.—A third stage of oxidation of the carbonaceous material exists by reason of the tendency of certain of the hydrocarbon compounds of coal to oxidize with the formation of carbon dioxide and water at temperatures in excess of 120° to 140°. This oxidation does not take place appreciably at ordinary temperatures. It is, however, a dangerous stage in the process of oxidation as the large amount of heat given out may quickly raise the temperature of the mass to the critical temperature. Any initial process which results in raising the initial temperature 50°C above the ordinary temperature would, in all probability, have enough material of the sort involved in such action to continue the action until the temperature had been raised another 50° and then this third type of oxidation would begin.

g. The fourth stage of oxidation may be indicated as occurring at temperatures above 200° to 275° and differs from the previous stages in that it is autogenous. Activity in this stage is further accelerated by the beginning of exothermic decomposition of the coal itself. Ignition begins at a still higher temperature, usually above 300° to 400°C.

Haldane and Meachem[1] are of the opinion that the carbon dioxide evolved when coal is oxidized is not due to the combination of oxygen with the carbon of the coal, but that it is due to decomposition of carbonates by means of sulphuric acid formed by oxidation of the pyrite.

The chemical reactions which take place when pyrite is oxidized are:—

$$4\ FeS_2 + 15O_2 + 8H_2O = 2Fe_2O_3 + 8H_2SO_4$$
and $$8H_2SO_4 + 8CaCO_3 = 8CO_2 + 8CaSO_4 + 8H_2O$$
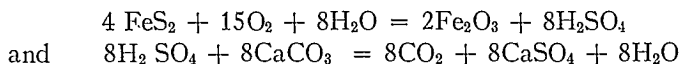
[1] T. I. M. E. Vol. 16, 1898, p. 457.

"It will be seen that for every 15 volumes of oxygen which disappear in this reaction 8 volumes of carbonic acid are liberated. It will be found on calculation that in air passing over such material, the ratio of diminution in oxygen and increase in carbonic acid will be 1:·74. This corresponds very closely to the average ratio observed in the air from old workings by Messrs. Haldane and Atkinson, and in the return air from most pits."

The reasons given to support this theory are numerous. Among them are the fact that some pyrites in coal does oxidize when exposed to air, the fact that sulphuric acid is thus formed and that this sulphuric acid will attack any carbonates with which it comes in contact, and the fact that the proportion of carbon dioxide thus formed is about sufficient to account for what is actually found to be liberated. This theory also explains how there can be absorption of oxygen without evolution of carbon dioxide. Against this theory, however, we have a great mass of recent observation and opinion as already set forth on pages 31 to 43.

A recent paper by **Lamplough and Hill**[1] on the slow combustion of coal dust describes some ingenious experimental work which was well carried out. Their experiments and results, in so far as they bear on the matter under discussion, may be summarized as follows.

The evolution of heat and the absorption of oxygen were measured by placing a weighed quantity of coal[2] in a pint Dewar vessel (vacuum flask) filled with oxygen and fitted with a sensitive electric thermometer consisting of a four junction copper constantan thermopile inserted in the coal. The flask was connected with an oxygen reservoir of about double its capacity, and provision was made for automatically registering the gas pressure continuously throughout the experiment, so that the quantity of oxygen absorbed from time ·to time could be calculated. The whole absorption system was enclosed in a water thermostat which could be kept approximately constant at any desired temperature, and provision was also made to replenish the supply of oxygen from time to time from an external source, the quantity added being calculated from the changes in pressure, etc.

The gases in the apparatus were measured and analysed at the beginning and end of each experiment to determine the amount of carbon dioxide produced and methane envolved.

Lamplough and Hill experimented with ten samples all told, six of them being from different parts of the Barnsley seam and one from the "Bullhurst" seam; the eighth coal was an anthracite. The additional samples were: a Barnsley top soft carrying 43% of pyrites and a sample of pure lump pyrites collected from the rubbish in a coal yard. The results of their experiments, which were conducted at 45°, are summarized in the following tables and conclusions copied from their paper.

---

[1] Trans. Inst. Min. Engrs. Vol. 45, 1913, pp. 629-657.
[2] The coal was ground to pass through a 30 mesh sieve "and 300 grammes were used in most of the experiments." In the earlier experiments so much marsh gas was given off that very little oxygen could enter, and thereafter the coal previous to its introduction into the apparatus, was heated in a florence flask in vacuo to 47° for a day. The gas evolved was measured and allowed for by analysis.

TABLE XLI.

Summary of Results

(Lamplough and Hill)

(1)	(2)	(3)	(4)	(5)	(6)
Description of coal.	Ash. %	Iron. %	Oxygen absorbed[1]. c.c. dry at normal T. & P.	Heat evolved[1]. Calories.	Calories evolved per cubic centimetre of oxygen absorbed.
Top softs, containing 43 per cent of pyrites[2]	40	20·2	321	1,158	3·6
Anthracite	—	—	132	495	3·6
Top coal	1·1	0·1	459	1,275	2·8
Bullhurst	3·2	1·2	60	234	3·8
Hard coal No. 1	6·0	0·1	195	705	3·6
Top softs:—					
First part	2·8	0·8	534	1,684	3·2
Second part	—	—	1,041	3,089	3·0
Hard coal No. 2	4·0	0·1	1,110	3,196	2·9
Slack	3·2	1·4	31	115	3·7
"Iron pyrites"[2] from coal	—	—	240	800	3·3

[1] The paper states that the amount of coal used in "most of" the experiments was 300 grammes, and it is probable that the figures in these two columns refer to this quantity in all cases, but unfortunately the paper is not specific on this point. It is unfortunate also that the several experiments were not of equal length although the time averaged about 12 hours.

[2] The word "pyrites has been used throughout to designate the sulphide FeS_2, without prejudice as to its nature. From its crystalline form it was evident that some of the material used in the last experiment was pyrites and not marcasite."

TABLE XLII.

Summary of Results

(Lamplough and Hill)

(1)	(2)	(3)	(4)	(5)	(6)	(7)
Description of coal.	Oxygen absorbed.	Carbon dioxide evolved.	Carbon dioxide evolved per 100 cubic centimetres of oxygen absorbed.	Initial rate of absorption per hour.	Final rate of absorption per hour.	Final temperature.
	c.c.	c c.	c c.	c c.	c.c.	°C.
Top softs, containing 43% of pyrites	321	118·0	37·0	54·0	55·0	51·2
Anthracite	132	0·0	0·0	59·0	32·0	49·4
Top coal	459	5·4	1·8	46·0	46·0	52·7
Bullhurst	60	0·4	0·6	11·2	7·7	47·2
Hard coal No. 1	195	2·7	1·3	18·6	22·0	50·0
Top softs:—						
First part	534	3·6	0·7	186·0	—	—
Second part	1,041	20·8	2·0	—	189·0	66·4
Hard coal No. 2	1,110	12·1	1·0	90·0	78·0	62·5
Slack	31	0·02	0·06	14·0	13·7	46·0
"Iron pyrites" from coal	240	102·0	43·0	475·0	—	—

"General conclusions:—(1) The heat which was evolved when coal-dust was heated in an atmosphere rich in oxygen was nearly proportional to the volume of oxygen absorbed, the mean value being 3·3 calories of heat produced during the oxidation brought about by the absorption of 1 cubic centimetre of oxygen.

(2) The production of heat may be attributed to two chemical changes, namely, the oxidation of iron pyrites and the oxidation of carbonaceous matter.

(3) The oxidation of carbonaceous matter in coals practically free from iron was not so rapid as in those containing much iron, but continued for a long time, comparatively little carbon dioxide being evolved, so that eventually there was considerable evolution of heat even in the absence of ventilation.

(4) The oxidation of iron pyrites picked from coal was at first very rapid, but soon almost ceased, because the flask became choked with carbon dioxide, which prevented further admission of oxygen. With conditions under which there is diffusion of air through the coal-dust, and when a considerable amount of iron pyrites is present, the oxidation of this mineral would possibly be the predominant factor in the spontaneous heating of such coal-dust.

(5) Oxidation of coal-dust takes place in contact with gas containing much less than the normal proportion of oxygen present in air.

(6) The oxidation of carbonaceous matter and the total changes occurring in pyrites during the absorption of a given volume of oxygen produce about the same amount of heat, so that the rate at which heat is given off in the oxidation of coal-dust due to either process may with surprising nearness be determined by the volume of oxygen absorbed."

Lamplough and Hill's experiments are very interesting and their observations regarding pyrite (marcasite) are no doubt largely justified in the case of coals carrying considerable quantities of very finely divided pyritic material; but their conclusions go very far in view of the amount of work done and it would seem reasonable to offer the following criticisms.

Referring to the experiment with pyrites they say: "It was seen from the pressure curve that the greater part of the carbon dioxide was evolved after most of the oxygen absorption had taken place. It may be concluded from this that the carbon dioxide is produced as a result of a reaction brought about by the products of the oxidation of the pyrites." The above pyritic material was possibly free from carbonaceous matter, but unfortunately an analysis is not given either for carbonate or coaly matter and no microscopic examination was made. The large evolution of carbon dioxide from this material in the short period over which the experiment lasted might indicate long previous exposure or the presence of a considerable amount of carbonate. It may be also noted that the amount of carbon dioxide evolved from the various coals appears from the table to have no relation whatever to pyritic content.

Considering the experiments with "Top softs containing pyrites" and Top coal; if pyrites in coal has such a large effect in the generation of heat spontaneously how is it these two experiments are so similar: the one coal containing 43% and the other 0·2% pyrites. Both, however, contain similar carbonaceous matter differing only in proportion.

Reference to column 6, Table XLI would seem to justify Dr. Harger's remarks in discussion of the paper to the effect that it is inconceivable that "Top softs" and anthracite should give the same value of 3·6 cals. per c.c.

of oxygen absorbed, when the one evolves·so much carbon dioxide and the other none at all. Harger further finds no evidence in the paper justifying conclusions Nos. 2 and 4.

Had the experiments been longer and all of equal duration much more useful information might have been obtained, as some of the coals would probably have eventually commenced to split off oxygen again as carbon dioxide.

In the cases where the experiment was stopped owing to accumulation of carbon dioxide, the suspension of a small vessel containing some carbon dioxide absorbent in the container with the coal might have been tried; this would perhaps have permitted longer experiments.

The chief weakness which appears in the method is this accumulation of carbon dioxide and methane in the vessel with the coal and the consequent lowering of the partial pressure of oxygen. The coal is therefore subjected to an atmosphere of rapidly changing composition. This difficulty was avoided in the method employed at McGill University, in October 1912, the coal being subjected to the influence of an atmosphere of constant composition and the products of combustion being continuously replaced by fresh gas, while the quantities of carbon dioxide and water vapour and hydrocarbons in the gas discharged were determined immediately after leaving the coal. Experiments may thus be continued for a considerable time so that any products indicating oxidation of pyrites or loss of carbon and hydrogen may be more easily detectable by analysis.

A final criticism is that no figures are given which make it possible to estimate the effect of errors in sampling in the several experiments. We have already seen that such errors usually exist and that their correction often increases the intelligibility of the results.

Winmill has just published[1] the results of some experiments on Barnsley "hard" coal at temperatures of 30°, 40°, 50° and 60°C. showing a very great increase in the rate of oxidation as the temperature rises. A description of these results and a series of tables will be found on pages 86-101 at the end of an abstract of his work, the main part of which was on the same coal at ordinary temperatures.

PORTER, BILLINGTON, AND CAMERON EXPERIMENTS.

Porter, Billington, and Cameron carried on a series of tests on the behaviour of coal in an atmosphere of oxygen at elevated temperatures at McGill University from 1912-14. Their work will now be set forth in considerable detail as it has not heretofore been published.

The investigation was undertaken by Dr. Porter as a supplement to his economic study of the coals of Canada, and in its initiation he had the advice and assistance of Mr. Edgar Stansfield, Chief Chemist to the Fuel Testing Division of the Mines Branch of the Department of Mines, Ottawa, who has been his chief chemist on the original research. The laboratory

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work which was conducted in the Mining Department of McGill University, was done at first by Mr. E. E. Billington, and later by Mr. A. E. Cameron, successively holders of Douglas Research Fellowships in Mining. The following report is largely made up from the notes of these gentlemen.

<div align="center">DESCRIPTION OF APPARATUS AND ITS USE.</div>

The research as outlined in advance was as follows:—

1. That each sample of coal be taken at the mine face, and be hermetically sealed at once under mine water in a bottle.

2. That this coal be crushed immediately before use, every precaution being taken to prevent the access of air.

3. That a portion of the wet sample so obtained, be placed in a suitable container through which gases, either dry or moist, at a constant temperature, could be passed.

4. That the container be of such a nature as to prevent radiation of heat to or from the coal and gas during the experiment.

5. That the coal be thus first brought to a constant physical condition by passage of a quantity of a neutral gas through it; i.e., the moisture in the coal should arrive at a state of equilibrium with the moisture —if any—of the entering gas; also any methane or other hydrocarbon physically emitted by the coal at that temperature should be removed, or the velocity of such emission be determined.

6. That the entering gas should first be passed through a suitable gas-washing apparatus to insure its purity.

7. That when the coal and the entering neutral gas reached a condition of equilibrium, the entering gas should be changed to oxygen, which had been previously suitably purified.

8. That any rise in temperature in the coal or its atmosphere of oxygen should be noted by two thermometers placed, the one in the gas inlet of the container, and the other in the gas outlet of the same.

9. That further, any substances emitted by the coal due to chemical action with the oxygen, should be collected by a suitable absorption apparatus.

Diagrams of the apparatus are shown in Figs. 25, 27A, and 29. The original plan called for suction as the means of inducing a current of gas; this meant that when in use the container was under a considerable reduction in pressure, and in practice it proved difficult to prevent leakage of air into the apparatus. It was, therefore, decided to prepare in advance a large quantity of the gas required under pressure, and the apparatus was thereafter so run that the purifying train was under a slight pressure, the absorption under a slight vacuum, and the container as nearly as possible at atmospheric pressure.

The Gases, Purifying Train, and the Oxidation Apparatus and Accessories.

The Gases were at first produced by chemical methods, and after some experimenting both oxygen and nitrogen of good quality were produced satisfactorily, but it was later found possible to buy both gases of a high degree of purity under high compression (120 Atm). The oxygen contained but $0 \cdot 2\%$ of impurity chiefly nitrogen, and the nitrogen only about $0 \cdot 5\%$

(*Porter and Billington.*)
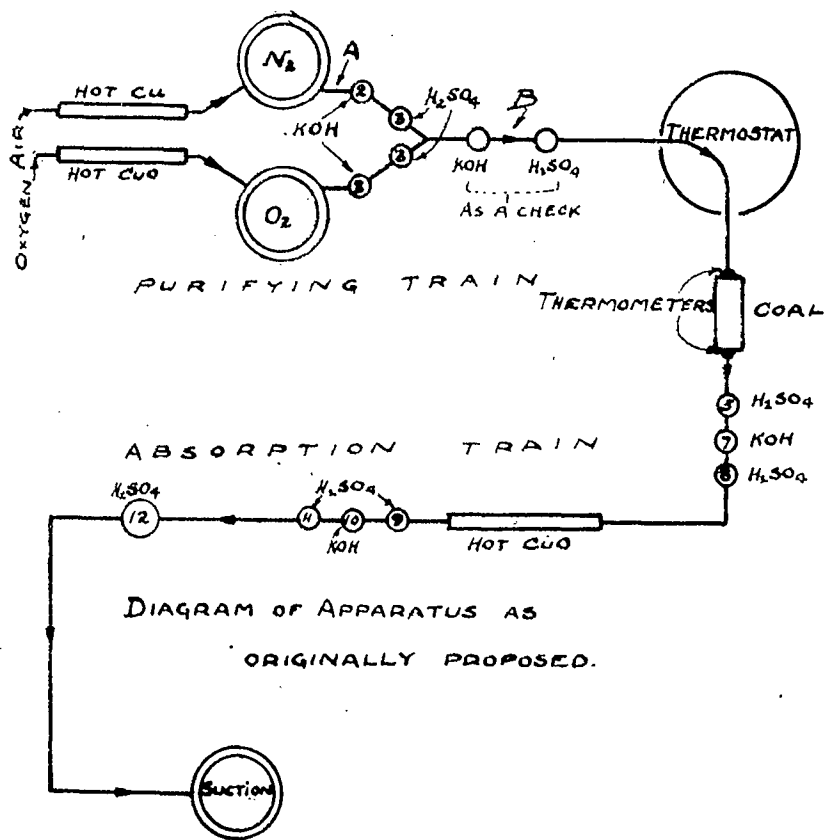
Fig. 25. Diagram of original apparatus.

of impurity, which could easily be removed as it was chiefly carbonic acid and oxygen. All waste of time in preparing oxygen and nitrogen was thus done away with, and a supply of gas of constant composition assured.

The Purifying Train as used underwent but very few alterations throughout the whole series of experiments, the only important change being the substitution of a large U tube containing stick phosphorus (No. 1, Fig. 29), as more satisfactory than the bottle containing pyrogallol solution (A, Fig. 25) in the nitrogen train; this U tube being kept in a dark container to prevent formation of red phosphorus.

THERMOMETERS

SADDLE FELT

COTTON WASTE

HINGE

FELT

WATER LINE

HEATER

COTTON WOOL

TOLUOL REGULATOR

STIRRER

SAWDUST

1" BOARD

SAWDUST

SAWDUST

(Porter and Billington.)
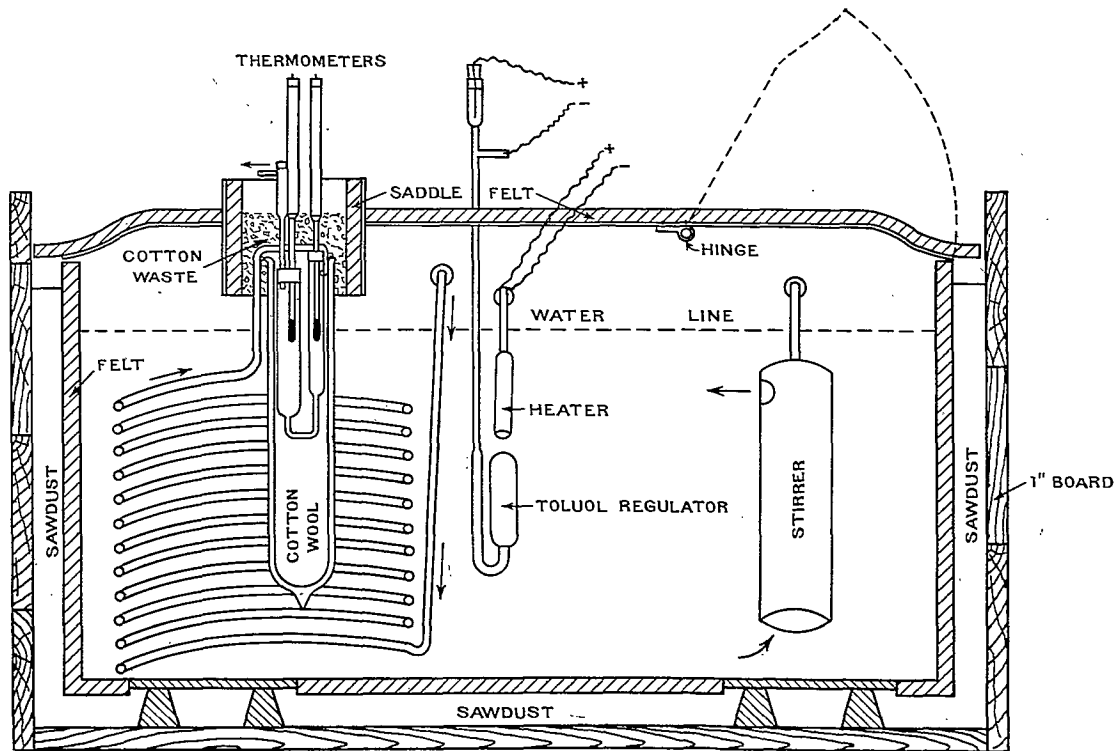
FIG. 26. Original thermostat and contents.

The Thermostat consisted of a tin-lined copper vessel, $36'' \times 13'' \times 13''$; fitted with a tinned lid. For the arrangement of apparatus in the thermostat, see Fig. 26.
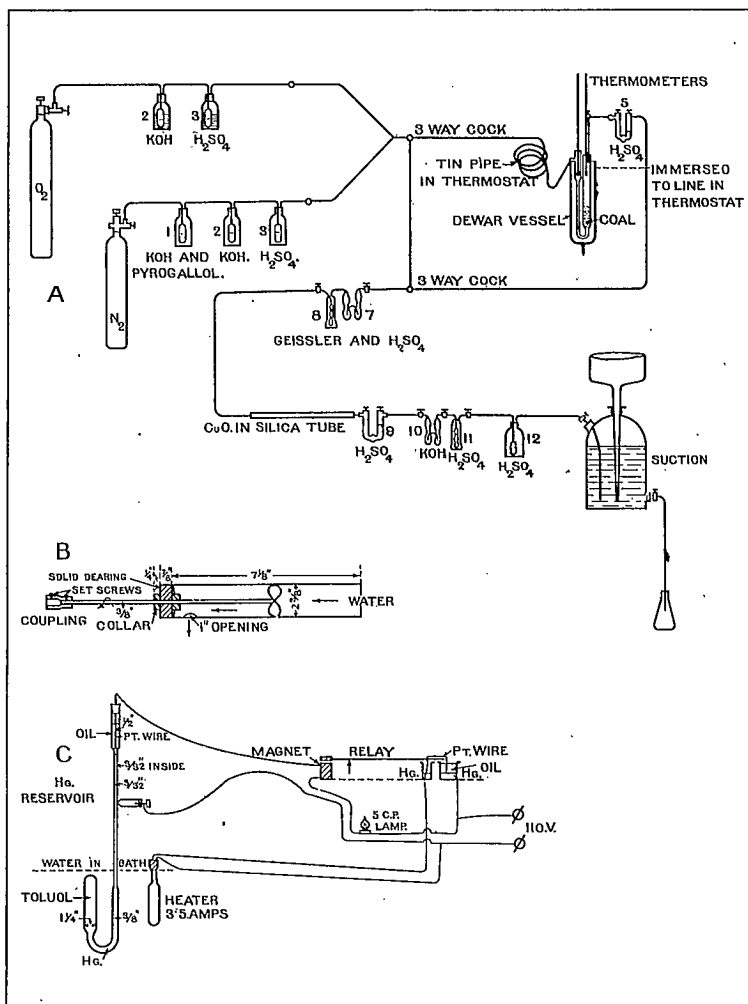
FIG. 27. A—General diagram of apparatus.
B—Stirrer.
C—Thermo regulator diagram.

The thermostat contained water up to a convenient level, and was fitted with a water gauge, so that loss by evaporation might be detected before injury to the heater occurred. The temperature was controlled by means of a toluol mercury regulator, operating a 110 volt, 3:5 amp. water-heater by means of a relay. (Fig. 27C). The water was agitated by means of a motor driven stirrer. (Fig. 27B).

The gas before entering the coal container was led through a 50 ft. spiral of $\frac{1}{8}$ inch diameter tin pipe coiled in the thermostat bath. The container stood in a deep Dewar vessel, which in the first season's experiments was immersed to within a few inches of its top in the water of the thermostat, to minimize change of temperature of the gas, between the place where the tin pipe left the water and the inlet of the container.

The thermostat was insulated by being completely enclosed in a jacket of thick saddle felt; and stood upon a number of corks in a large box, 32″ × 15″ × 17″, having walls 1″ thick. The space between the felt and the walls and bottom of the box was filled with dry sawdust. The lid was fitted with a wooden box 6″ × 6″ × 6″, having a hole in one end, through which the Dewar vessel which exactly fitted was introduced at will. (Fig. 28B). The other end of the lid was so hinged as to allow of easy access to the stirrer and heating apparatus in case of necessity, without any disturbance of the container and coal.

The Thermoregulator and Heater originally made by Mr. Billington, restricted the fluctuation of bath temperature to a range of 0·2°C. After working excellently for two months the glass of this regulator crystallized and broke in the middle of an experiment; its place was taken by another one of similar design (Figs. 26 & 27C), but made with glass tubing of $\frac{3}{16}$″ outside diameter, and $\frac{1}{8}$″ bore, whereas the original tubing had been of $\frac{11}{32}$″ diameter, and $\frac{1}{16}$″ bore. The later experiments were all conducted using this regulator, which permitted fluctuation of bath temperature over a range of 0·6°C.

It may be worthy of note that the regulators always did better work when the stirrer was in operation, as a certain amount of vibration made the mercury contact more prompt.

The spark at make and break between the platinum wire and mercury surface was extinguished by means of heavy transformer oil. This oil required cleaning out every six hours, as the sparking caused sediment to form which interfered with efficient regulation.

The Stirrer (Figs. 26 & 27B) was made entirely of brass, and was operated by a $\frac{1}{6}$ H.P. Crocker and Wheeler motor, belted to a countershaft, from which the stirrer was driven by means of a variable speed friction drive.

The Container was changed several times before a satisfactory form was devised. The first suggestion was the use of a vacuum vessel fitted with an inlet at the bottom, in which the coal might be placed without the use of any inner vessel. (Fig. 28A). This very simple arrangement was abandoned because it necessitated the use of a submerged connexion between the vessel and the end of the tin pipe; it also was found to be too cumbersome to allow of accurate weighing of the coal and vessel when desired.

The form of container finally adopted was that shown in Figs. 26 and 28B. Into this apparatus the coal was at first placed in a tight-fitting gauze
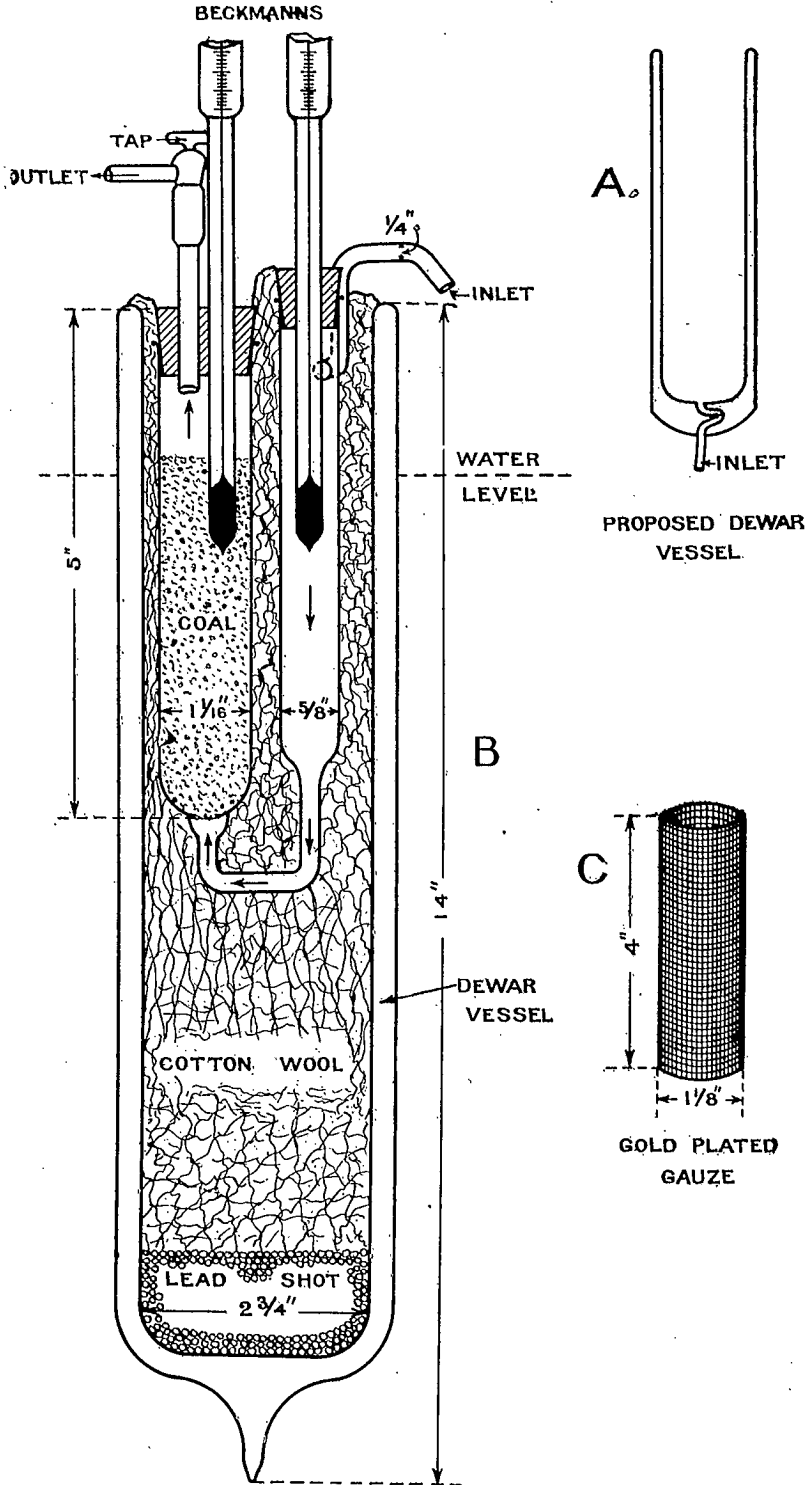
FIG. 28. Details of apparatus.

(Porter and Billington.)

receptacle, 4″ long by about 1⅛″ diameter made of 60-mesh gauze which had been previously gold plated (Fig. 28C). The idea in using the gauze was that both gauze and coal might be readily removed for weighing, and quickly replaced, no gas connexions having been disturbed. This method was given a good trial, but proved troublesome, as in spite of the fact that the gauze was a very tight fit in the glass container, too much gas passed between the gauze and the wall of the vessel, instead of through the coal. When, during this trial, it was required to determine the weight of the gauze and coal, they were quickly put into a special weighing tube in which the air could be replaced at will by nitrogen.

In the later experiments the gold gauze was not used, the coal being simply introduced into the container on a bed of glass wool, (Fig. 28B), and container, coal and special stoppers were weighed together when required.

The Dewar vessel was fitted into the box Fig. 26, by means of a piece of rubber cloth wedged in with cotton waste, to prevent the admission of too much moist air into the container box. The container itself was packed into the Dewar vessel with fine cotton wool. See Fig. 28B.

The Beckmann thermometers, Figs. 26 and 28, were lent by Dr. H. T. Barnes, F.R.S., Director of the Department of Physics at McGill University; they were tapped before reading by an electric buzzer. Readings were taken by means of a telescope from a distance of four feet.

The Absorption Train.

By reference to Figs. 25, 29, and 34 it can be readily seen that this train underwent considerable changes during the preliminary experiments. Fig. 25 represents the train as originally designed, Fig. 29 the form used for the first series of experiments, and Fig. 34 its 1914 form. The changes were mainly substitutions of dry or solid absorbents for the wet ones in order to lessen the weight of the train and reduce the head to be overcome by suction.

The reactions which might take place between coal and gas during any experiment were assumed to be as follows:—

When the coal is submitted to the action of dry nitrogen, purely physical changes occur:—

      (1) Mechanical drying or evaporation of moisture;
      (2) Evolution of carbon dioxide, if, as is commonly the case, this gas was contained in the original coal under pressure;
      (3) Evolution of methane or other hydrocarbons (C_nH_{2n+2}) from the coal, these gases almost always existing in the coal as it occurs in the seam.

When oxygen is being passed over the coal, oxidation of some of its constituents usually takes place, the substances formed by this chemical

FINAL FORM OF APPARATUS

BILLINGTON.

(*Porter and Billington.*)
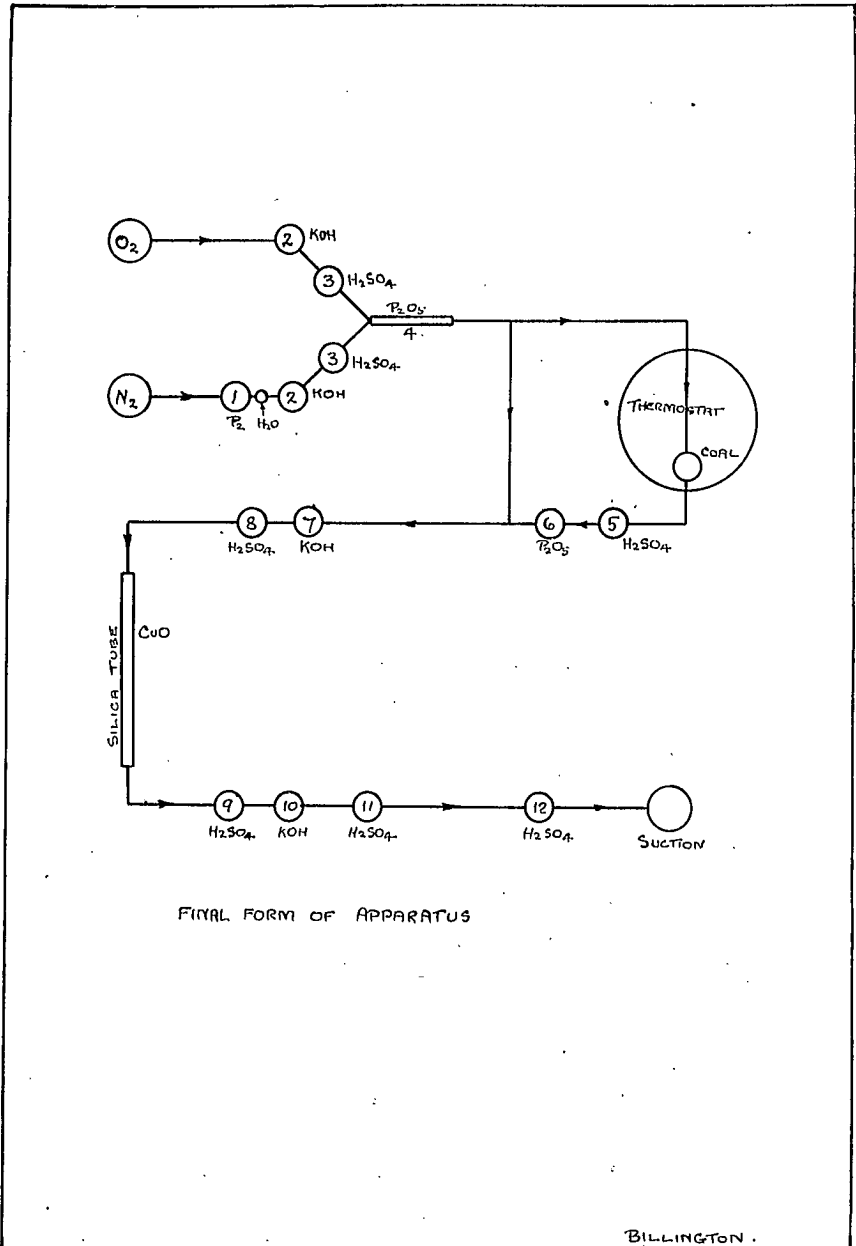
FIG. 29.   Second form of apparatus.
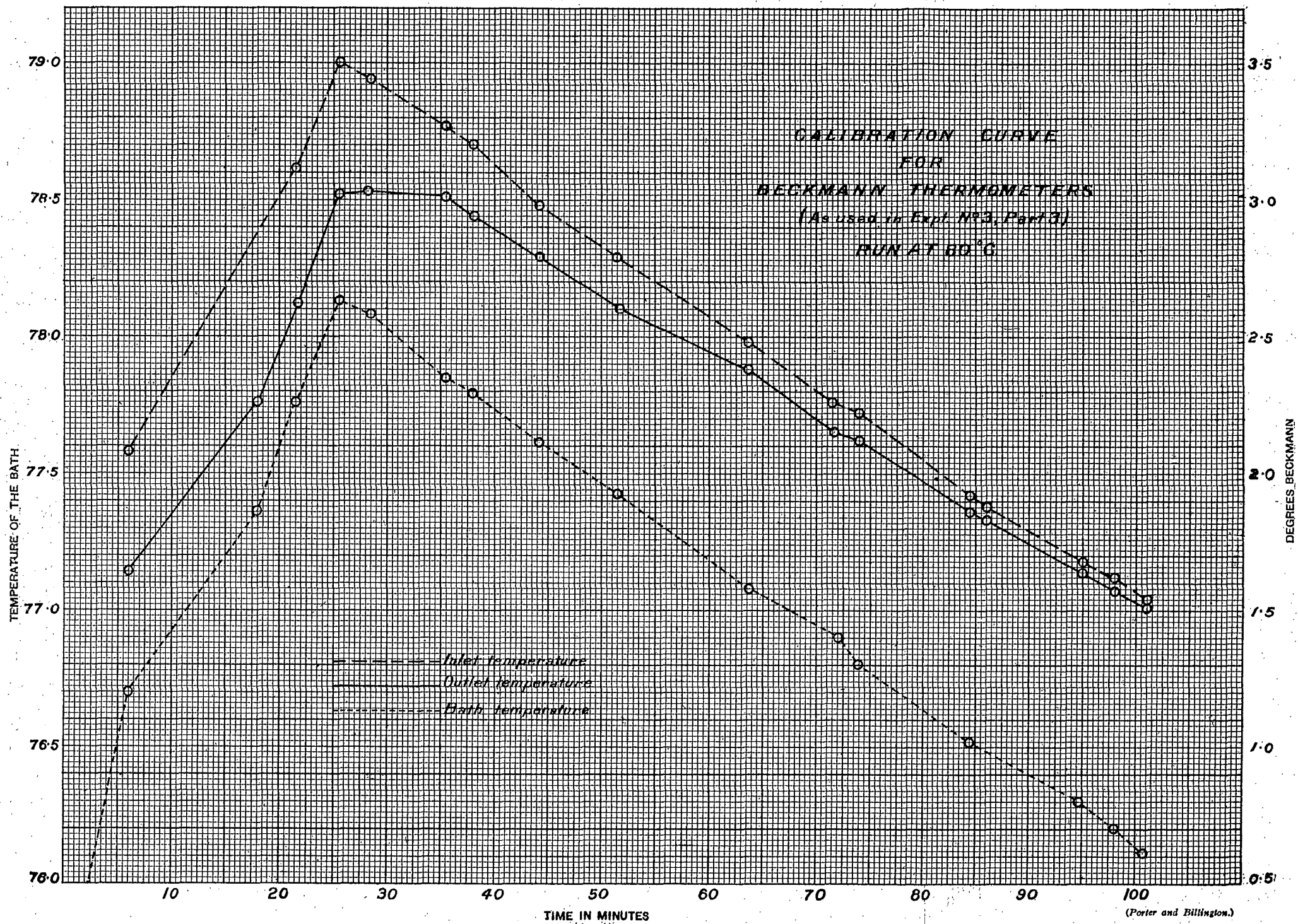
FIG. 30. Calibration curve of Beckmann thermometers.

Expt. III, Part I

Expt. III. Part 2
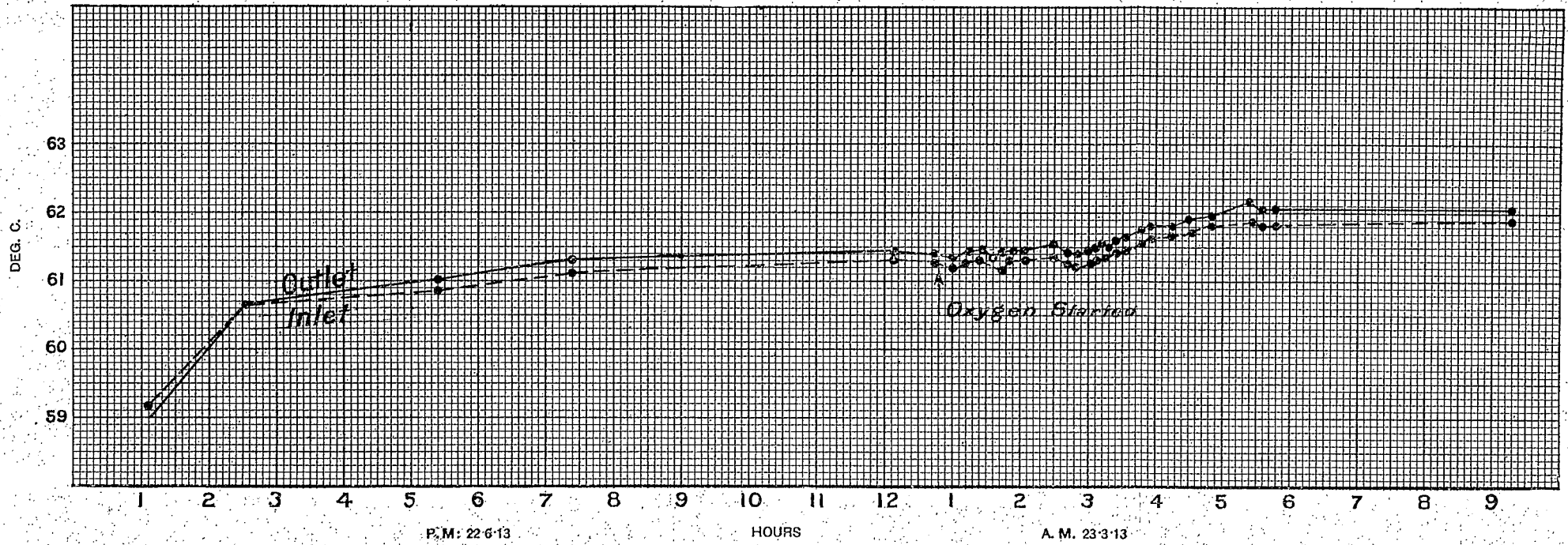
(Porter and Billington.)
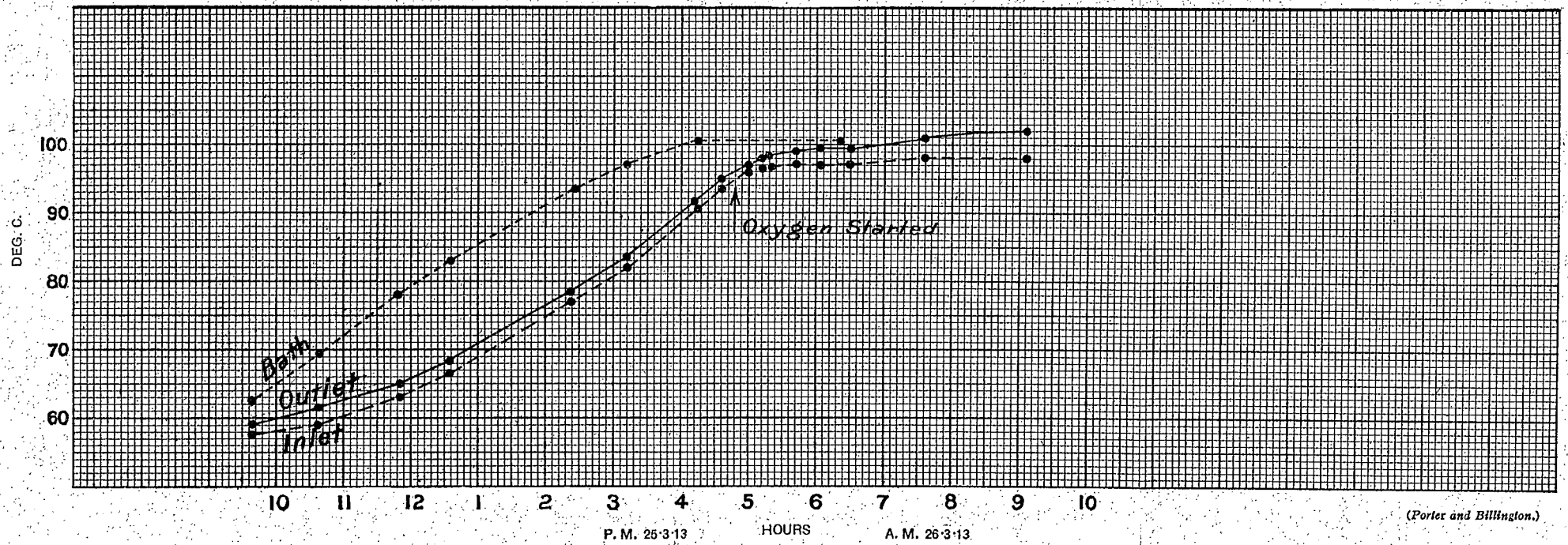
Fig. 31. Graphic record of experiment III, Parts 1 and 2.

EXPT. Nº 3, THIRD PART

RUN AT 80°C.

Thermometer pushed into the container

Thermometer removed from container

Probable Curve

Probable Curve

Outlet

No gas

Inlet

No gas O₂

No gas

Operator omitted tapping of Beckmanns

DEGREES BECKMANN

DEGREES BECKMANN

No gas

N₂

Inlet

No gas

Outlet

O₂ No gas O₂

O₂

Bath

Container filled with an atmosphere of Nitrogen

Container filled with an atmosphere of Oxygen

Supply of fresh gas shut off — Gas on — Gas supply shut off — on off on — Gas off on — Gas supply shut off — on

90
85

87

88

HOURS

P.M. 27·3·13

A.M. 28·3·13

P.M. 28·3·13

(Porter and Billington)

FIG. 32. Graphic record of experiment III, Part 3.
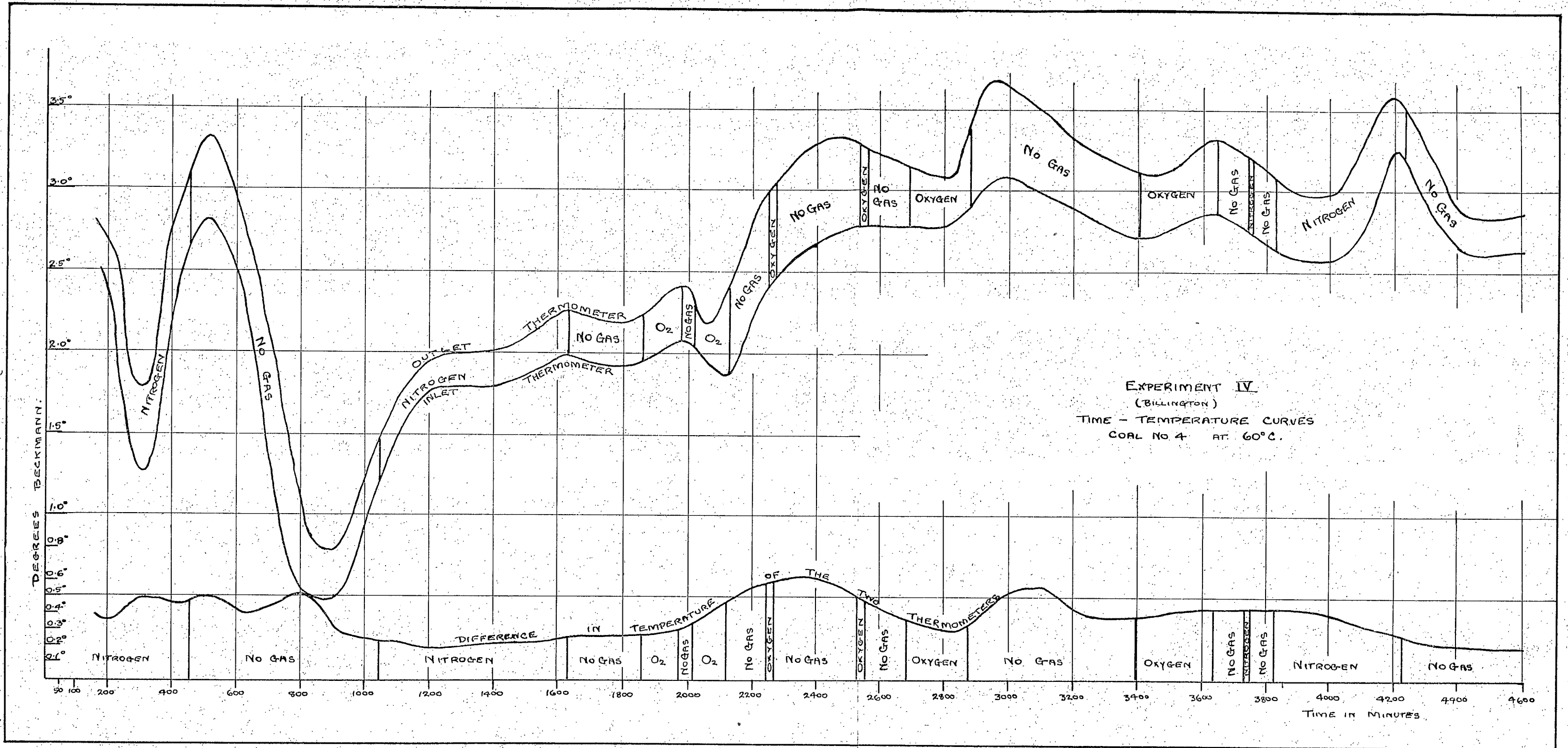
FIG. 33. Graphic record: experiment IV.

(Porter and Billington)

action would probably consist of water, carbonic acid and hydrocarbons split off from the coaly matter.

> Any water evolved, either physically or through chemical action, was absorbed in sulphuric acid and phosphorus pentoxide, (tubes Nos. 5 and 6 in Fig. 29).
>
> Carbon dioxide was absorbed by the Geissler bulb containing potassium hydroxide, (tube No. 7 in the diagrams) any moisture lost by No. 7 was collected in the guard tube of sulphuric acid (No. 8).
>
> The silicon combustion tube containing red-hot copper oxide was assumed to burn up all hydrocarbons to carbon dioxide and water, which products were collected by means of potash bulbs and a sulphuric acid tube similar to those described above.

Before weighing each piece of apparatus it was wiped with a clean linen cloth, and allowed to stand ten minutes in the balance case. The weights were counted as they lay on the pan, and checked by observing the blank spaces in the weight-box.

With the apparatus as described above, Mr. Billington carried out a first series of experiments the results of which are clearly shown in the appended curves and table. The coal used was a semi-lignite from Kipp, Alberta. The sample was taken at the face of the workings by Mr. de Hart, and immediately packed in mine water and sealed as were all other samples dealt with in both series of experiments. In all, four experiments were run. Of these the first two were of a preliminary nature, made to test the apparatus and gain experience, and are not reported, as no results were obtained which justified publishing.

The curves Figs. 31 and 32 show the results of the third experiment which was run in three parts. In this experiment no attempt was made to calculate the ratio of evolved substance to the oxygen absorbed, but attention was paid solely to the temperature rise with oxygen.

In the fourth experiment a complete test was made over some 72 hours. The results of the absorption train calculations are shown in Table XLIII, p.124. The original Time-Temperature record drawn by Mr. Billington, was some twelve feet long and this has been considerably reduced and reproduced in Fig. 33.

The third curve in Fig. 33 has been obtained by plotting the difference between the ordinates of the outlet and inlet thermometer curves in order to more clearly show the temperature rise in oxygen, so that it may be directly comparable with the results obtained by Mr. Cameron in the later experiments.

As shown by the last curve, the maximum temperature rise obtained with oxygen was of the order of $0.7°C$. There was, however, an average difference of $0.2°$ C. between the inlet and outlet thermometers at all times,

so that in reality the temperature rise was of the order of $0 \cdot 5°C$. with oxygen and not $0 \cdot 7°C$. as shown. The curve has not been corrected for the average difference in temperature throughout the experiment.

The results obtained by Mr. Billington in the above tests should be considered preliminary to a second series of tests made by Mr. Cameron in the winter and spring of 1913-14. The results of both series will be considered in drawing final conclusions.

TABLE XLIII.

Record of Results—Experiment IV.

(Porter and Billington)

Coal taken: $20 \cdot 6335$ grammes.   Temperature of bath: $60°C$.

Time in minutes.	Water evolved.	Carbon dioxide evolved.	Hydrogen in hydrocarbons evolved.	Carbon in hydrocarbons evolved.
0	Atmosphere in	apparatus is nit	rogen	
946	·0185	·0133	·0112	·0416 ?
1,750	·0075	— ·0023	·0000	— ·0029
1,860	Atmosphere in	apparatus chan	ged to oxygen	
2,118	·0155	·0056	·0035	·0006
2,880	·0060	·0102	— ·0021	·0073
3,634	·0000	·0050	·0020	·0047
4,571	·0205	·0223	·0191	·0176

NOTE,—Apparent gain in weight of coal $= 0 \cdot 4858$ gramme.

Apparent gain in weight of coal per gramme of coal $= 0 \cdot 0236$

Real gain in weight of coal, including weight of C and H evolved $= 0 \cdot 7071$ gramme.

CO_2 evolved weighed $0 \cdot 0541$ and therefore accounts for less than $\frac{1}{10}$ the O_2 absorbed.

The analyses of coal before and after the experiment showed no detectable difference.

Before beginning the second tests several changes were made in the apparatus to meet difficulties which developed in the earlier work.

Changes in the Apparatus.

Fig. 34 shows the general layout of the apparatus as reconstructed. A comparison with Fig. 29 will show that the purifying train underwent no alteration with the exception of the removal of the long phosphorus pentoxide tube (4). This was done to economize space and simplify the apparatus, it having been found by analysing the gases that this phosphorus pentoxide tube was an altogether unnecessary guard, there being no trace of moisture in the gas after it left the last sulphuric acid bottle on its way to the thermostat.

Considerable change, however, was made in the thermostat, the principal one, as shown by comparison of Fig 26 with Fig.35, being the removal of the Dewar vessel from its position in the bath to a separate box attached to the end of the thermostat. This was done on Billington's suggestion
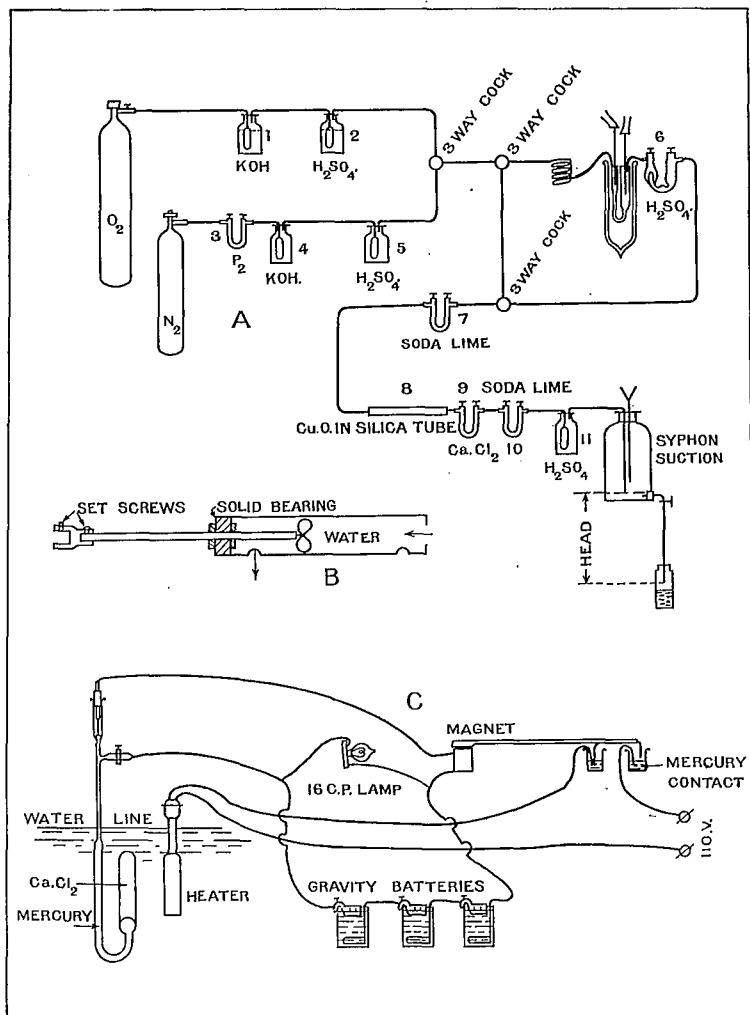
(Porter and Cameron.)

FIG. 34 A—General diagram of final apparatus.
B—Stirrer.
C—Thermo regulator diagram.

in order to make the gas connexions more accessible and to minimize any chance of moisture from the bath water finding its way into the Dewar vessel and thus possibly giving a variable temperature in that vessel.

When first put into the box the Dewar vessel was wrapped with 1 inch of felt and the whole packed around with sawdust, but it was soon found

that there was a sufficient difference in temperature between the inside and outside of the Dewar vessel to cause appreciable loss in temperature in the vessel, and consequently the box was further modified as shown in Fig. 35.
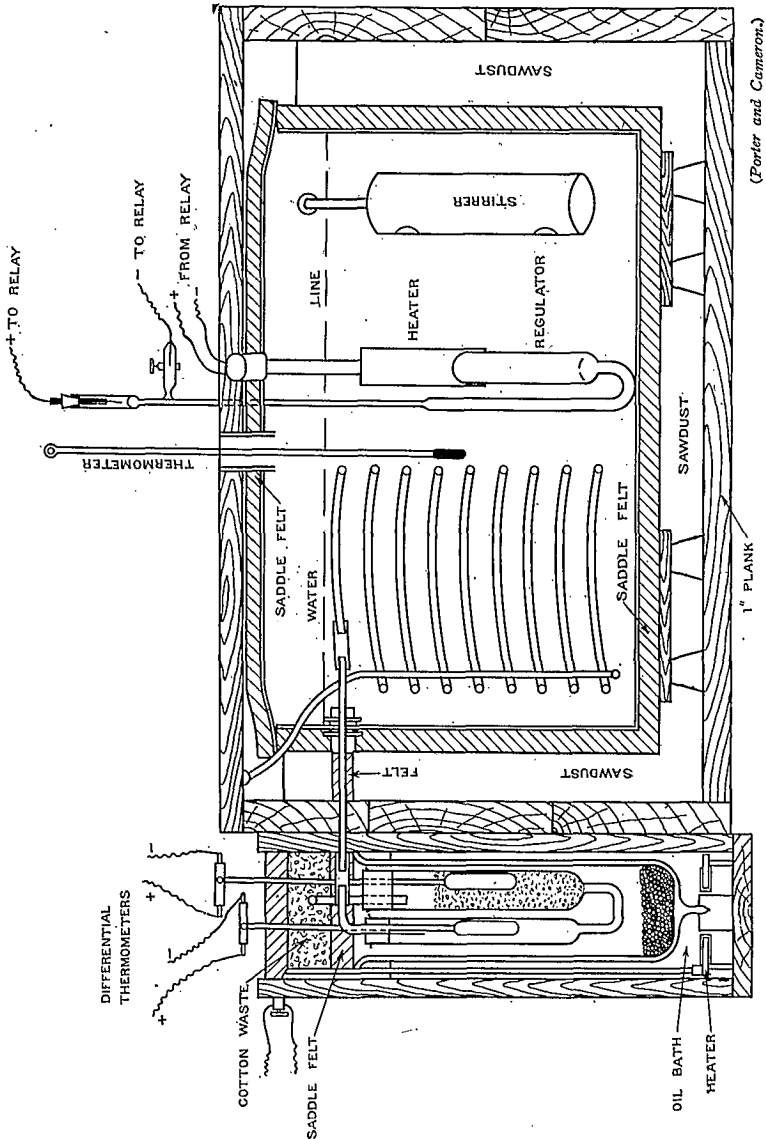
FIG. 35. Diagram of final thermostat and contents.

(Porter and Cameron.)

The box 6″ × 6″ × 18″ was made water-tight by lining with heavy galvanized sheet iron, and, after the Dewar vessel had been placed in position, was filled with a heavy transformer oil. In the bottom of the box, but insulated from contact with the lining, was placed a small electric heater

GLASS TUBE CARRYING COPPER LEADS

ASBESTOS BOARD

NICHROME WIRE

BRASS BINDING POSTS

A

B

NICHROME WIRE

ASBESTOS BOARD

ASBESTOS PAPER INSULATION
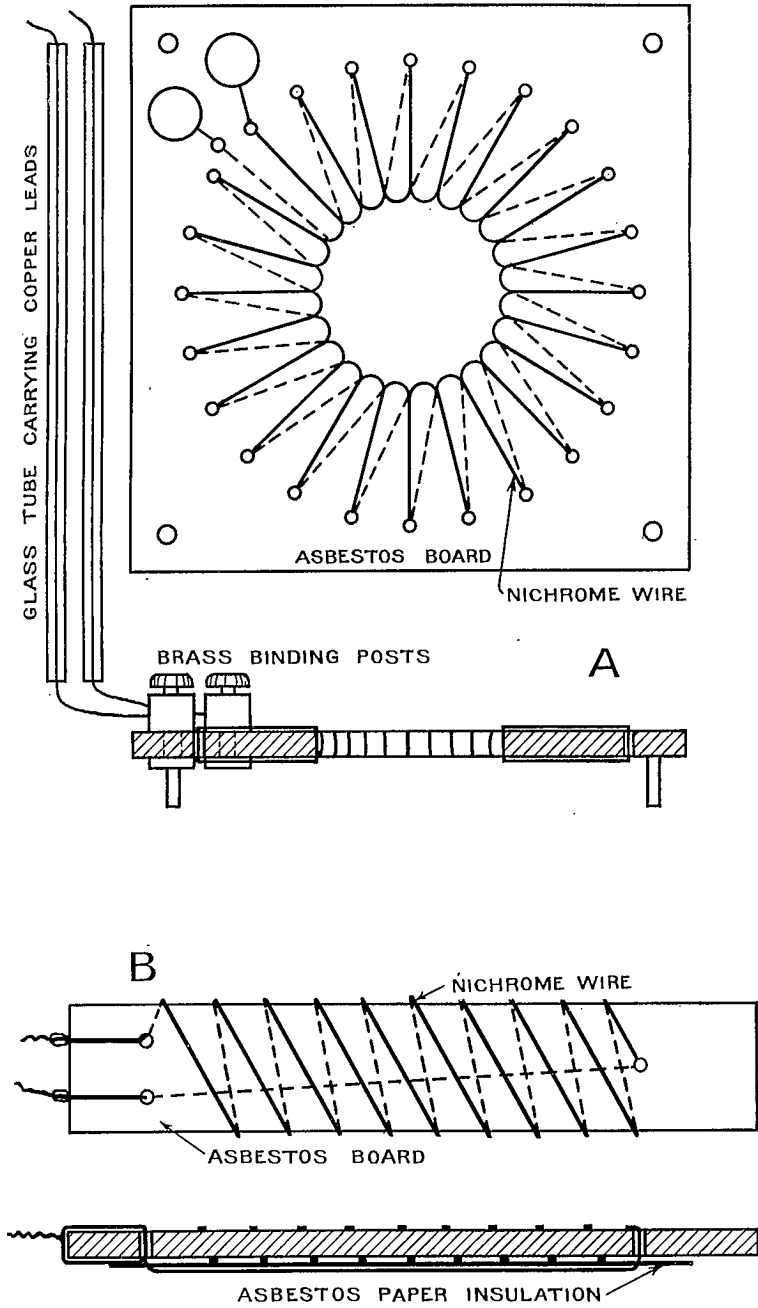
(*Porter and Cameron.*)

FIG. 36. Electric heaters for oil bath and container.

which, when connected to the electric current through a variable resistance in the form of a bank of lamps, was able to keep the oil bath at any desired temperature. This heater is shown in Fig. 36A and consists of a piece of asbestos shingle $4'' \times 4'' \times \frac{1}{8}''$ upon which is wound 6 feet of "Nichrome" high resistance ribbon wire. The shingle is cut square on the outside and a $1\frac{1}{2}''$ diameter circle cut out of the centre and nicked to receive the wire. A ring of small holes was punched $1\frac{3}{4}''$ from the centre all around and as close as possible together and the wire threaded as shown in the diagram. In this way the wire is insulated on the outside edge from contact with the iron lining of the box. The whole is supported from the bottom by four short wooden pegs. Thin glass tubes carry the bare copper wire leads from the heater to the top of the box where they are connected to the bank of lamps by permanent screw terminals. When in position the heater is so placed in the box that a cork placed on the bottom of the Dewar vessel just fits into the circle cut out of the centre of the heater.

A current of $5 \cdot 0$ amperes was used to heat the oil up to the required temperature (about 80°C.) and thereafter $2 \cdot 0$ amperes were continually applied to make up for radiation losses through the box. The heater being placed at the bottom of the box convection currents generated in the oil are sufficient to heat the oil uniformly throughout, no mechanical stirring being necessary.

In order to save the large amount of time that would be necessary for the gas alone to heat the container to the desired temperature, a second small heater, as shown in Fig. 36B, is used to heat up the inside of the Dewar vessel. It consists of a flat piece of asbestos board $1'' \times 3'' \times \frac{1}{8}''$ around which is wound about 2 feet of "Nichrome" wire, the whole being insulated by a covering of thin asbestos paper wrapper. The leads, connecting the heater to a pair of terminals situated on the outside of the box, are made of ordinary flexible insulated lamp cord with solder connexions to the "Nichrome" wire.

This heater was also run through a bank of lamps, and it was found after some experiment, that the same bank would do for both. The oil bath was first heated up to a little above the desired temperature and the connexions then transferred to the second heater. This one heated up much quicker and the resistance of the bank of lamps was then arranged to keep it at a constant temperature only breaking the connexion occasionally to heat up the oil bath as it cooled below a certain point. Thus by altering the connexions occasionally it was a comparatively easy matter to keep both temperatures fairly constant. At the end of about an hour it was found that the thermometer in the Dewar vessel would no longer fall upon breaking the connexions, but would remain constant because by then the walls of the Dewar vessel, the container, and the coal had all reached the same temperature, and there being but very little radiation this loss was counteracted by the heating effect of the incoming gas. When this condition was obtained the connexions were made permanently to the heater in the oil bath.

A further modification of the Thermostat consisted in the substitution of a battery of 3 gravity cells supplying the current necessary to operate the relay in the heater circuit of the bath (Figs. 27C and 34C) in place of taking current from the 110 volt mains. By this means sparking was completely done away with in the glass regulator thus minimizing the possibility of delay due to the regulator burning out.

The Absorption Train.

The train suffered a few minor changes from Billington's design, as can be seen by Figs. 27A, 29, and 34A.

In the first Cameron experiment dry absorbents alone were used; $CaCl_2$ for moisture and soda lime for CO_2, but it was found that the U tube containing $CaCl_2$ clogged early in the experiment stopping the flow of gas, so a vessel of H_2SO_4 (6, Fig. 34 A) was substituted in the later experiments. It was also felt that H_2SO_4 made a better dryer for the comparatively large amount of water coming over from the coal as the bubbles rising through the liquid gave better and surer contact between the gas and the absorbent. For the very small quantities of water produced from the burning of the hydrocarbons the dry absorbent was found very satisfactory and was used throughout the tests.

As mentioned above the dry absorbents used were $CaCl_2$ for moisture and soda lime for CO_2. Calcium chloride was substituted for P_2O_5 as used by Billington solely because a good supply was found ready at hand in the laboratory. Soda lime (7 and 10, Fig. 34 A) was considered a better absorbent for the gas than a solution of KOH, and moreover its use eliminated the necessity of weighing an extra moisture absorbent after each CO_2 absorbent. The upper half of the second arm of the U tubes containing soda lime was filled with $CaCl_2$ to take care of the moisture developed by the reaction of CO_2 upon the soda lime.

Temperature Readings.

In order to obtain very accurate readings of the temperature differences between the incoming gas and the coal, two differential electric resistance thermometers specially designed by Dr. H. T. Barnes, and made by Mr. N. T. Pye in the Macdonald Physics Building of the University, were used in place of the Beckmann thermometers used by Billington. Differences of temperature of one five-hundredth of a degree were easily observable with these instruments.

This apparatus consisted essentially of three parts, as shown diagrammatically and in detail in Fig. 37.

1. The two differential thermometers.
2. A specially constructed Wheatstone's Bridge.
3. A Broca galvanometer.

The thermometer as shown in Fig. 37B consists of a thin silver tube, 2″ long, encasing a coil of very fine platinum wire of 38·50 ohms resistance wound about a mica centre. The thermometer is connected to a glass tube 8″ long and $\frac{3}{16}$″ diameter. The leads, consisting of fine silk in-
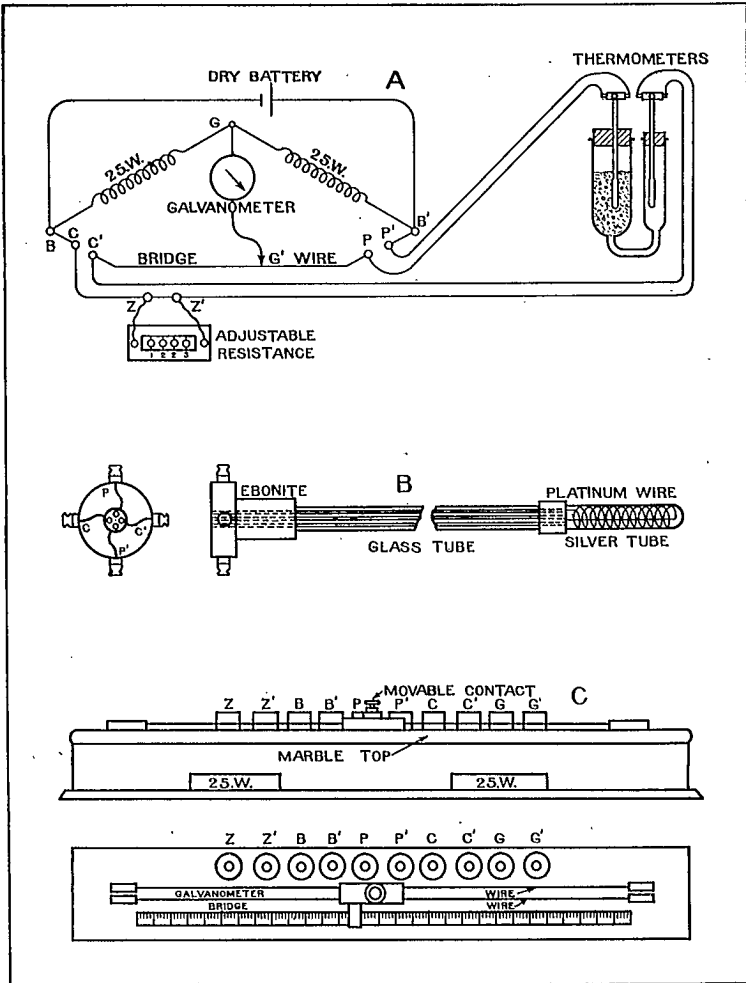
A — DIAGRAM OF THERMOMETER CONNECTIONS (Porter and Cameron.)
B — DETAILS OF THERMOMETER
C — DETAILS OF WHEATSTONE'S BRIDGE

FIG. 37. Details of electric thermometers.

sulated copper wire are further insulated from contact with each other in the glass tube by being carried in $\frac{1}{32}$″ glass tubing to the terminals at the top of the thermometer. Each thermometer also has in it a pair of compensator leads connected to separate terminals at the top so that the two

instruments may be used either together as differential thermometers or separately for measuring actual temperatures. In the experiments they were always used differentially and, therefore, the compensators were not needed. A diagram of the thermometer connexions is shown in Fig. 37A.

The Wheatstone's Bridge is shown in detail in Fig. 37C. It consists of a wooden box $3'' \times 3'' \times 24''$ having a solid marble top. The two equal arms of the bridge of 25 ohms resistance each are placed inside the box and all connexions are led to terminals on the marble top. The wire itself is of such size that a temperature difference of 1°C between the thermometers is equivalent to a movement of the sliding galvanometer connexion of 60 mm. and the wire being 600 millimetres long a possible temperature difference of 5°C on either side of the zero reading is shown directly upon the scale. A further resistance box made of the same wire as the Bridge wire may be inserted in series with one of the thermometers, and is so arranged as to give readings of anything from one to ten degrees, so that with the apparatus it is possible to read with great accuracy any temperature difference between the two thermometers up to 15°C.

The galvanometer used was of the standard Broca type, obtained, equipped complete with Nernst lamp and scale, from the Cambridge Scientific Instrument Company.

As mentioned above, the Bridge was designed to have a movement of 60 mm. for every degree of temperature difference, but before starting the experiments, calibration tests were made by taking a series of readings with the thermometers in baths of different temperature, using standard mercury thermometers, reading to one-tenth of a degree. All readings were made simultaneously and upon calculation it was found that the average movement was 60·15 mm. per degree, which is well within the limit of accuracy of reading the mercury thermometers.

The Coals used.

In order that close comparison might be made with Lamplough and Hill's work it was decided that at least one of the coals used should be as nearly as possible the same as some that they experimented on, and therefore samples were obtained, through the kindness of Mr. George Blake Walker and Sir William Garforth, from various collieries in England working the Barnsley seam. These coals were used for five experiments Nos. V to IX. It was also thought advisable to experiment with some Canadian coal especially liable to spontaneous combustion, and for this purpose the sample used in experiments X and XI was obtained through the kindness of Mr. Cadwallader Evans, from the Acadia Coal Company workings on the Cage Pit seam at Stellarton, Nova Scotia.

Directly after reaching the laboratory the samples, which were sent from the mines in sealed vessels filled with mine water, were crushed under mine water to about 10—30-mesh and hermetically sealed in glass bottles, stored under water.
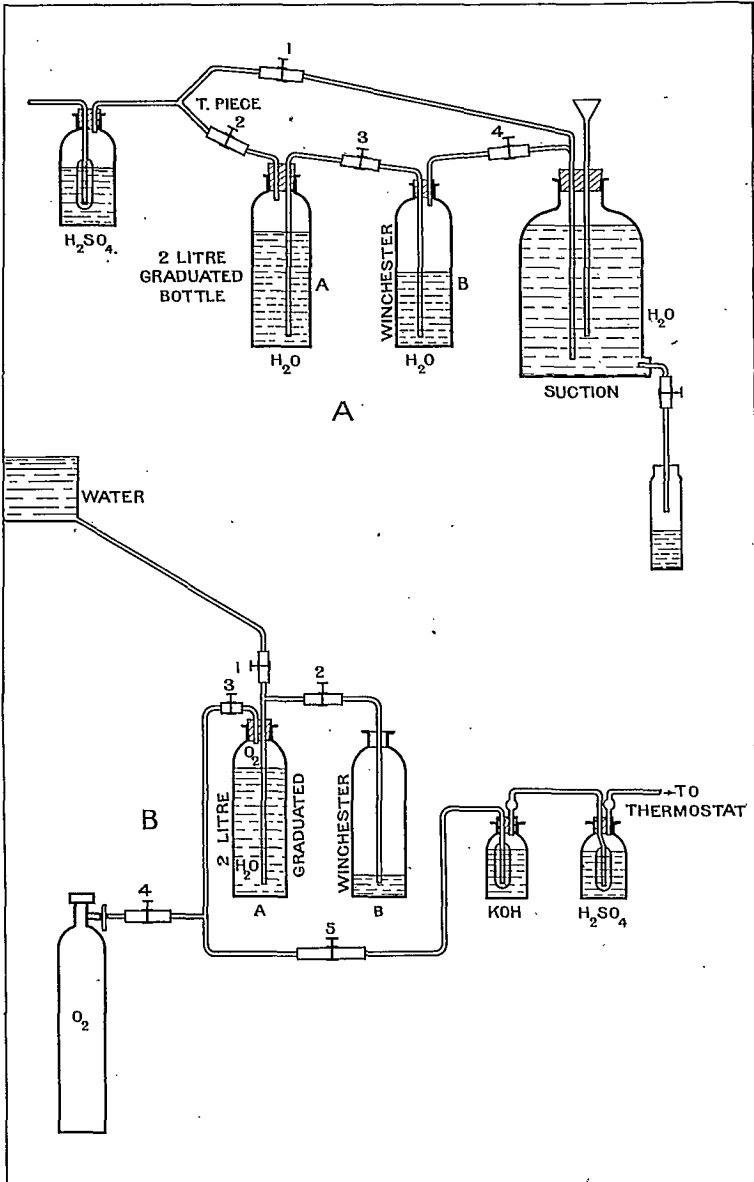
(*Porter and Cameron.*)

FIG. 38   A—Apparatus for measuring rate of flow of gas.
         B—Apparatus for supplying oxygen.

The Experiments.

Before starting the experiments it was decided that some means should be had of determining the approximate rate of flow of the gas through the apparatus, and for this purpose Dr. Porter designed the apparatus shown in Fig. 38A.
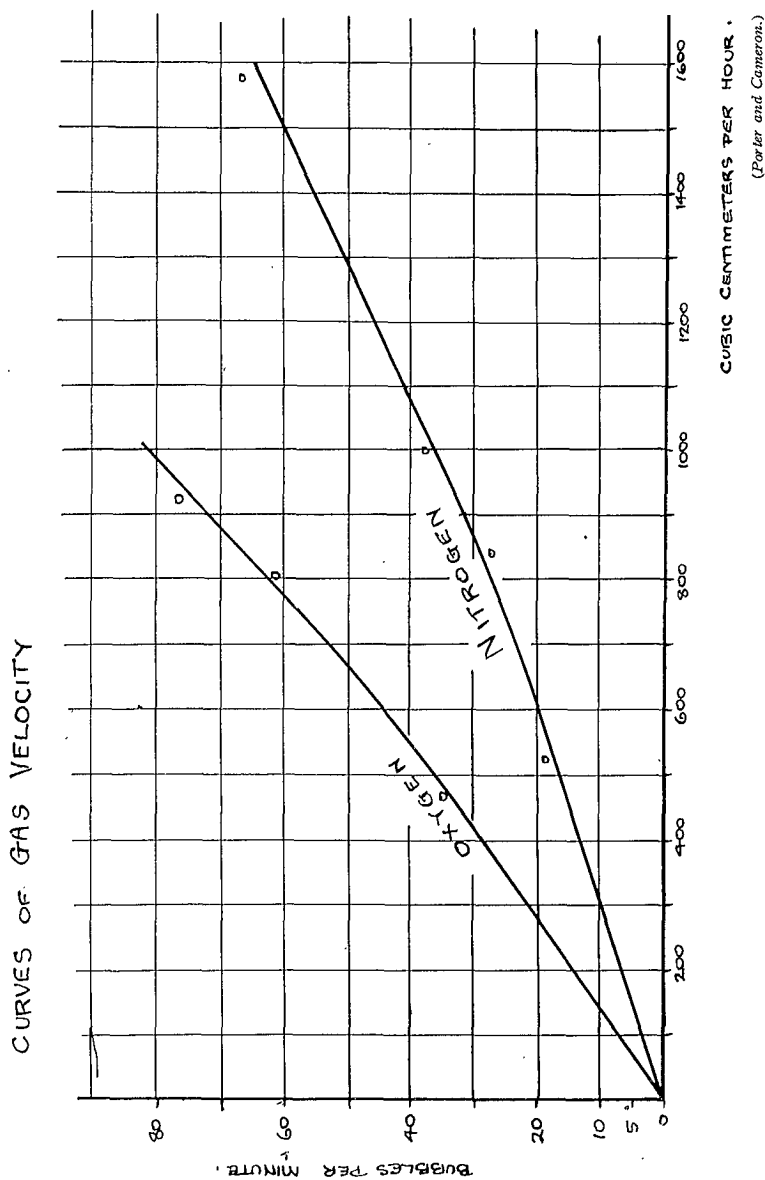
FIG. 39. Curves showing gas velocity.

It was inserted at the end of the absorption train between the last H$_2$SO$_4$ bottle and the suction (Fig. 34A), and consisted of a graduated bottle (A) connected by means of a syphon to an ordinary Winchester (B), which

in turn was connected by a T-piece to the suction. A by-pass (I) was inserted so that the gas could flow direct from the train to the suction when measurements of the rate of flow were not being taken. A was filled with water to the cork and B was placed at a slightly lower level than A in order to help the suction overcome the extra head of water. With cock 1 closed and cocks 2, 3, and 4 open, the suction causes a suction in B, which causes the water from A to flow over into B making a slight vacuum in A which in turn draws gas from the train. The flow will of course be no faster than the gas is fed to the purifying trains from the storage tanks, and, therefore, different rates of flow of gas can be correlated with the number of bubbles passing some bottle in the purifying train, and the rate thereafter determined by counting these bubbles from time to time. In this way the curves, Fig. 39, were obtained. The oxygen curve shows the rate of flow of oxygen through the H_2SO_4 bottle 2, Fig 34A, in bubbles per minute, and the nitrogen curve, the rate of flow of nitrogen in bubbles per minute through the H_2SO_4 bottle No. 5, Fig. 34A.

This is of course by no means an accurate determination, but it proved sufficiently reliable for the purpose and with a little care about the adjustments the experiments could all be made under approximately identical conditions.

In order to obtain reliable results the coal had first to be thoroughly dried, and before all experiments this was done in the following manner.

The coal on being taken from the storage bottle was first placed in a filter for a few moments to allow surface water to drain off. From here it was transferred to a large sheet of coarse filter paper for a brief time and as much more moisture as possible extracted. Then it was placed in an atmosphere of nitrogen in a small flask and tightly corked with a rubber stopper through which projected a capillary glass tube. The flask was then placed in an oven and kept at a temperature of 105-110°C. for from three to five hours until upon cooling and weighing the coal was found to remain constant as to weight. In this way all moisture was removed with very little contact with air and consequent absorption of oxygen.

The primary object of the experiments being a study of the heat evolution due to the action of oxygen, they were run only long enough to produce a decided rise in the temperature of the coal, and usually a period of some 15 hours sufficed. No attempt was made to determine the rate of absorption of oxygen as this would have necessitated long extended experiments such as No. IV of Billington's work. Moreover, owing to the short period of time over which each experiment extended it was thought unnecessary to make a detailed study of the rate of evolution of the various gases coming from the coal, as Billington did in experiment IV, and only the total amount of evolved substances was obtained at the end of each experiment.

Two series of experiments were made, one showing the effect of dry gas upon the coal and the other the effect of a saturated gas. In both cases, of course, the coal was previously thoroughly dried in order that

the true weight of coal should be known. It had been hoped to experiment with several different coals, but unfortunately owing to delays, the length of time necessary to construct and test the apparatus and other unforeseen difficulties, reliable results were obtained from three coals only.

Seven experiments in all were made, four using dry gas and three using saturated gas. The bath temperature for all experiments was 80°C. as it was felt that at this somewhat elevated temperature more rapid oxidation would probably take place and definite results would be more quickly forthcoming.

In the experiments with saturated gas a slight change in the apparatus was necessary. For saturating the gas at the temperature of the bath a small gas wash bottle containing distilled water was inserted in the thermostat between the coil of piping used to heat the gas and the pipe leading to the coal container. This was so connected that the gas bubbled through the water. It was also necessary to insert a condenser between the container and the first sulphuric acid bottle in the absorption train to collect the excess moisture coming over. The condenser consisted simply of an air tight bottle set in an ice bath.

The gas being dry until it reached the wash bottle it was expected that, as the change in weight of the bottle, and the weight of water coming over into the condenser were known it would be a simple matter to calculate the amount of water absorbed by the coal; but unfortunately it was found that in all cases some water worked back into the coil of tin piping in the thermostat probably by diffusion. Moisture determinations therefore had to be made on the coal after the experiments.

Calculations.

The weights of the water, carbonic acid and hydrocarbons given off during the experiment are obtained by very simple calculations from the weights of the respective elements of the absorption train before and after the test. The weight of oxygen absorbed is obtained by adding the sum of the three above items to the algebraic[1] increase in weight of the coal as determined by weighing the container before and after the test. The volume of oxygen absorbed is then calculated from the following formula:—

$V = W \times 22400 \div 32$ where

V = volume of oxygen at 0°C and 760 mm. pressure.

W = weight of oxygen absorbed.

This very simple formula gives the volume directly, and shows the great advantage of using gravimetric methods of analysis over the volumetric methods as used by Lamplough and Hill, and Winmill.

The calculated results of all the experiments have been assembled and are shown in Table No. XLIV, p. 145, but curves showing the relation between temperature and time have been drawn for each experiment,

[1] In the majority of the tests made in this particular investigation the coal actually lost weight owing to the loss of moisture, etc., exceeding the absorption of oxygen. In these cases the "increase in weight" would be a minus quantity and the absorption of oxygen would therefore be less than the sum of the three items evolved.

and will be explained and discussed in detail before going into a more genera
discussion of the results as a whole. By temperature is meant the difference
of temperature between the incoming and outgoing gases in the coal con
tainer.

It should be noted that the experiments are numbered to follow thos
made by Billington, thus Cameron's first is numbered V and his seventh X

Experiments V and VI.

The curves Fig. 40 show the results of the first two experiments wit
the final apparatus. Both were run as nearly as possible under identica
conditions; the first one on a sample of coal from the Barnsley seam a
Tankersley, and the second on coal from the Silkstone seam, Normanton
England. The gases used were thoroughly dry and the bath temperatur
80°C. The Barnsley coal on analysis contained 0·45% sulphur and th
Silkstone coal 0·26%, both being low sulphur coals.

The curves show the striking similarity of the results obtained. Bot
coals started at a temperature slightly cooler than the incoming gas and a
no time did they rise above the temperature of the gas. About two hour
after the oxygen had been admitted the coals had reached a point of max
mum temperature, and from there on each curve approximates a straigh
line. A maximum rise of 0·18°C. on oxygen as compared with nitroge
was obtained in experiment V, and of 0·29°C. in experiment VI. Thi
greater rise in the second case is probably to be accounted for by the fac
that in experiment VI the coal was subjected to a slower rate of flow c
oxygen and less heat was carried off by the gas. The absorption result
shown in Table XLIV, p. 145, tend to bear out this opinion.

Experiment VII.

This experiment was run on the same coal as experiment VI and unde
the same conditions, with the exception that the gas was first saturate
with water vapour. The curve Fig. 41, p. 138, shows the temperatur
results obtained. It was found that the presence of the moisture rendere
it practically impossible to establish temperature equilibrium while th
nitrogen was passing, and after running for some hours without getting
perfectly uniform temperature the attempt to do so was abandoned an
oxygen was turned on. The results obtained are very characteristic an
show clearly the effect of moisture upon the temperature rise in oxygen
Owing to certain peculiarities in the running conditions of this experimen
the calculated oxygen absorption as shown in Table XLIV, p. 145, is no
very reliable, but is given as at least showing the order of the amount
absorbed. From the results of this and other experiments there seems t
be no doubt that the presence of a small amount of moisture greatly in
creases the activity of the absorption reaction and consequently the hea
evolution.

The temperature results of these three experiments on similar coal
show, as would be expected, that the increase of temperature is inversel

proportional to the rate of flow of gas so long as enough of the l atter is supplied, and as the amounts of oxygen supplied were greatly in excess of that needed for absorption, the temperature differences obtained were
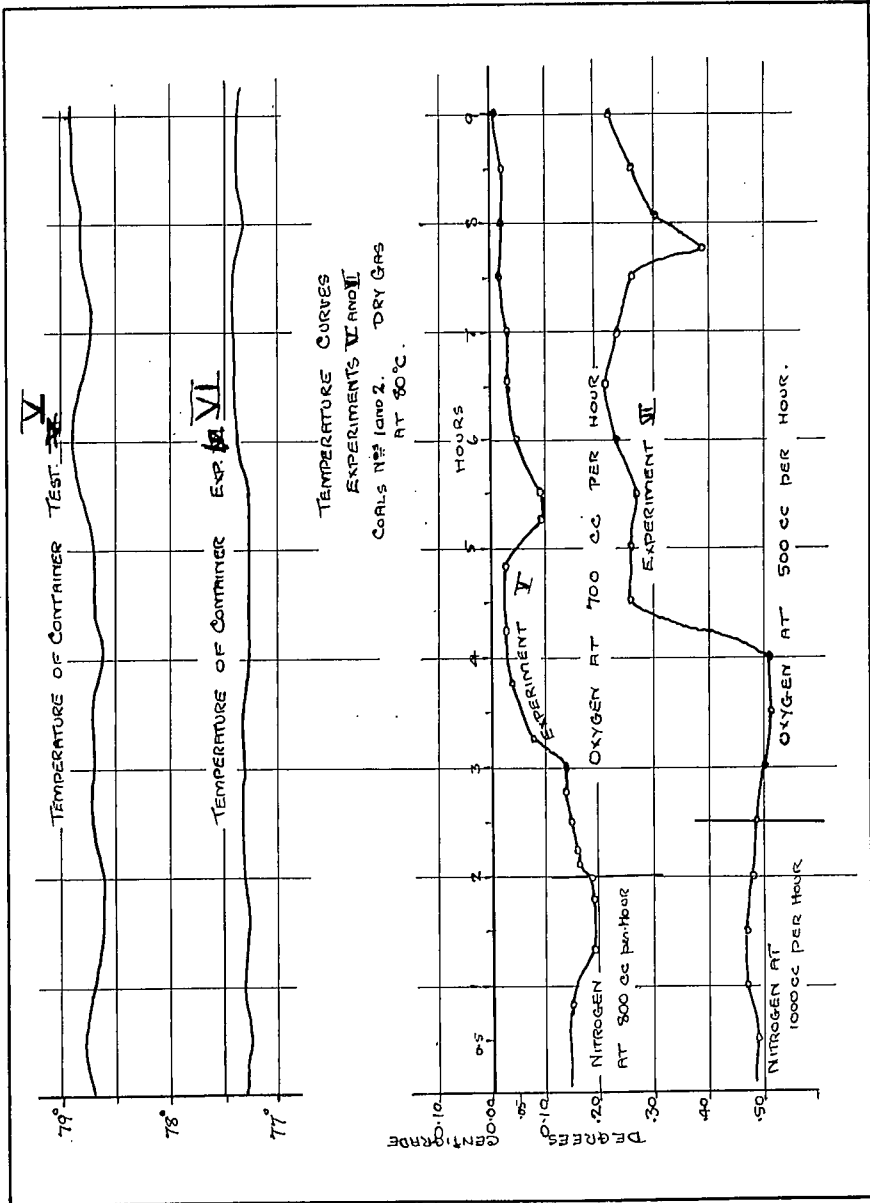
FIG. 40. Graphic record for experiments V and VI.

therefore of a very small order. It was therefore decided that in the future experiments means must be devised for giving an exceedingly slow rate of flow for the oxygen. For this purpose the apparatus shown in Fig. 38

(B) was designed by Dr. MacIntosh.   It was inserted between the oxygen cylinder and the first absorption bottle of the purifying train (1, Fig. 34A)
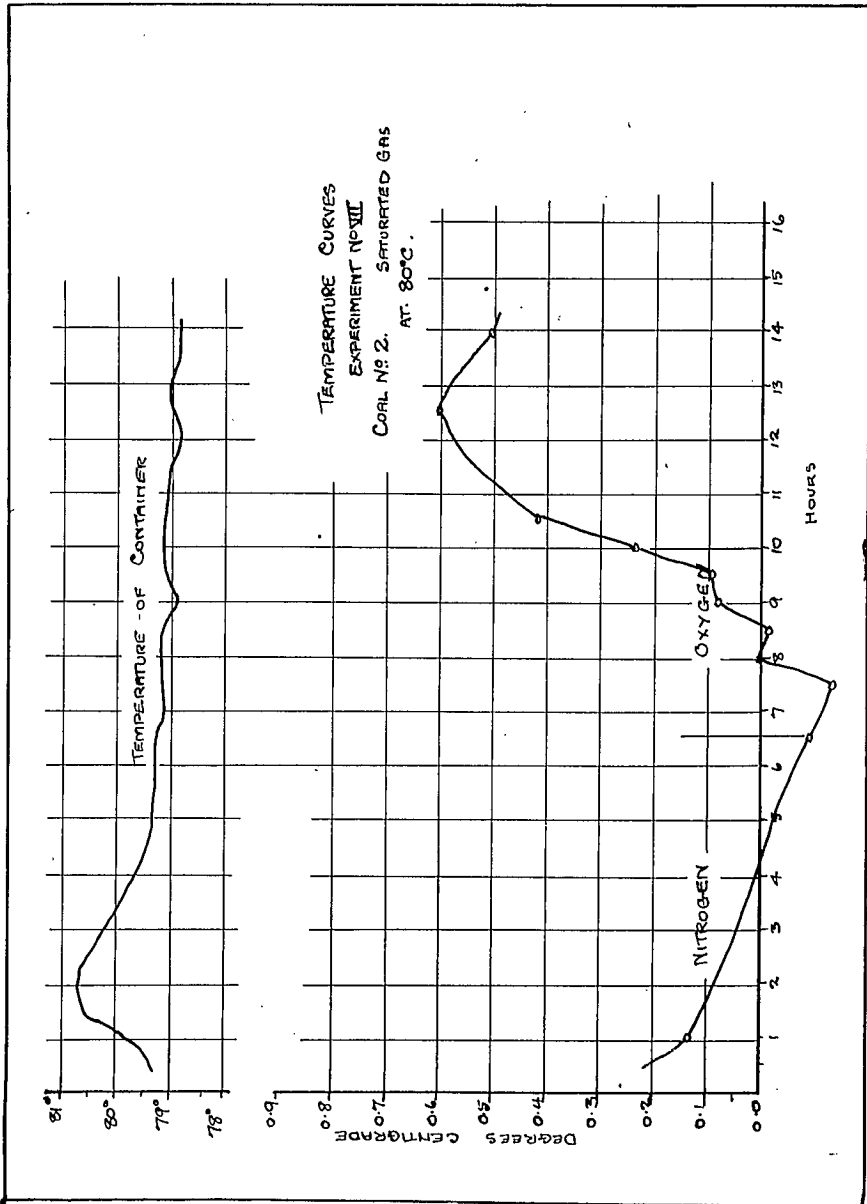
Fig. 41.   Graphic re ord for experiment VII.

(Porter and Cameron.)

and consists of a graduated bottle A connected by a syphon and T-piece to an open Winchester B.   The third arm of the T-piece is connected through a pinch cock to a tank of water arranged to give a constant head.

A by-pass from the oxygen cylinder is arranged so that the apparatus may be swept out clean with oxygen direct from the cylinder.

The two-litre bottle being filled with distilled water, cocks 1 and 5 are closed, and oxygen from the cylinder allowed to flow into the bottle causing the water to syphon over to the Winchester. When sufficient oxygen has been collected the cylinder valve 4 is closed, the level of the water in the Winchester raised to the same level as that of the water in the graduated bottle, and cock 2 closed. In this way the oxygen in the graduated bottle is at atmospheric pressure. Then by opening cock 5, and regulating the flow of water through cock 1, any desired rate of flow of the gas can be obtained.

Experiment VIII.

The coal from the Normanton Silkstone seam was again used for this experiment which was a duplication of experiment VII, except that the above described apparatus was used, and it was made solely to find out what effect a reduction in the quantity of the oxygen passing through the coal has upon temperature rise. In this experiment the total amount of oxygen passed was less than 900 c.c. during the sixteen hours of the experiment, whereas in experiment VII the gas was flowing at the rate of 400 c.c. per hour. The curve Fig. 42 shows clearly the results obtained. A comparison with curve Fig. 41 for experiment VII shows how greatly the temperature rise is influenced by the rate of flow of the oxygen.

Experiment IX.

This experiment was the same as experiment VIII, except that dry gas was used. It was, therefore, a duplication of experiment VI using the improved oxygen control. The temperature rise is shown in curve Fig. 43. By comparison with the previous curves it may be noted that the rise obtained is greater than that obtained for either dry or saturated gas with a high velocity flow, but not so great as that shown in experiment VIII with a saturated gas and the same velocity flow.

These last four experiments show clearly two things:—

(1) That, as would be expected, the rise in temperature with oxygen is dependent upon and varies inversely as the rate of flow of the gas so long as the supply suffices for oxidation.

(2) That the presence of a small amount of moisture materially increases the evolution of heat due to the absorption of oxygen by the coal.

Moreover, the coal being very low in sulphur (0·26%) the experiments show[1] that the moisture does not play its part solely by oxidation of pyrite or other sulphur compounds present, but is a direct aid to the absorption of the oxygen by the coal itself and the consequent production of heat.

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[1] See conclusion 3, p. 146.

Experiment X.

The coal used for this experiment, and for the one following was from the Cage Pit seam of the Acadia Coal Company, Stellarton, Nova Scotia.
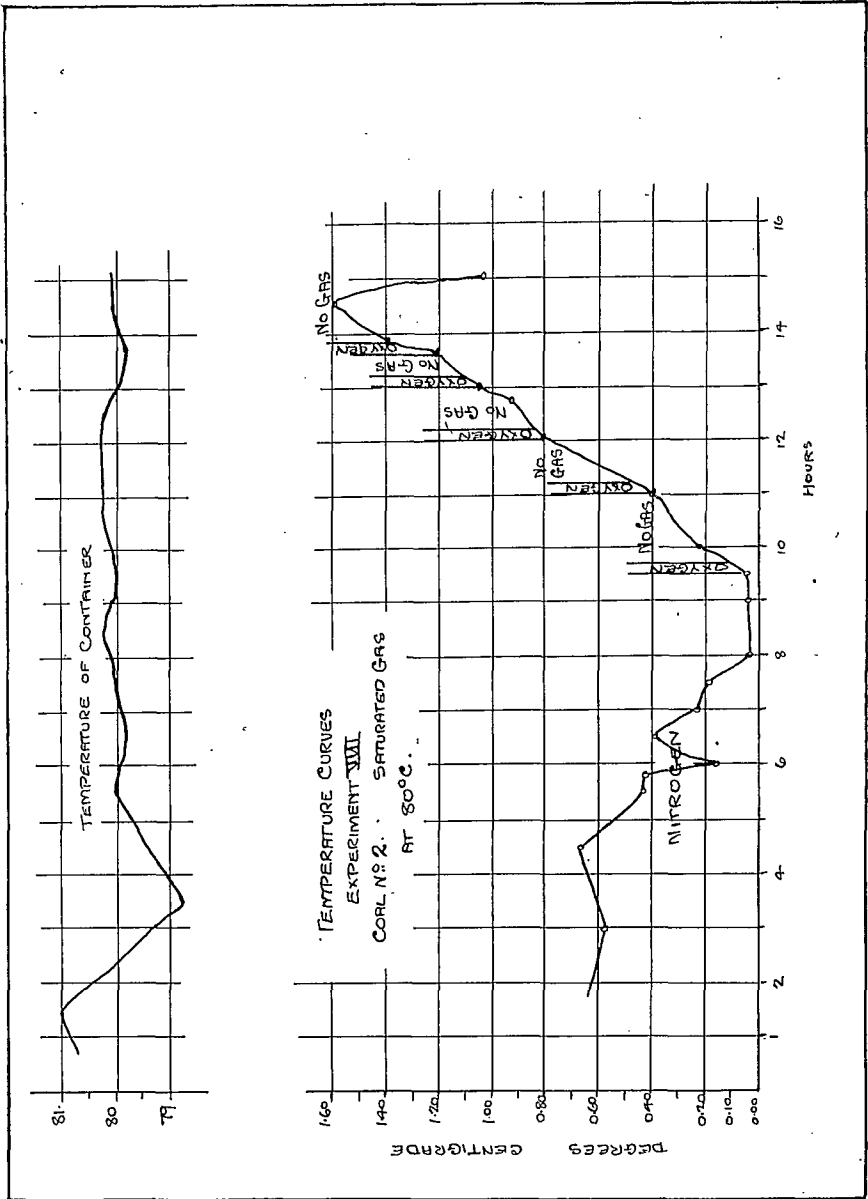
FIG. 42. Graphic record for experiment VIII.

(Porter and Cameron.)

The experiment was run with dry gas and as nearly as possible under the same conditions as the previous ones. The temperature rise with oxygen

is shown in curve Fig. 44. The total amount of oxygen passed during
the experiment was less than 1000 c.c. over a period of eight hours. The
bath surrounding the coal container and therefore the coal itself was main-
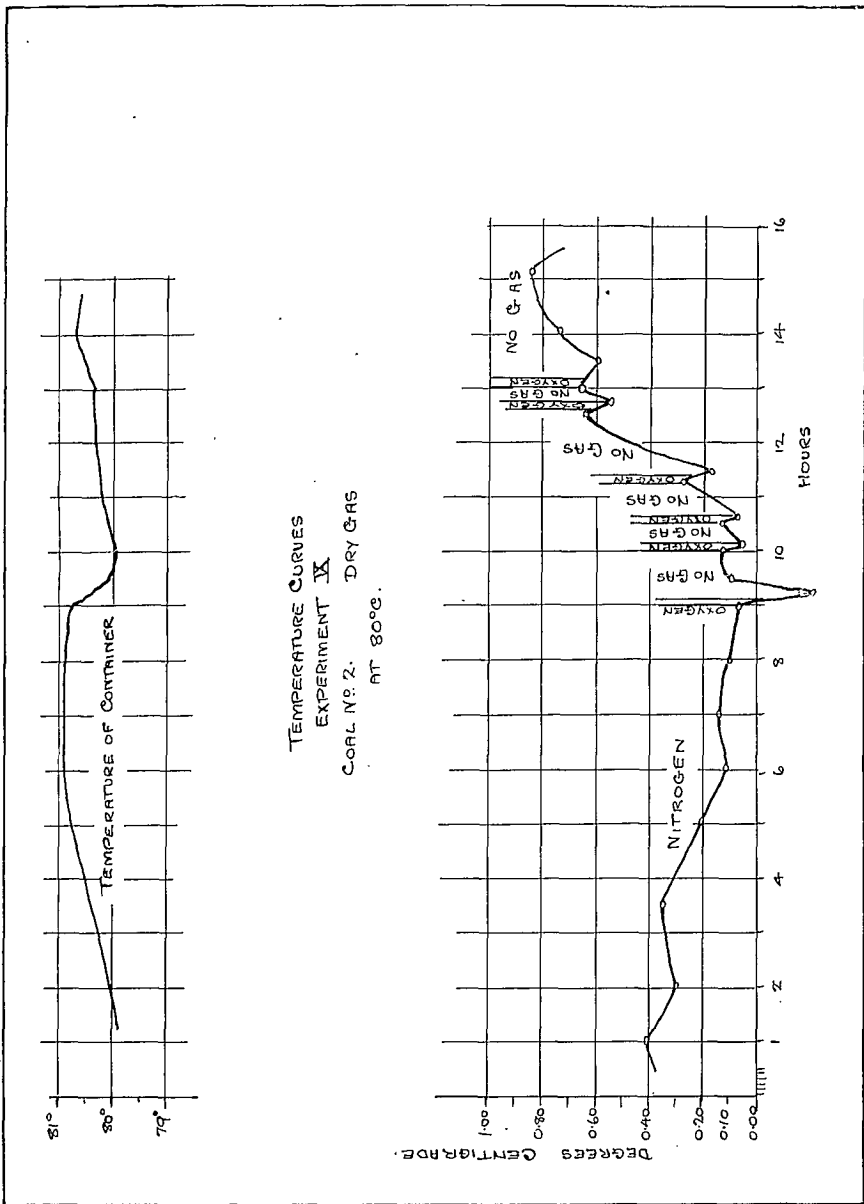
FIG. 43.   Graphic record for experiment IX.

(Porter and Cameron.)

tained throughout the experiment at a temperature of 0·6°C. above that
of the incoming gas and a maximum temperature rise of 0·6°C. was ob-
tained when oxygen was passed.

Experiment XI.

This, the last experiment was run on the same coal as experiment X, and under identical conditions with the exception that saturated gas
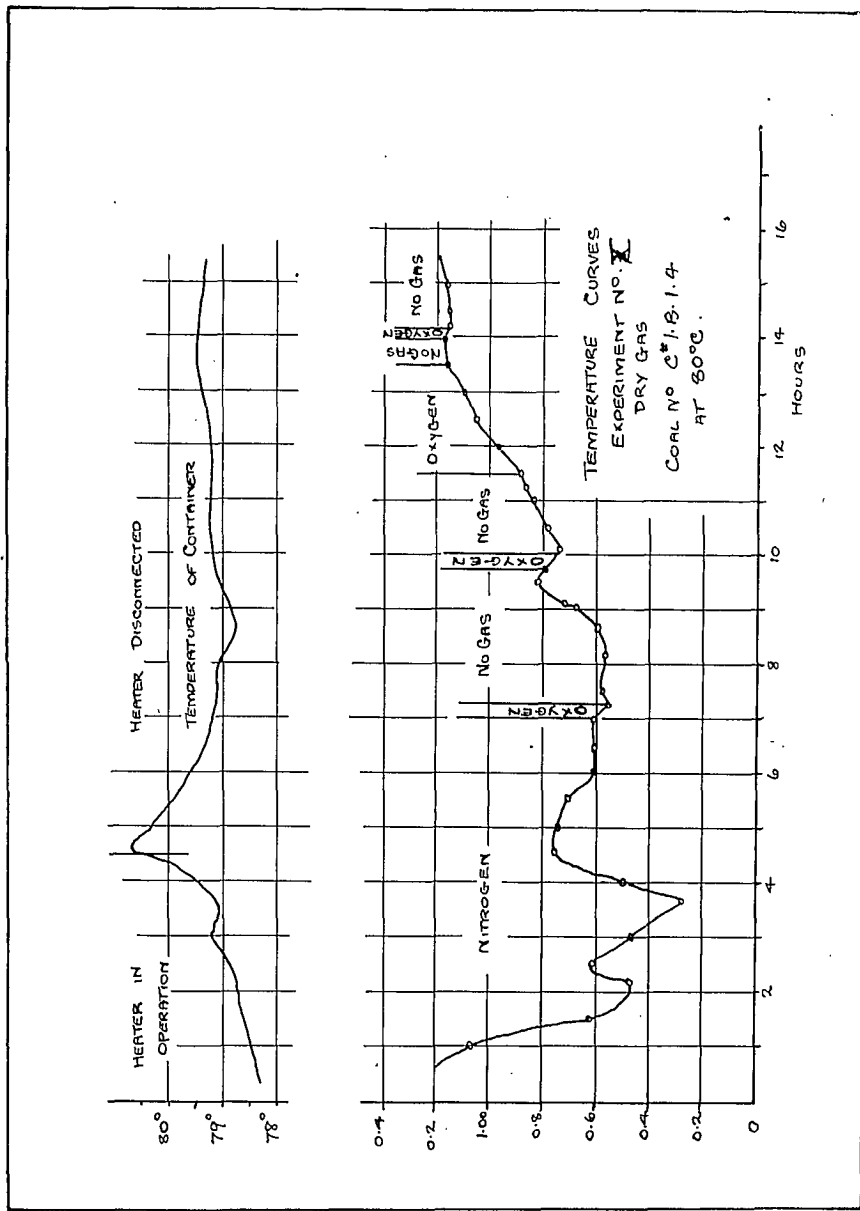
FIG. 44. Graphic record for experiment X.

(Porter and Cameron.)

was used. As in the previous "wet tests" no serious attempt was made to obtain temperature equilibrium while the nitrogen passed, but as soon as

a fairly constant condition was obtained the oxygen was turned on. The curve Fig. 45 shows the results obtained. Comparison with the curve for experiment IX shows that these results are very similar to those ob-
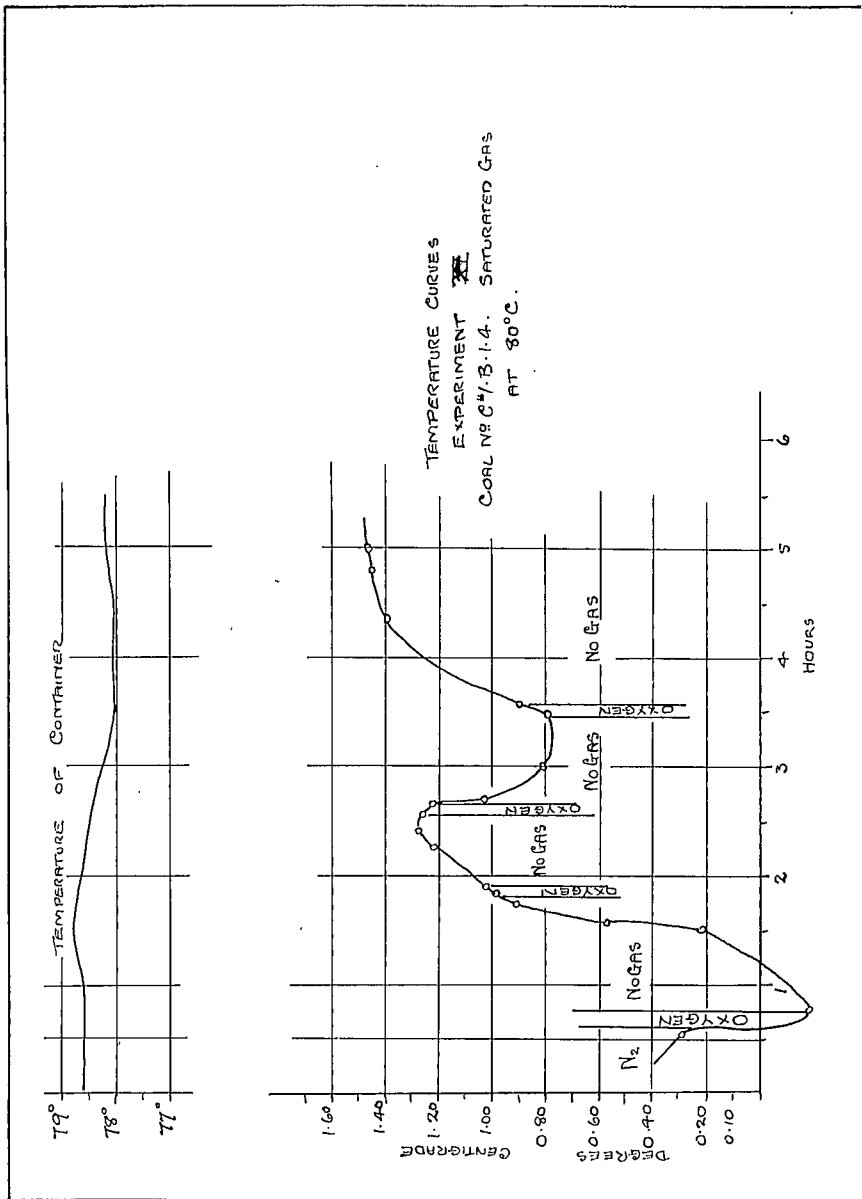
FIG. 45. Graphic record for experiment XI.

tained with the English coal. In this experiment the maximum temperature rise for the eight hours with oxygen is $1 \cdot 2°C$. an increase of $0 \cdot 6°C$. above that obtained with dry gas.

Another point of interest brought out by the various curves is that when oxygen is admitted even in very small quantities the temperature tends first to drop slightly and then to rise above the starting point. Moreover as soon as the oxygen in direct contact with the coal has all been absorbed the temperature begins immediately to drop again and will not rise until sometime after more oxygen has been applied.

The Calculated Results.

The results obtained from the absorption train for all coals are shown in Table XLIV, p. 145. A study of this table clearly brings forth the fact that the rate of absorption by the coals experimented with depends upon the presence of some moisture, and is influenced by the rate at which oxygen passes through it.

That the first condition holds is shown by comparing the results of experiment VIII with IX, and experiment XI with X. In both of these pairs of experiments we find that the one in which saturated gas has been used has shown, by quite an amount, an increase in the absorption of oxygen by the coal in spite of the fact that in each case the passing of gas has been continued for an appreciably longer time in the dry than in the wet condition. It will, however, be shown later that these experiments must not be interpreted as showing that "wet" coal oxidizes faster than "dry."

For evidence of the second statement let us consider experiments VI and IX. Here we have the same coal subjected to as nearly as possible the same conditions, except a change in the rate of flow of oxygen, and we find that in IX with a low velocity of flow over a period of 6 hours the absorption has amounted to $3 \cdot 69$ c.c. per gramme of coal, while in VI with a fairly high flow the absorption for $6\frac{1}{2}$ hours is appreciably less, being only $3 \cdot 55$ c.c. per gramme of coal.[1] The same result is even more apparent if we compare experiments VII and VIII, but as mentioned before there were certain difficulties encountered in VII which make it somewhat unreliable. The difference here, however, is so great that even allowing for possible errors it would appear that the same deduction could be made as is shown by experiments VI and IX.

Summary of Conclusions.

It is of course well understood that no general conclusions can reasonably be drawn from so limited a number of experiments, but on the other hand it is thought that the experiments show certain conditions which appear to govern, to a certain extent, at least, the absorption of oxygen by coal and the consequent production of heat. These are set forth below:—

1. Oxidation depends largely upon the presence of moisture. With absolutely dry gas and almost absolutely dry coal some oxidation does

[1] Mr. Cameron is quite right in stating that his experiments apparently support this second deduction, and there is no doubt whatsoever that an excessive oxygen supply, as pointed out elsewhere, by keeping down temperature does actually keep down oxidation. It is, however, open to question that the very small decrease in temperature noted by Mr. Cameron as resulting from the excess of oxygen in his earlier experiments, could have had even the small effect on the rate of oxidation which his experiments would seem to show.

TABLE XLIV.

Summary of Records, Experiments V-XI.

(Porter and Cameron)

Experiment No.	Coal No.	Weight of coal taken grm.	Condition of gas.	Average flow of O₂ per hr. c.c.	Time in oxygen hours.	H₂O evolved grm.	CO₂ evolved g.m.	Hydro carbons evolved grm.	Oxygen absorbed grm.	Oxygen absorbed per grm. coal in c.c. at N.T.&P.	Oxygen absorbed per grm. coal in c.c at N.T.&P.	Final wt. of coal grm.
V........	1	40·0240	dry	700	7	0·3506	0·0933	0·0454	0·2502	175·14	4·25	39·7849
VI........	2	43·6204	dry	500	6½	0·3165	0·0143	0·1272	0·2220	155·40	3·55	43·3844
VII.......	2	38·6400	wet	400	6	0·1400	0·0457	0·0142	0·1261	98·27	2·54	38·5662
VIII........	2	37·0210	wet	50	5½	—	0·0272	0·0615	0·3171	221·97	6·00	37·2494
IX........	2	42·9360	dry	50	6	0·4911	0·0238	0·0159	0·2265	158·55	3·69	42·6317
X........	3	45·9960	dry	100	8	0·3166	0·0226	0·0026	0·1813	126·91	2·49	45·8355
XI........	3	43·6080	wet	100	5	0·0293	0·0128	0·0122	0·4885	332·0	7·60	44·9422

Analysis for Sulphur:—

Coal No. 1.—Barnsley Seam, Tankersley, England.. 0·45%

Coal No. 2.—Silkstone Seam, Normanton, England... 0·26%

Coal No. C 1. B. 1·4 Cage Pit seam, Stellarton, N.S... 0·90%

take place, but it is clear that moisture greatly facilitates the reaction. Too much moisture will undoubtedly, however, hinder the oxidation and consequent production of heat, and it must be made quite clear that nothing in the experiments goes to indicate that "wet" coal oxidizes more rapidly than "dry" using these terms in the ordinary commercial sense. The wet tests just tabulated were really "dry" in the sense that the coal had been dried to above the boiling point, and the only moisture admitted was that of air saturated by passing through water. The total amount of moisture was therefore actually much lower than in any industrial dry coal storage. On the other hand the dry tests as conducted above involve an almost absolute exclusion of moisture: a condition quite impossible except in an elaborate laboratory experiment.

2. The absorption of oxygen by the coal and the consequent production of heat is apparently dependent upon, and to a certain extent proportional to the rate of flow of the oxidizing gas, i.e., too much oxygen or air, as well as too little, checking the action.

3. No exact information is obtainable as to how much of the oxygen, if any, went into combination with the sulphur of the coal, but the samples are all low in sulphur and No. 2 particularly has very little of this impurity, and calculation will show that even if all of the sulphur in the samples had been oxidized, which is of course an enormously exaggerated assumption[1]—the absorption of oxygen could not have been accounted for. In view of the work done by other experimenters on this subject it is probable that even in the "wet" tests, the oxygen was mainly absorbed by the resins and humus bodies which are known to form an appreciable part of the coals in question.

In conclusion it may be said that the experiments are but a small part of what will have to be done before the whole matter is cleared up. Much interesting work is yet to be done on pyritic coals and pyrite, with a view to finding out the true effect of this substance in the oxidation of such coals, and similarly pure hydrocarbons, resins, etc., as contained in coal and allied substances such as peat, etc., will have to be studied. It is hoped, however, that the above report will prove of some value, not only through its actual results of experiment, but also through its description of apparatus and methods.

Parr and Francis[2] experimented on the absorption of oxygen by coal at still higher temperatures than those employed by Porter and Cameron.

The apparatus used by them is shown in Fig. 46.

It consists of two towers filled with solid potassium hydroxide, and three wash bottles partially filled with a 50 per cent potassium hydroxide solution. That this solution thoroughly removed any traces of carbon dioxide which may have been contained in the oxygen, was proved by means of solutions of barium hydroxide in the two small flasks B' and B". A round 1500 cc Jena flask F, served as a heating chamber, a nickel calorimeter capsule, C, for holding the material to be tested was firmly fixed in a loop of heavy iron wire and suspended in the flask. Two thermometers were used, one T, to indicate the temperature

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[1] See pp. 42-43 ante.
[2] Univ. of Illinois. Eng. Expt. Sta. Bull. 24, 1908.

of the gas (oxygen), and the other T' was immersed in the coal within the capsule. The exit tube led the products into a test tube, B, containing a freshly prepared solution of barium hydroxide.

Normally it would be expected that the temperature of the surrounding gas would be slightly higher than that of the coal, the loss by convection and poor conductivity being shown by a slightly lower reading of the thermometer embedded in the coal. It is evident therefore, that any relative rise in temperature, as shown by the thermometer T^1, would be due to chemical activity within the capsule.
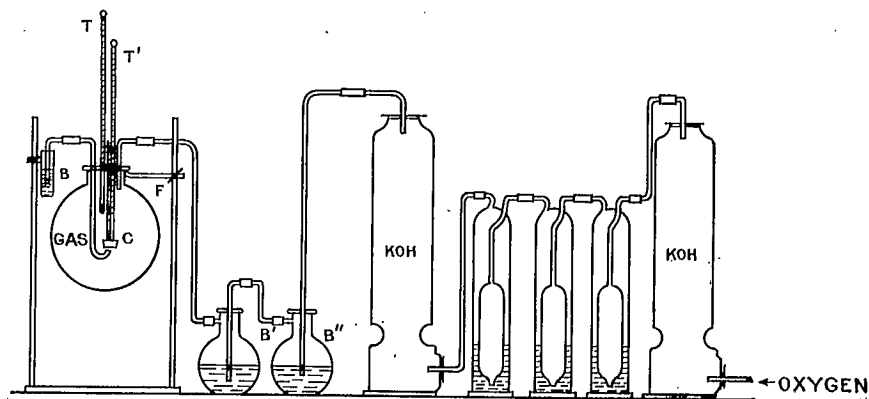
(Redrawn from Parr and Francis.)

Fig. 46. Oxygen absorption apparatus

Operation. The method of operation was as follows: Two grams of coal were placed in the nickel capsule and the apparatus adjusted as described. Oxygen was then admitted at the rate of approximately 150 bubbles per minute. The flask, F. was uniformly heated with a constantly moving Bunsen flame and readings of both thermometers were recorded every minute. The first appearance of carbon dioxide was noted in the test solution, B. This test tube was changed with sufficient frequency to indicate whether or not the evolution of carbon dioxide was continuous.

The temperatures shown by these two thermometers were plotted, and some of the curves obtained are reproduced below from the paper by Parr and Francis. The continuous line in each shows the temperature of the gas, while the dotted line shows the temperature of the coal in the capsule. In most cases there was a slight evolution of carbon dioxide at about 30°, but this ceased and did not begin again until about 125°. This first carbon dioxide is inferred to have been merely occluded gas. For convenience in charting this was omitted. This coal for Figs. 47, 48, and 51, contained:—

Moisture............................... 6·53 per cent.
Ash.................................... 7·76   "
Volatile matter........................33·86   "
Fixed carbon...........................51·85   "
Sulphur............................... 2·10   "

The coal used in Fig. 47 was a sample of Williamson county, Illinois, Carterville coal in a finely pulverized form. At the point indicated by the first cross (x) or 125°, there was a positive appearance of carbon dioxide, which continued until a temperature of 155° was reached, when the chemical activity became so great as to cause a much more positive evolution of carbon dioxide and a very rapid rise of the thermometer T^1. At 160° as represented by the delta, the coal showed the presence of fire and thermometer observations could no longer be taken.

Fig. 48 shows a repetition of the above test except that the coal used was buckwheat size. Carbon dioxide first appeared at 112° and the more copious evolution started at 147°. This rapid evolution continued over a much longer space and a red glow was not visible in the coal until the temperature was 258°. This shows that oxidation proceeds much more rapidly with finely divided coal than with lump coal.

Fig. 49 represents a similar experiment on a sample of Taylorville, Illinois, coal in the powdered condition. The appearance of carbon dioxide was first detected at a temperature of 153° C and at the same point the two curves cross. At a temperature of 157° C the coal was on fire. In this experiment no carbon dioxide was evolved at the lower temperatures, 120° to 130° as in the case of the other coals examined. The kindling temperature is practically the same as that at which oxidation begins, as judged by the evolution of carbon dioxide.

Fig. 50 represents a similar experiment in which powdered Pittsburgh gas coal was used. The figure shows that the temperature at which fire appeared was slightly higher than with the powdered bituminous coal of Fig. 47. "This suggests that the oxidation of hydrogen may also have a part in the chemical reactions involved as being perhaps, more readily available in coals of the strictly bituminous type."

A number of tests were also made, using air instead of oxygen. One set of results is reproduced (Fig. 51). They are for the same coal as was used in the experiments whose results are given in Figs. 47 and 48. It will be seen that the results are not essentially different from those obtained when oxygen was used. As would be expected, the activity of the oxidation is decreased so that the appearance of carbon dioxide was at 135° instead of at or about 120°. The voluminous appearance of CO_2 and the crossing of the lines occur at 165° instead of between 140° and 150°. At about 200° the external heat was withdrawn for a few minutes, the oxidation temperature dropped back in a similar manner. At 280°, however, the action had become entirely independent of external heating.

Apparently we have here an example of a type of combustion which occurs at a temperature far below the ignition point, and still is self-supporting and would be continuous with an adequate air supply.

FIG. 47. Absorption of oxygen by powdered Carterville coal in atmosphere of oxygen (8).

(From Parr and Francis)
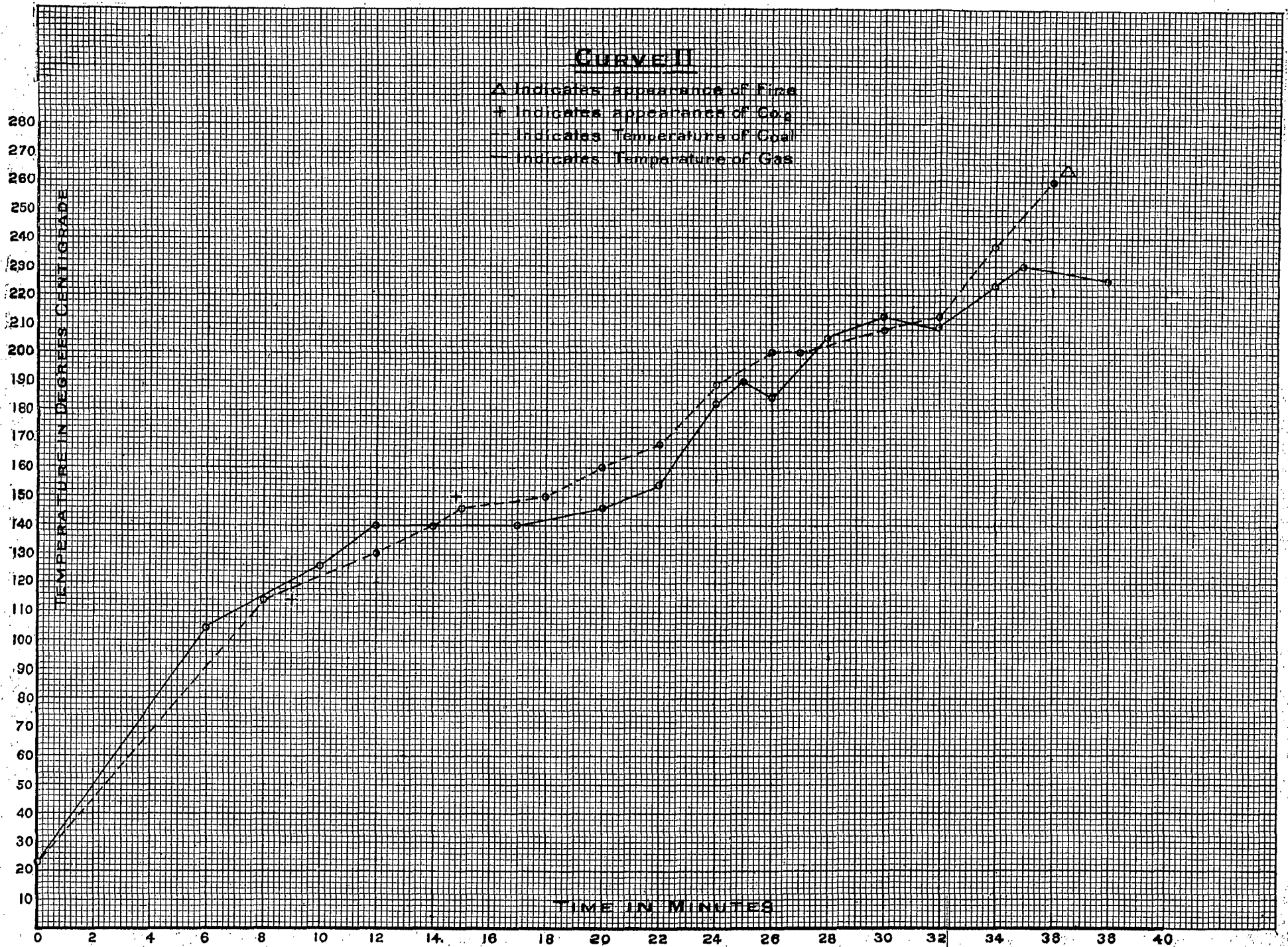
FIG. 48. Absorption of oxygen by buckwheat size Carterville coal in atmosphere of oxygen(9).

(From Parr and Francis)

CURVE III
A indicates appearance of fire
C indicates appearance of CO_2
— indicates Temperature of Coal
— indicates Temperature of Gas
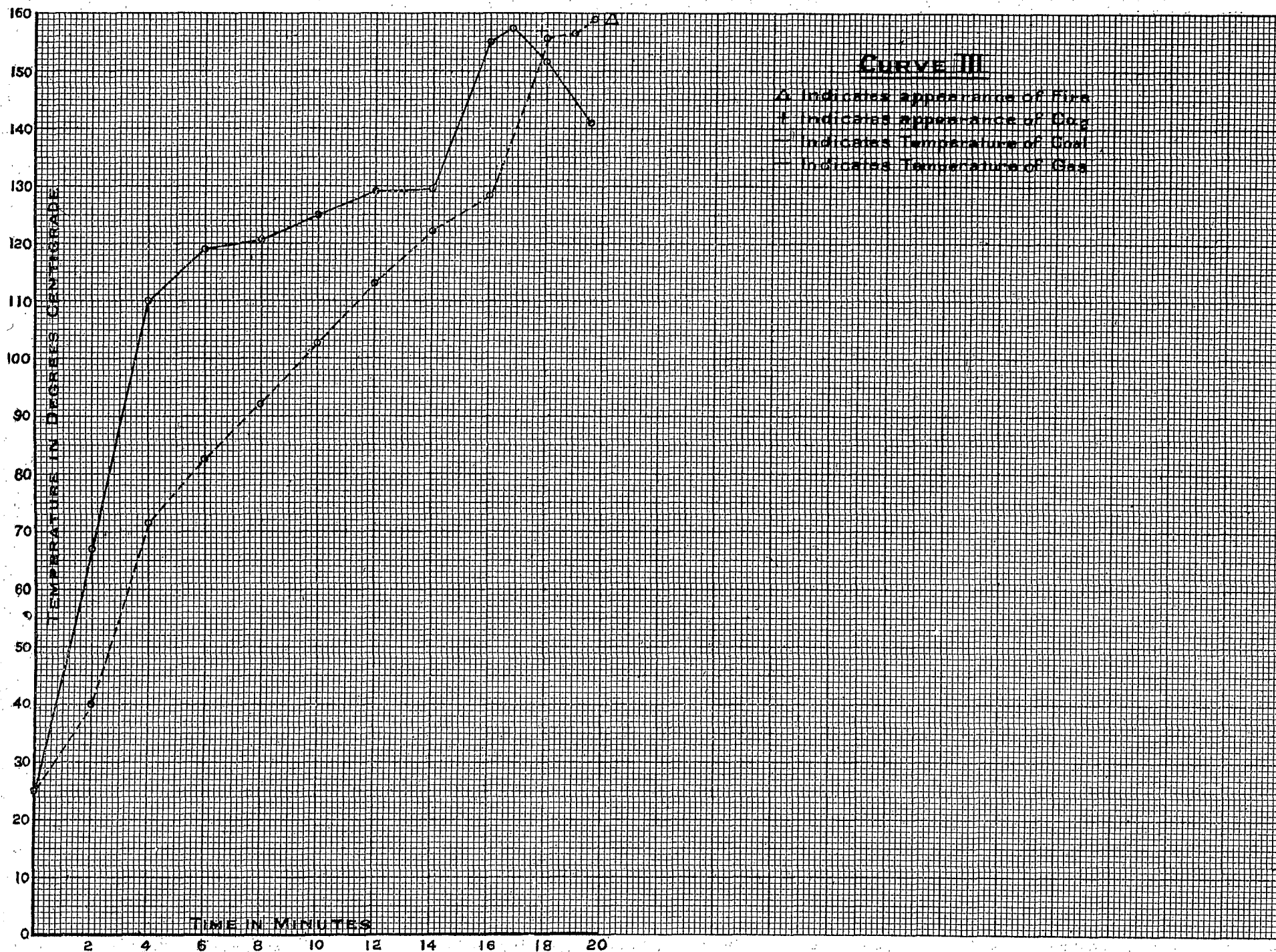
FIG 49. Absorption of oxygen by powdered Taylorville coal in atmosphere of oxygen (11).
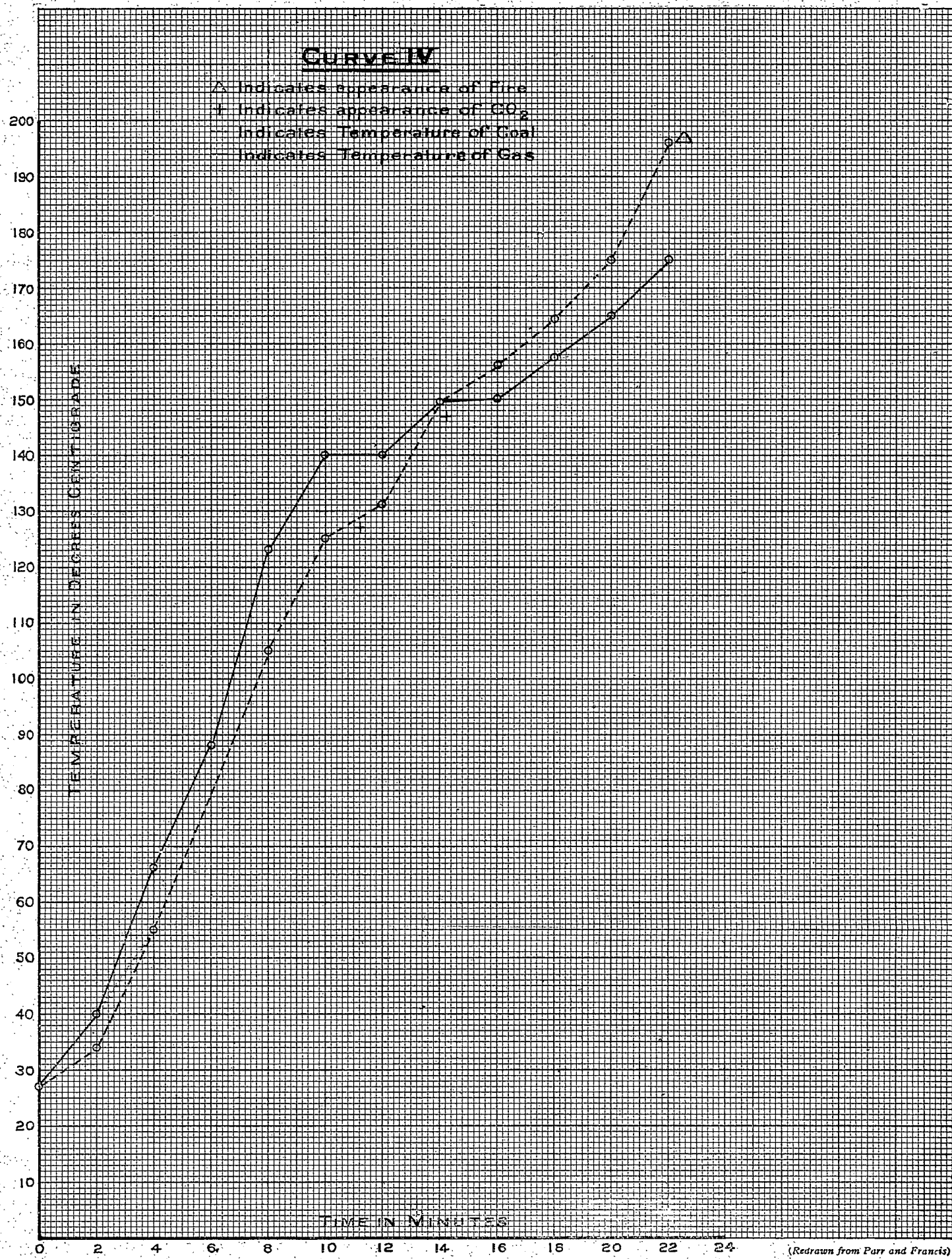
FIG. 50. Absorption of oxygen by powdered Pittsburgh gas coal in atmosphere of oxygen.

CURVE V

Ⓐ Indicates appearance of Fire
Ⓐ Indicates appearance of CO₂
Indicates Temperature of Coal
Indicates Temperature of Gas

FIG. 51.   Absorption of oxygen by powdered Carterville coal in air (15).

(From Parr and Francis)
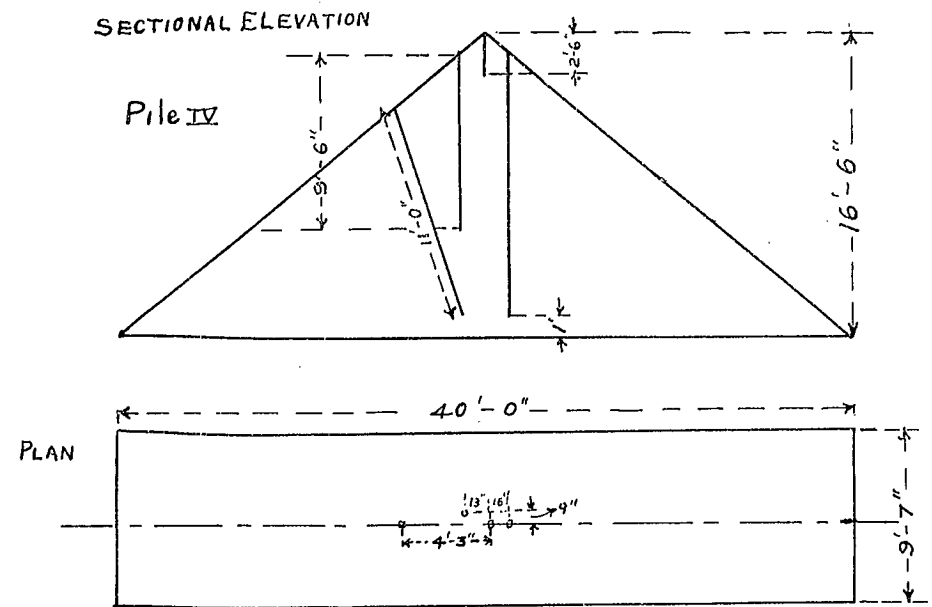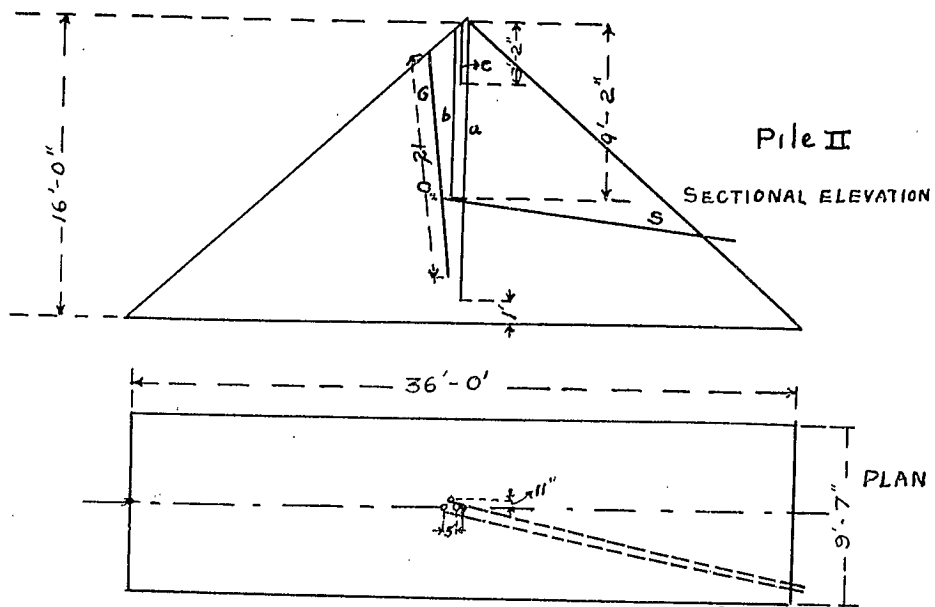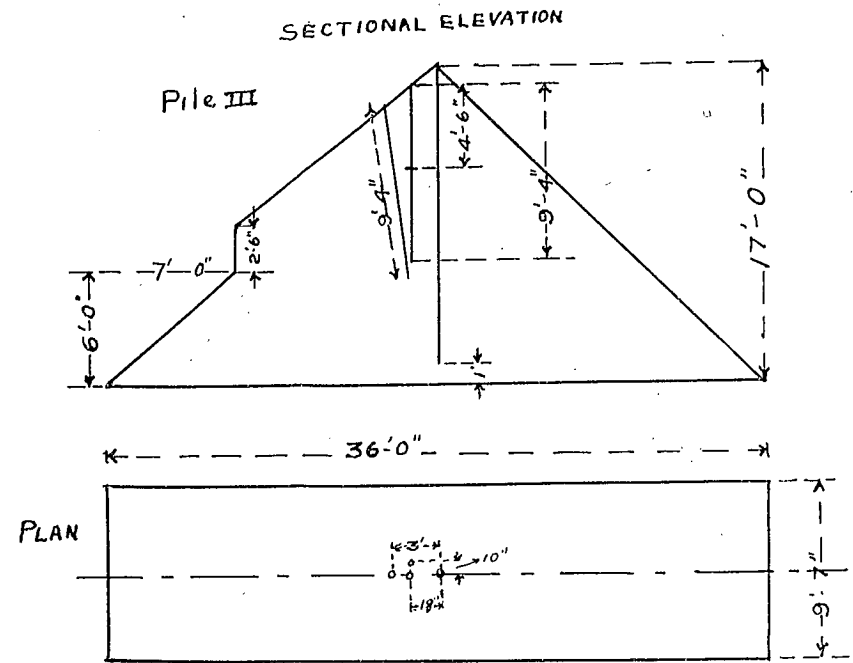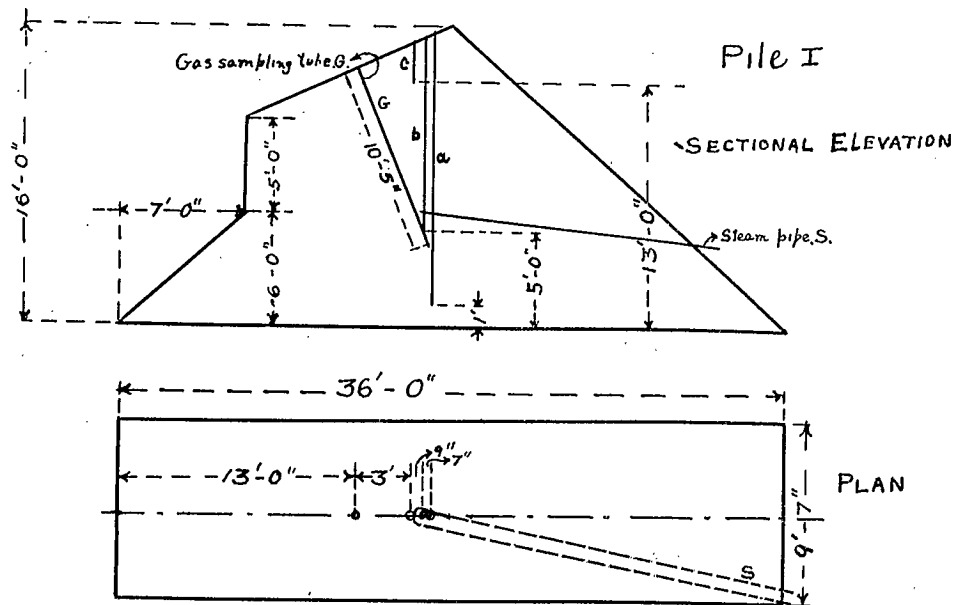
FIG. 54. Diagrams of coal piles, Glace Bay.

(Porter and de Hart.)

TABLE XLV.

Temperature and Pressure Readings—Glace Bay Storage.

(Porter and de Hart)

Date.	Relative humidity per cent.	Atmospheric temperature degrees C.	Atmospheric pressure Inches Hg:	Weather.	Temperatures (Deg. C.)											
					1A	1B	1C	2A	2B	2C	3A	3B	3C	4A	4B	4C
July 20......	97	17·6	29·95	Cloudy	—	—.—	—	13·5	13·5	13·5	—	—	—	—	—	—
21......	84	20·1	29·87	Fine	17·0	19·0	18·0	16·0	16·0	12·0	—	—	—	—	—	—
22......	78	18·3	29·90	Cloudy	16·0	18·0	17·0	14·0	14·0	10·0	13·5	14·0	16·0	20·0	—	—
23......	91	18·1	29·96	Showery	16·0	18·0	17·0	14·0	14·0	14·0	14·0	14·0	16·5	18·5	—	—
24......	57	19·9	29·97	Fine	17·0	19·0	18·0	14·0	14·0	14·0	14·5	14·0	17·0	20·0	—	—
26......	63	19·4	30·10	Fine	17·0	19·0	18·5	14·5	14·5	15·5	15·0	15·0	17·0	19·0	—	—
27......	48	21·3	30·33	Fine	17·5	19·5	19·5	14·0	14·5	17·0	15·5	15·0	18·0	20·0	18·0	—
28......	40	22·5	30·94	Fine	18·5	20·0	20·5	15·5	16·5	18·0	16·0	15·5	17·5	—	—	—
30......	65	21·7	30·10	Fine	—	21·3	—	—	17·0	—	—	—	—	—	—	—
31......	—	19·0	—*	Cloudy	17·5	20·5	21·0	15·5	16·0	18·2	15·5	16·0	18·5	19·0	18·5	—
Aug. 3......	63	15·8	—	Fine	18·0	20·5	22·0	15·5	17·0	18·0	15·5	17·3	19·5	21·0	19·5	—
10......	63	—	—	Fine	21·0	24·8	26·0	17·5	20·5	21·5	17·5	19·0	22·5	23·5	23·0	22·5
11......	—	19·1	—	Fine	—	—	—	—	—	—	—	—	—	—	—	—
13......	—	16·9	—	Fine	25·0	27·0	29·0	17·0	19·0	18·0	17·5	18·5	21·5	22·0	21·5	22·0
15......	64	18·7	—	Fine	25·0	28·0	30·0	17·0	20·0	17·0	17·5	18·5	21·5	23·0	22·5	23·5
16......	90	18·7	—	Wet	—	—	—	—	—	—	—	—	—	—	—.—	—
19......	90	17·5	—	Wet	25·0	28·0	32·5	19·0	20·5	16·0	17·5	19·5	20·0	23·5	22·5	24·0
20......	66	14·2	—	Cloudy	—	—	—	—	—	—	—	—	—	—	—	—
24......	54	16·9	—	Fine	29·0	32·0	35·0	17·5	20·0	16·5	17·0	17·0	17·0	24·5	20·5	23·5
27......	74	15·7	—	Fine	28·0	33·0	35·5	18·0	21·0	18·0	17·5	19·0	19·0	23·5	22·0	20·5
29......	96	21·5	29·79	Cloudy	30·5	33·0	37·0	19·5	22·0	19·0	19·0	21·0	20·5	25·0	24·0	27·0
31......	—	14·3	30·20	Fine	—	—	—	—	—	—	—	—	—	—	—	—
Sept. 3......	90	18·3	29·57	Showery	31·0	35·0	38·0	19·0	22·0	15·5	18·0	20·0	20·0	25·0	23·0	28·5
5......	—	15·1	—	Fine	—	—	—	—	—	—	—	—	—	—	—	—
9......	59	13·1	30·16	Fine	29·0	34·0	36·0	20·0	22·0	14·0	17·0	18·8	18·5	25·0	22·0	27·0
13......	—	16·3	29·70	Showery	29·5	34·0	37·0	18·5	21·0	17·0	18·0	18·0	19·0	23·0	21·5	25·0
15......	—	9·9	30·13	Fine	27·5	33·8	35·5	20·0	22·5	14·0	—	—	—	—	—	—

*No barograph readings were obtained between July 30 and August 28 owing to the fact that the barograph had been sent away for repairs.

CHAPTER VI.

THE PREVENTION OF FIRE IN STORED COAL.

The prevention of fire and even of serious deterioration of coal in storage is a matter of such great practical importance that it has engaged the serious attention both of Governments and private individuals for many years.

It is necessary to store very large quantities of fuel at all of the more important naval bases and at all industrial centres, and ordinarily these stores are in the form of piles of considerable height and of large extent completely exposed to the weather; but it has long been known that the majority of coals cannot safely be so stored in tropical climates, and that many coals are unsafe in large piles even in temperate lands.

The practical method of meeting the difficulty, so far as tropical stores are concerned, has been to use anthracite coals only, or when this has been impossible, to limit the size and particul .rly the depth of the storage piles, and to shovel the pile over, or otherwise ventilate and cool it whenever heating begins. Either of these expedients makes the coal very costly, and it has often been pointed out that any coal could be safely stored under water, either in large tanks and water-tight bins or actually below sea-level in docks properly constructed to contain the coal, and provided with the necessary filling and dredging appliances.

Submerged Storage.

The British Admiralty is more deeply concerned than any other single body in the matter of tropical storage, and it has accumulated a great mass of detailed information on the subject. Much of this information is necessarily confidential, but in general it may be said that in all cases submarine storage has been found to be effective in preventing decomposition and of course fire, but that the cost of the necessary equipment and the additional expenses in handling the coal are very considerable, added to which there are difficulties in many places from the contamination of the coal by silt, sewage, etc., contained in the water. It must also be remembered that the risk of fire is not confined to the coaling station; the coal ordinarily has to be sent out in cargo ships and later is bunkered in the ships that use it, and as submergence under these conditions is not practicable it is unsafe to attempt to use coals which heat, quite irrespective of the method of storage employed at the station. The general practice of the Admiralty is, therefore, to send out to tropical stations only such coals as have been proved to stand shipment and storage with a reasonable degree of safety, and to this end the various available coals have been carefully studied.

In more temperate climates a much wider range of coals can be safely stored, but for industrial purposes economy of handling is of great importance, therefore the piles are made as high as possible to lessen the first cost of the storage yards and cheapen handling. The result is that heating is common and fires not infrequent, and various devices have been tried such as submerged bins, ventilation channels through the coal, etc.
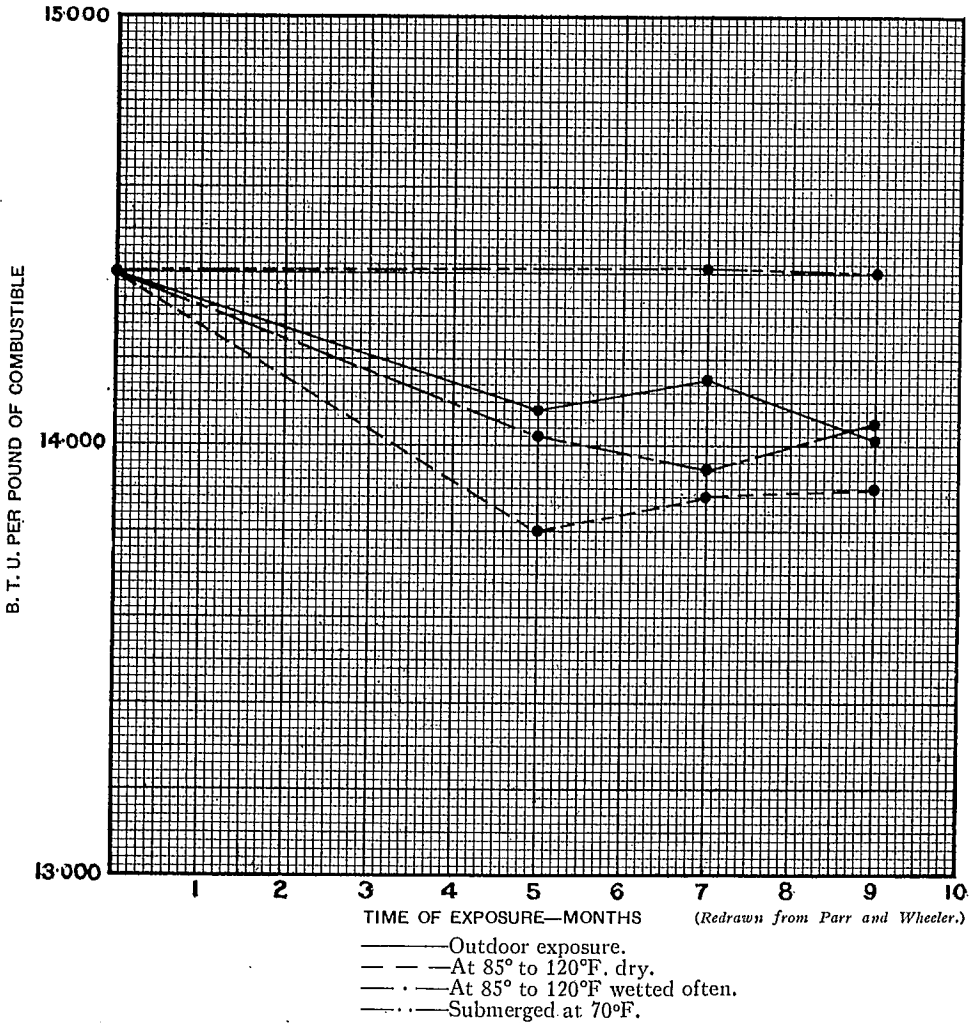
Fig. 52. Calorific power of exposed vs. submerged coal.

————Outdoor exposure.
— — —At 85° to 120°F. dry.
—— · ——At 85° to 120°F wetted often.
——·· ——Submerged at 70°F.

Some tests made by the British Admiralty[1] to determine the weathering losses of coal stored in the air and of coal submerged under water have been made public. In May, 1903, twenty-one tons of coal were selected from storage piles. Ten tons were stacked in heaps and covered with tar-

[1]Eng. News, Vol. 56, 1906, p. 17.

paulins and ten tons were placed in two-ton crates and submerged in one of the navy yard basins at Portsmouth. The remaining ton was burned carefully under a test boiler, observations being made of its calorific and evaporative qualities. The crates were taken up at intervals and the coal was tested by burning in comparison with the coal stored on dry land for the same length of time. The actual figures are not available, but it is reported that in every case the results were in favour of the submerged coal.

A test made by the Fuel Engineering Co.[1] of Chicago on coal stored under water for two years, and similar coal exposed to the atmosphere for two years, showed calorific values as follows:—

Submerged coal 11,937 B.Th.U., weathered coal 11,718 B.Th.U., or a difference of about 1·9 per cent. Since both samples contained 15·9 per cent of ash the two results are directly comparable.

Parr and Wheeler[2] refer to the storage of coal by the Western Electric Company, whose 15,000 ton concrete bins contain coal which is kept altogether submerged. This coal shows an advantage of 1·9 per cent in heating value in favour of the coal stored under water, after a period of two years. The same authors had previously[3] published some curves from Hamilton's experiments—Fig. 52— showing that coal stored under water for almost one year suffered no appreciable alteration.

In spite of ample evidence that submergence either in fresh or sea water not only protects coal from fire, but also retains its full heating power indefinitely, practical difficulties have thus far prevented any extended commercial use of this system, and it is doubtful whether it will ever be employed very largely for ordinary coals except perhaps at tropical naval bases; but there is undoubtedly a large field for this method of storage in the case of lignites and lignitic coals, which not only heat readily, but also disintegrate and lose a very appreciable fraction of their value on weathering. Such coals can be kept virtually intact under water, and it is probable that in the course of time it will be found commercially expedient to provide submerged stores at places where such coals can be produced or sold at much lower prices than more stable fuel. There are immense quantities of lignitic coal in many parts of the world—as for example in Alberta and Saskatchewan in central Canada; and although they have lower calorific value than bituminous coal, their geographical situation renders them the logical fuel for large areas. As a matter of fact these coals are already much used at points where a fresh and reliable supply can be secured. By suitable system of storage their use could be very greatly extended, and arrangements to this end will no doubt be made comparatively soon, unless in the meanwhile some cheaper method of preservation is developed, or we come to burning coal at the mines and transmitting its heat and power electrically or otherwise.

[1] Eng. News, Vol. 60, 1908, p. 729.
[2] "The Weathering of Coal." Bull. 38, University of Illinois Experiment Station, 1909.
[3] The Deterioration of Coal. Journal American Chemical Society, Vol. XXX, 1908, pp. 1027-33.

Ordinary Storage.

Many authorities recommend as an alternative to submergence that the coal be stored in sheds affording protection from both sun and rain. It is by no means clear that rain is harmful (see p. 27), although there is a widespread belief that it precipitates heating, but there is no doubt that exposure to the sun is dangerous at least while the pile is being made, as coal, owing to its blackness, absorbs heat rapidly, and if it is then covered by a fresh layer of coal this heat is retained and greatly accelerates subsequent oxidation. When the quantities to be stored are comparatively small or the conditions particularly severe this expedient of storing under cover is worthy of consideration; but when the quantities are large the cost of the sheds becomes a serious item, and there is usually also a considerable increase in the handling expenses owing to the increased complexity of the loading and unloading arrangements. It is therefore very unusual to have large covered storage plants except perhaps at certain tropical naval stations where cost is of secondary importance. It should, however, be noted in this connexion that enclosed storage even on a fairly large scale is frequently practised for reasons having little or nothing to do with oxidation and heating. It is quite customary to have loading bins of large capacity at railway and steamship coaling stations; but these are to enable supplies of fuel to be quickly loaded by gravity, and under ordinary conditions no one lot of coal remains long enough in such storage to run risk of heating.

In cold and wet localities it is also occasionally expedient to house coal supplies, as otherwise the fuel would freeze into a solid mass of mixed coal and ice.

When submerged storage is impracticable and the coal is piled either in sheds or in the open it is clear that the air cannot be excluded and heating is liable to occur. Provision must then be made for conducting the heat generated away from the pile. This can be done in two ways, first, by piling the coal in shallow heaps, or second, by ventilating the coal pile. It has been found by practical experience that shallow coal piles will not ignite spontaneously, the particular height to which any coal can be safely piled can, however, only be determined experimentally. The same result can be obtained in deeper piles by providing air ducts whereby the coal is so well ventilated that the supply of air is so greatly in excess of that needed for oxidation that the incoming air will keep the pile cool.

A method of storing coal and ventilating it has been developed by the **Canadian Pacific Railway**[1] whereby fires have been virtually eliminated. The method in general is: first to level off a triangular piece of ground so that temporary tracks may be laid upon it and a steam shovel used if desired. A track is then laid in and hopper-bottom coal cars unloaded on this track, which is then raised on the coal and the operation repeated until an embankment of considerable height is made, with an inclined track from the apex of the triangle to the main line. When a sufficient height is reached,

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[1] See plates I, II, VI, and pp. 159-163.

PLATE II.

General view of storage pile at Angus.

the coal is side dumped or side shovelled and the track is gradually shifted to one side and the width of the pile thus increased to any desired extent. The height of the pile on the approach increases from nothing to about 16 feet, and this latter height is maintained for the major portion of the pile.

As soon as possible after each portion of the pile reaches its full height it is ventilated by driving pointed iron rods, $1\frac{1}{2}''$ or $2''$ in diameter, vertically down through it. After the rod reaches the bottom a bell-shaped collar is slipped over it and forced down about six inches into the coal, as shown in Fig. 53, p. 153. The rod is then tapped to compact the coal around it and to loosen the rod itself and both collar and rod are withdrawn. A rough funnel of tar paper is then put in the bell-shaped top of the hole to prevent pieces of coal falling in or being washed in by the rain. The walls
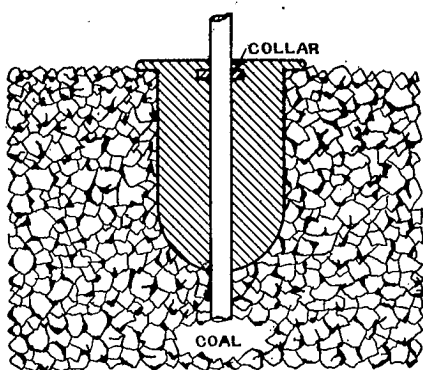
(*Porter and Brunton.*)

FIG. 53. Apparatus for ventilating storage piles.

of the lower part of the hole maintain themselves without protection, and holes driven in this way ordinarily last for many months. The distance between the holes varies somewhat with the circumstances; but generally it is about $16''$ from centre to centre, and the cost, which is almost wholly labour, amounts to approximately 5c. per ton.

Another method, which is frequently effective, and in certain cases economically possible, is to pile the coal in layers of about 2 feet, allowing each layer to be exposed to the air for at least two days, and if possible much longer, before it is covered by the next layer. This method is usually effective in preventing fire, if the piling is done in cool weather, but in mid-summer, particularly in hot and sunny weather, it is of doubtful value to say the least. Porter and de Hart have experimented on this method of storage, see pp. 154-159.

In order to obtain detailed information on deep storage piles a series of experiments were made by the author and his assistants, Messrs. Brunton and de Hart, on Nova Scotia coals from the Dominion Coal Company, these coals being selected because they form the main part of the ordinary fuel supply of eastern Canada. These tests were carried out under two

heads: (1) to study the storage of fresh coal at the mines; and (2) to study the behaviour of coal which had been shipped in cargo lots to Montreal and stored there.

Porter and de Hart experiments, Glace Bay.

The experiments at the mines were made at Glace Bay, Nova Scotia, in the summer of 1911, by Mr. J. B. de Hart working under Dr. Porter's personal direction. Four similar piles were made by dumping coal cars from a railway trestle. Each pile contained about 90 tons and was built as follows:—

Pile No. 1. The coal used was fresh "run-of-mine" from No. 4 mine of the Dominion Coal Company. (Phalen seam). It was mined the day before the pile was built, and was exactly as it came from the mine except that it became damp owing to rain, which fell during the transfer.

Pile No. 2 was made with coal from the large stock pile of the Dominion Coal Company. This coal had been mined in February and was chiefly but not wholly from the Phalen seam. This coal was also damp when piled.

Pile No. 3 was built of two kinds of coal. First, nine or ten feet of stock coal, as in pile 2, was dumped, and on top of that five or six feet of freshly mined run of mine coal from No. 4 colliery as in pile 1. Both coals were damp.

Pile No. 4 was the same as pile No. 1 except that the coal was piled in layers about 3 to 5 feet thick, an interval of two days being left between the dumping of successive layers.

The piles were situated between successive bents of a trestle. The coal was not in contact with the wood of the trestle, however, as the bents between which the coal was dumped were boarded up and protected by galvanized iron. The location can be seen from photographs. (Plates III, IV, and V.

The method of piling the coal was by dumping it from hopper bottom cars on top of the trestle and then "trimming". In some cases the coal tailed out over the tracks at the side of the trestle and had to be held back by a low wall of planks as can be seen in the photographs above mentioned. These planks constituted the only wood in contact with the coal. The coal for piles 1 and 4 and the top half of 3 was mined on July 19, 1911. The dumping of pile No. 1 was commenced on July 20, and finished July 21. Pile No. 2 of stock was dumped on July 20. The stock coal in Pile No. 3 was dumped on July 20, and the fresh coal on July 21. Pile No. 4 was built in layers as follows: July 21, 30 tons; July 24, 15 tons; July 26, 15 tons; July 28, 15 tons; and July 31, 15 tons.

As each pile was made three $\frac{1}{2}$ inch iron pipes were put in. They were 8 feet, 14 feet, and 20 feet long respectively. These pipes were open at the bottom and were threaded at the top and were kept closed by caps or wooden plugs. Their positions are shown in plan and elevation in Fig. 54. Two pipes (S) in the form of a U were also placed, one in pile 1, and one in pile 2. They were open at the ends which projected into the air.

PLATE III.
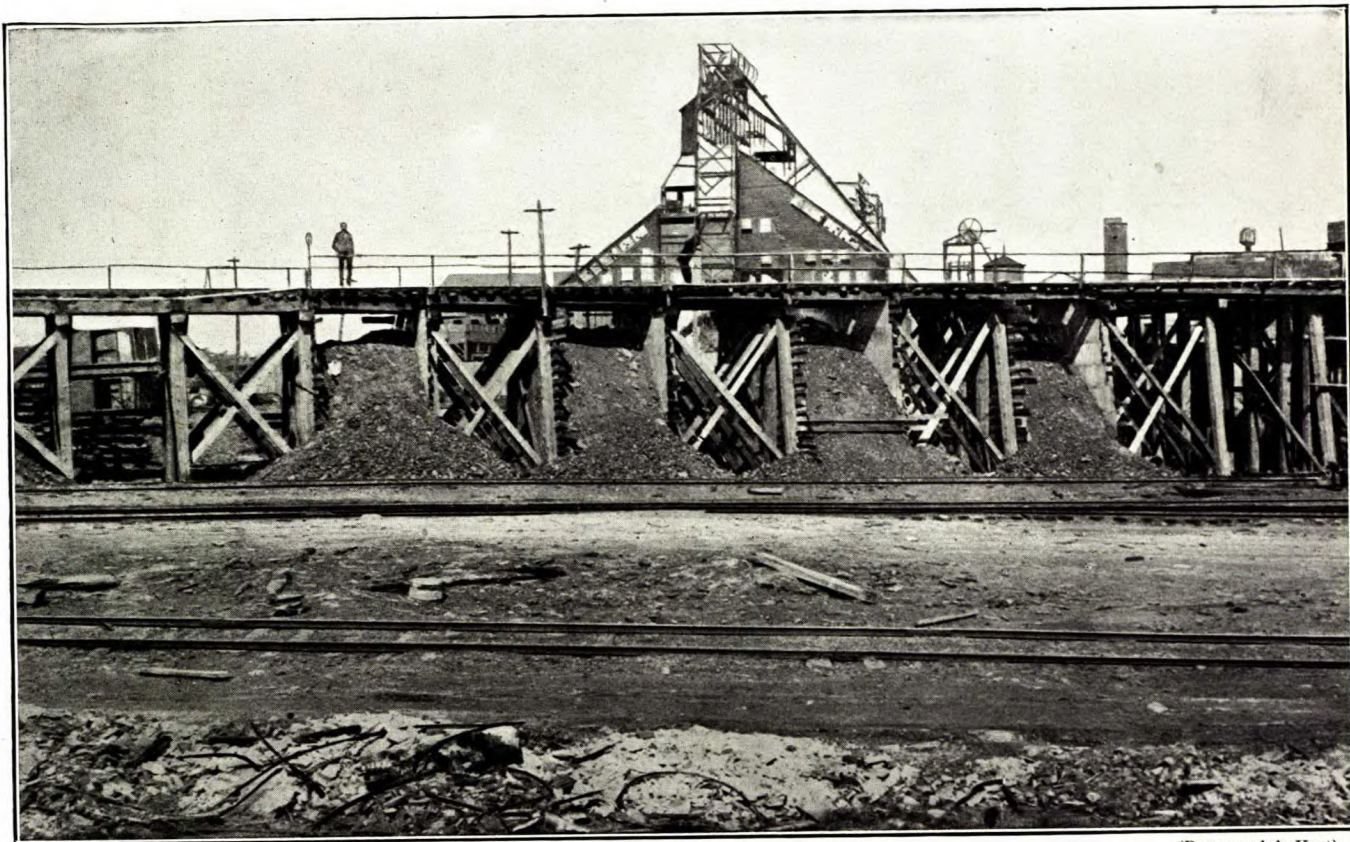
(Porter and de Hart)

General view of experimental piles at Glace Bay.

PLATE IV.

(Porter and de Hart)

General view of experimental piles at Glace Bay.

Their use will be explained later. A brass tube G, $\frac{1}{8}$ inch internal diameter was forced to the centre of each pile after it had been completed. These brass tubes were used to draw off gas samples from the interior of the piles. All these pipes and tubes are shown in Fig. 54.

Temperatures were taken at frequent intervals in the $\frac{1}{2}$ inch pipes. It will be well to refer to these pipes by symbols. All the long pipes will be called A, the medium pipes B, and the short pipes C. Thus the top pipe in pile 1 will be called 1C, and in pile 2, 2C, and so on. The middle pipe in pile 3 would be 3B.

The atmospheric temperature and pressure were recorded by a thermograph and barograph respectively, and the relative humidity was taken at intervals. The results of these observations, together with notes on the weather, are given in Table XLV.

The temperatures and pressures given are the average for the 24 hours obtained from the thermograph and barograph curves. All temperatures are given in degrees centigrade. The temperatures in the $\frac{1}{2}$ inch pipes were taken by maximum recording thermometers which were let down to the bottoms of the respective holes by strings. When the temperature in the holes was less than the atmospheric temperature it was impossible to use these thermometers, hence an ordinary centigrade thermometer was employed, and was pulled up and read as rapidly as possible. The error thus introduced was probably less than one degree except in one case noted. The temperature readings have been plotted on a time base as per Figs. 55-61, p. 156, and in this way the rise of temperature can perhaps be most readily seen.

A point which is clearly shown by these figures is the fact that the coal which was piled in layers heated less than the coal which was piled quickly. Unfortunately, the coal in none of the piles heated to any great extent, and it is, therefore, impossible to tell whether piling the coal in thin layers at intervals of several days would prevent spontaneous combustion in a case where it would otherwise occur. The difference in temperature rise, however, is considerable. The maximum temperatures attained in piles 1 and 4, which were almost identical except for the length of time taken in building, were as follows:—

1A 30·8°	1B 35°	1C 38°
4A 24·3°	4B 22·75°	4C 27·5°

It seems probable, therefore, that piling the coal in layers and exposing each layer to the air would, in many cases prevent spontaneous combustion. Unfortunately in the majority of cases economic considerations prevent the adoption of this method of piling the coal, as ordinarily the pile is made by dumping the coal out of railway cars run on a track laid on the pile and shifted as the pile grows. In such cases the above method would involve a disproportionate expense for track moving. The method, however could be used without much added expense where the piles are made by an overhead travelling grab.

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The higher temperature of piles which have been built quickly is probably due to the fact that absorption of oxygen and consequent heating is exceptionally rapid in the first few hours of exposure. If the coal is covered in by fresh coal at this stage it retains its heat, whereas, if it is left exposed for a longer period, the rate of oxidation decreases and the coal is free to cool off to approximately atmospheric temperatures. If, however, the pile is built in hot weather and particularly in bright sunlight, slow piling is likely to result in even greater heating than quick piling. As a matter of fact coal piled in summer and in dry, i.e., sunny weather, is found to be especially liable to give trouble.

It is interesting to note the times taken to attain the maximum temperatures. They were approximately as follows:—

TABLE XLVI.

Dates of Maximum Temperature in Glace Bay Storage.

(Porter and de Hart)

Pipe.	Date of max. temp.	Time since completion of pile.
1A	September 4	45 days
2A	„ 17	59 „
3A	August 27	38 „
4A	September 4	35 „
1B	„ 4	45 „
2B	„ 17	59 „
3B	August 29	40 „
4B	„ 30	30 „
1C	September 3	44 „
2C[1]	„ 17[1]	59[1] „
3C[1]	August 28[1]	39[1] „
4C[1]	September 4[1]	35 „

[1]Records too irregular to enable any smooth curve to be drawn. Probably due to some extent to the enforced use of a non-maximum thermometer.

We may say that roughly, Pile 1 reached its maximum temperature on September 4, Pile 2 on September 17, Pile 3 on August 28, and Pile 4 on September 4.

On September 16, temperatures were taken in the pipes in pile 1 every foot down. These temperatures showed the maximum temperature to be about three or four feet below the surface. The same general location had been observed by Porter and Brunton previously at Angus, and was later found to be true of a C.P.R. coal pile at Outremont. Probably above the depth of maximum heating there is too rapid radiation and ventilation to allow of the maximum temperature being attained, and below this point there is insufficient oxygen to enable the coal to oxidize freely enough to yield high temperature.

In order to determine the absorption of oxygen and evolution of methane and other gases, gas samples were drawn from the centre of the pile and analysed. The samples were sucked out through the brass tubes
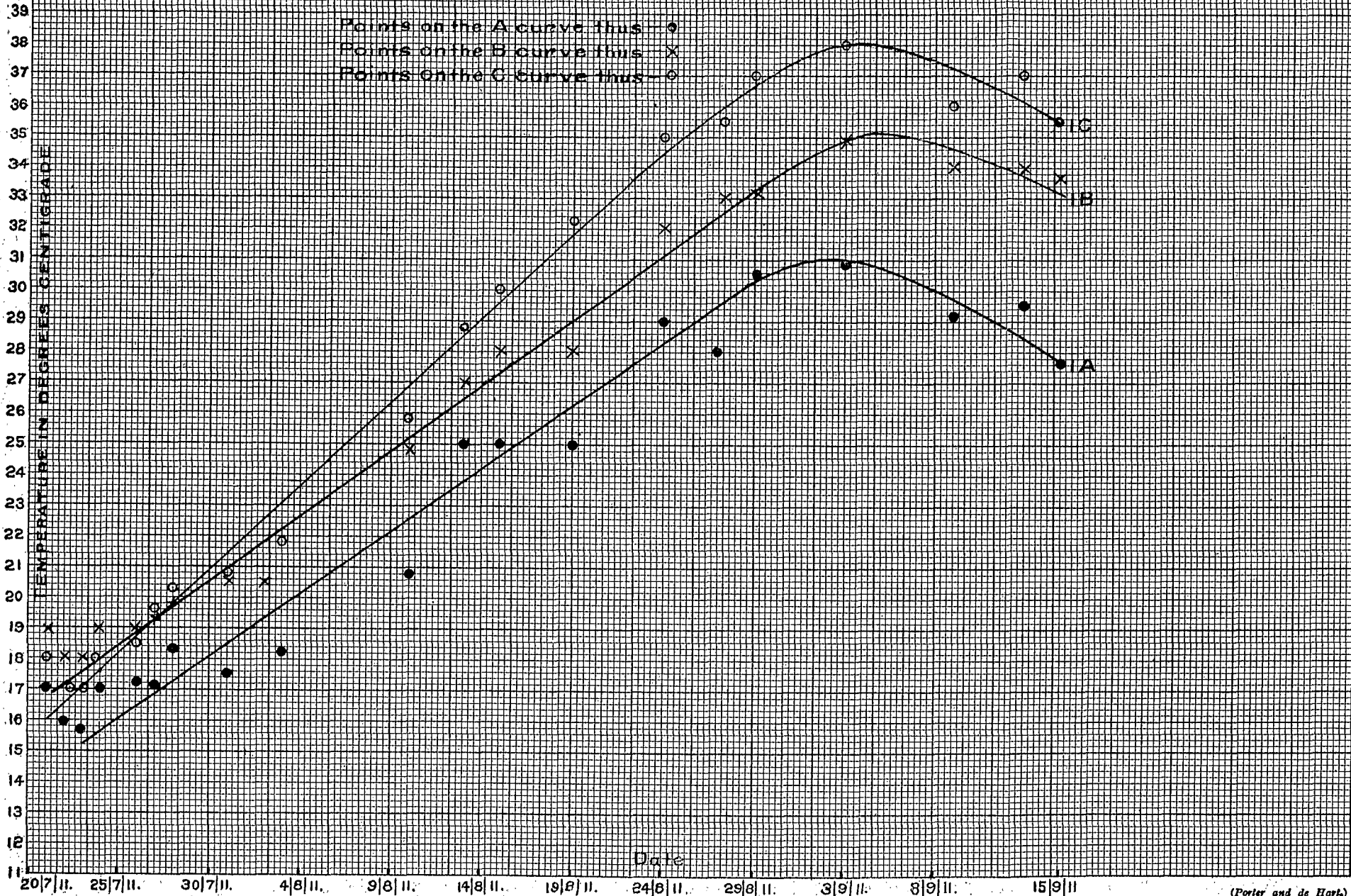
FIG. 55. Graphic record of temperature in Pile No. 1, Glace Bay, N.S.

FIG. 55. Graphic record of temperature in Pile No. 1, Glace Bay, N.S.

(Porter and de Hart.)

FIG. 56. Graphic record of temperature in Pile No. 2, Glace Bay, N.S.

CURVES SHOWING
TEMPERATURES IN PILE 3

Points on the A curve thus—o
Points on the B curve thus—x

FIG. 57.   Graphic record of temperature in Pile No. 3, Glace Bay, N.S.

CURVES SHOWING
TEMPERATURES IN PILE 4

Points on the A curve thus ×
Points on the B curve thus ●
Points on the C curve thus ○
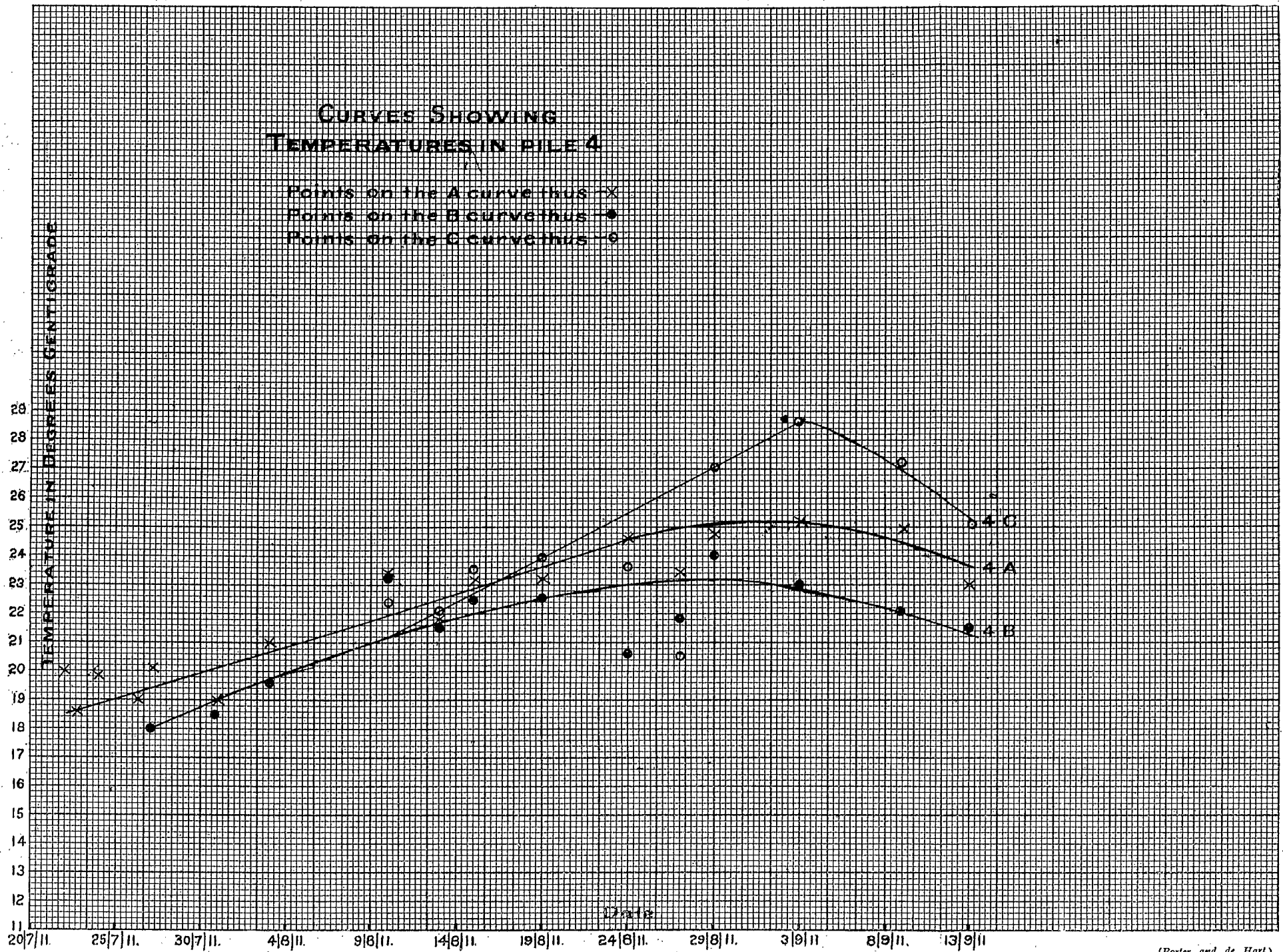
FIG. 58. Graphic record of temperature in Pile No. 4, Glace Bay, N.S.

(Porter and de Hart.)

CURVES SHOWING
TEMPERATURES IN "A" PIPES

Points on the "1A" curve thus = ○
Points on the "2A" curve thus = ●
Points on the "3A" curve thus = ✕
Points on the "4A" curve thus = ▢
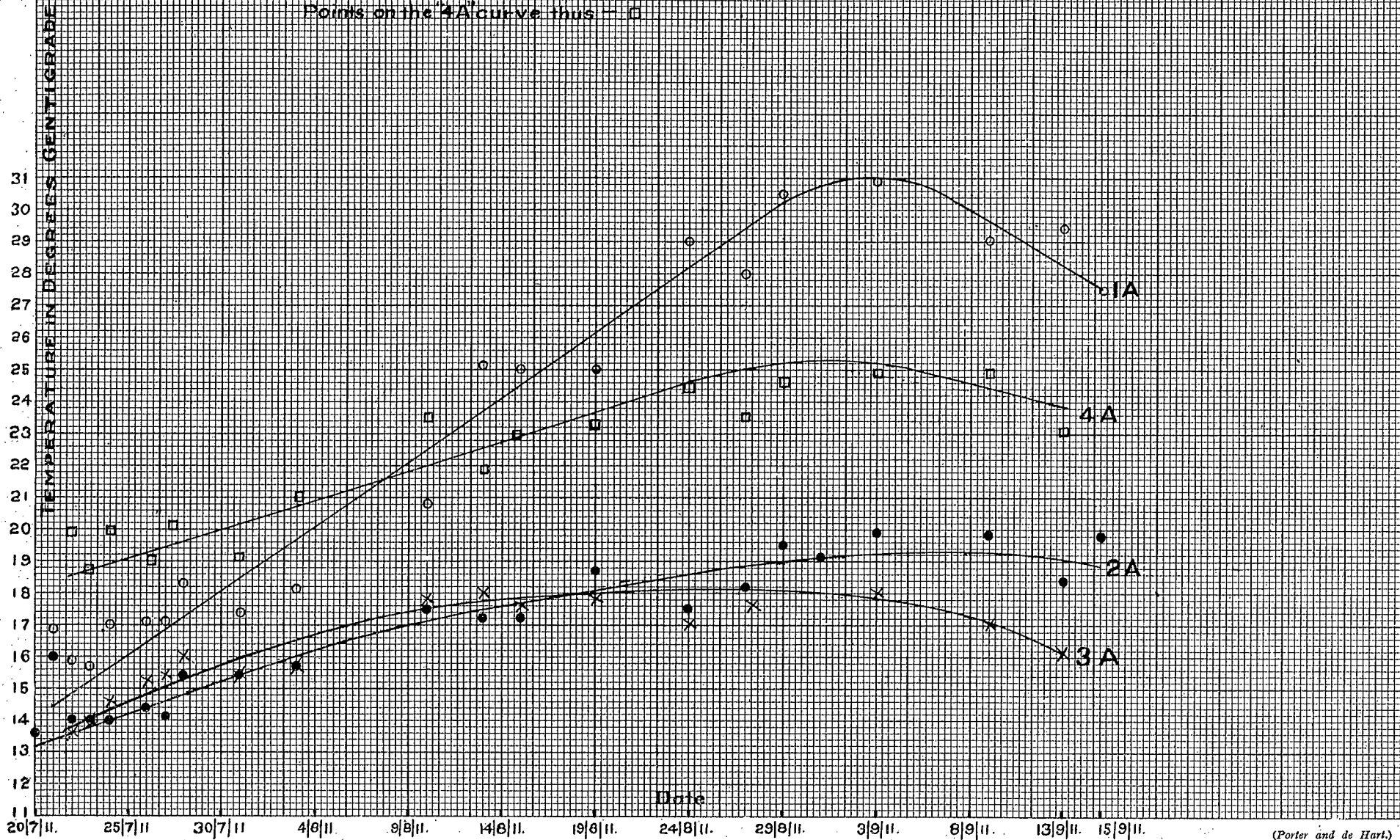
FIG. 59. Graphic record of temperature in A pipes, Glace Bay, N.S.
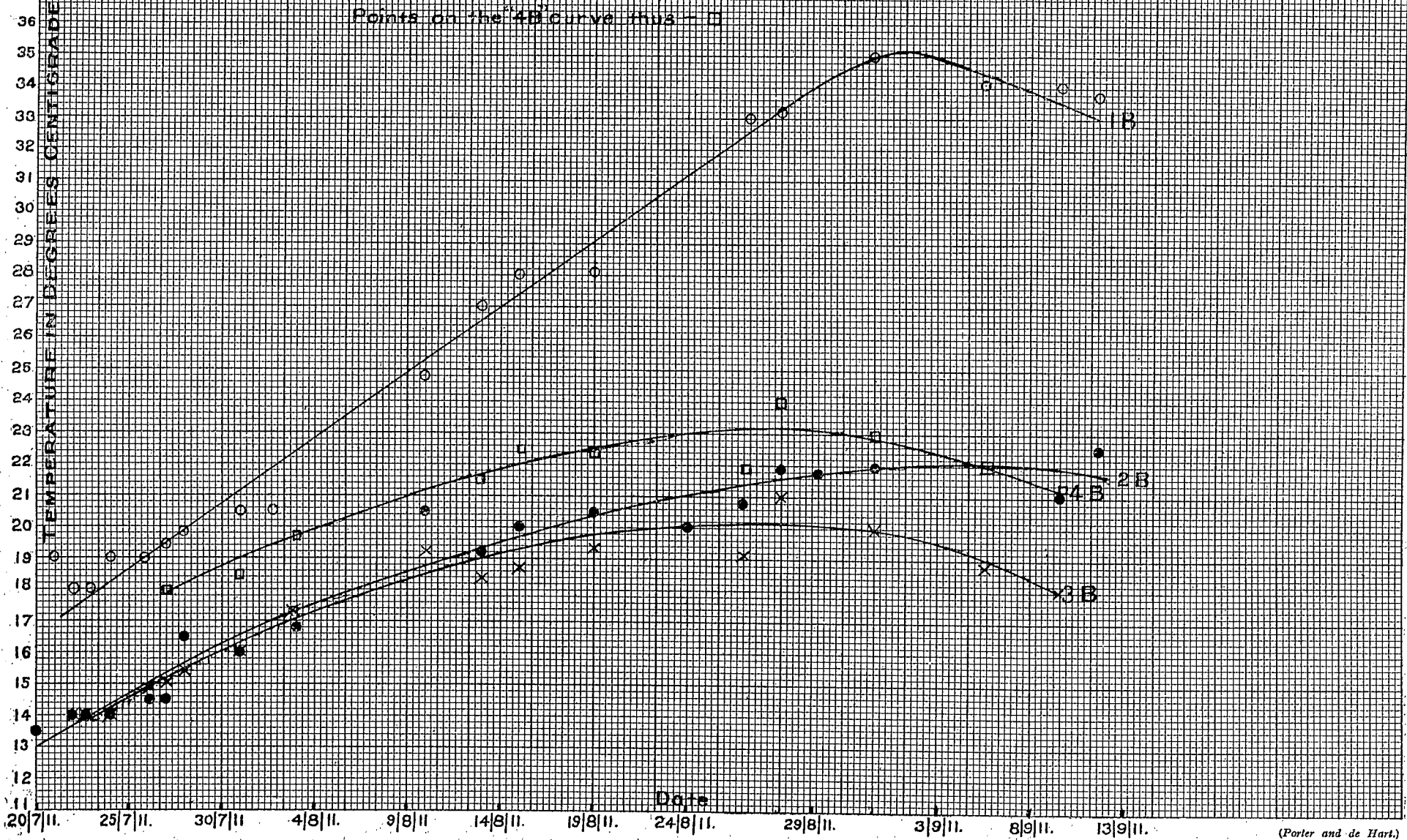
(Porter and de Hart.)

Fig. 60. Graphic record of temperature in B pipes, Glace Bay, N.S.

CURVES SHOWING
TEMPERATURES IN C PIPES

Points on the IC curve thus— o
Points on the 4C curve thus— •
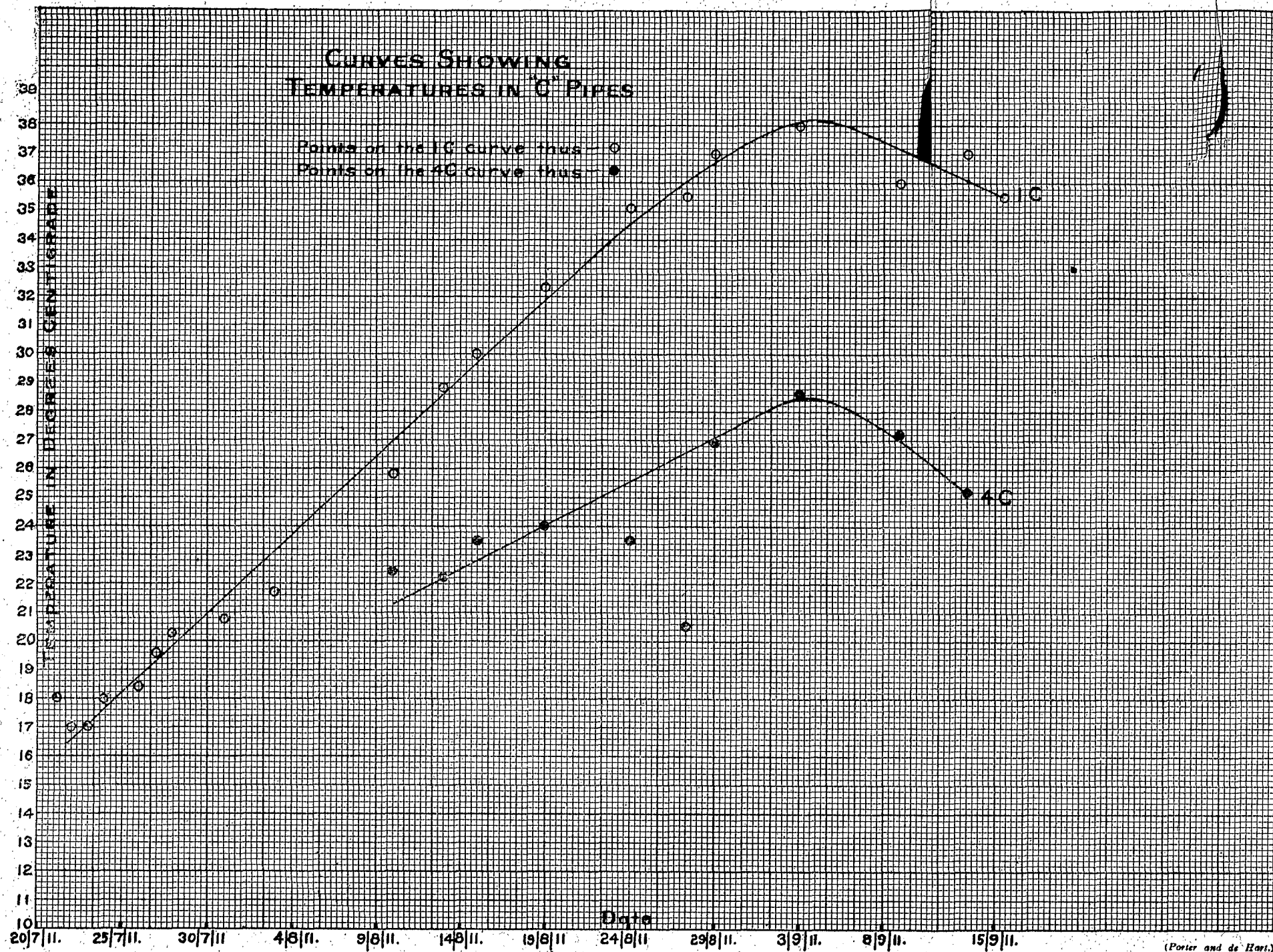
FIG. 61. Graphic record of temperature in C pipes, Glace Bay, N.S.

(Porter and de Hart.)

mentioned above. About 250 cubic centimetres were first drawn off and discarded in order to ensure the removal of all air from the tube. Then 250 c.c. of gas were taken. The standard methods of analysis with absorption pipettes were employed. Practically no carbon dioxide or heavy hydrocarbons were found in the gases evolved, but even in the case of the stock coal the oxygen content was always low. It has been noted that the oxygen content is very variable, but there seems to be no connexion between its variations and the pressure, temperature or relative humidity readings, these consequently are omitted from Table XLVII.

TABLE XLVII.

Oxygen in Gas Samples from Glace Bay Storage Piles.
(Porter and de Hart)

OXYGEN IN PER CENT.

Date.	Pile 1.	Pile 2.	Pile 3.	Pile 4.
Aug. 13........................	19·8	20·8	20·6	20·6
Aug. 16........................	19·2	20·0	20·4	18·9
Aug. 20........................	20·3	20·6	20·6	20·5
Aug. 24........................	20·7	20·4	20·4	....
Aug. 27........................	20·1	20·6	20·4	20·2
Aug. 29........................	20·1	20·2	20·4	20·8
Aug. 31........................	19·9	20·2	20·4	19·9
Sept. 3........................	20·4	20·3	20·2	20·1
Sept. 7........................	20·3	20·3	20·3	20·2
	20·1	20·4	20·4	20·2
Sept. 8........................	20·1	20·4	20·4	20·3
	20·2	20·3	20·4	20·3
Sept. 10........................	20·2	20·4	20·4	20·3
	20·2	20·3	20·3	20·3
Sept. 11........................	20·4	20·4	20·4	20·6
	20·5	20·3	20·6	20·4

After September 3, duplicate sample tubes were filled with g. s, one immediately after the other in order to check the analysis. The results of both analyses are given.

These figures show a slight depletion of oxygen. Although the samples from pile 1, which became hotter than any of the other piles, shows the lowest oxygen content, the oxygen of the samples does not appear to diminish as time goes on, and oxygen from the air must therefore have obtained access to the interior of the pile.

Attempts were made to determine the relation of the gas-pressure in the heart of the pile to the atmospheric-pressure outside by means of the small pipes already referred to. The apparatus used was that which had been employed by Porter and Brunton at Angus, see page 159. It was found almost impossible to get satisfactory readings except in very quiet weather, as the small, but frequent changes in the external pressure due to the wind masked the still smaller differences in pressure in the piles. Owing to this difficulty the number of reliable readings obtained is far too small to prove anything, they are, however, given here as an indication of the amount

of pressure or suction, and in the hope of stimulating further experimental work along this line.

TABLE XLVIII.

Pressures in Interior of Glace Bay Storage Piles.

(Porter and de Hart)

Date	Pressure in inches of water.			
	Pipes			
	1B	2B	3B	4B
Aug. 11.....................	−0·0066	−0·0091	−0·0054	−0·0048
Aug. 16.....................	+0·0195	+0·0113	+0·0136	+0·0082
Aug. 20.....................	−0·0174	−0;0206	−0·0162	−0·0000
Aug. 24.....................	−0·0223	−0·0131	−0·0022	−0·0264
Aug. 27.....................	+0·0438	+0·0024	−0·0000	−0·0000
Aug. 29.....................	+0·0012	−0·0000	−0·0000	−0·0000

+ signifies pressure, — signifies suction.

August 21 being a very still day it was found possible to take readings with one limb of the U tube open to the air, and in all four cases these readings checked exactly.

It will be noted that there is no case in which some of the piles showed pressure and others showed suction. Hence it is natural to look to external causes for the changes in pressure. A study of the barometric and thermometric readings and of the relative humidity shows that there may be some relation between the atmospheric conditions and the pressure changes in the pile, but, owing to the very small number of readings obtained and their small amount, it is unwise to attempt to draw any conclusions of weight from the records.

No barometer readings were taken on August 11, as the barograph was not available on that date. With the exception of the reading 1B on August 27, however, the records show no suction when the barometer was falling and no pressure when it was rising.

At the conclusion of the Glace Bay experiments above outlined, Mr. de Hart observed the loading of a collier belonging to the Dominion Coal Company, one hatch of which was loaded with freshly mined coal from a single one of the Company's mines, while the remainder of the cargo was made up of ordinary mixed coal as it came to the loading pier.

Mr. de Hart then went to Montreal on the collier and observed the unloading, and saw that all of the coal from the particular hatch under observation was shipped to the Canadian Pacific Railway's storage yard at Outremont, Montreal, where in turn he saw it piled according to the standard Canadian Pacific Railway method, detailed on page 152. He then put observation tubes in the pile and connected them up with the apparatus which had been used by Porter and Brunton a year before,

PLATE V
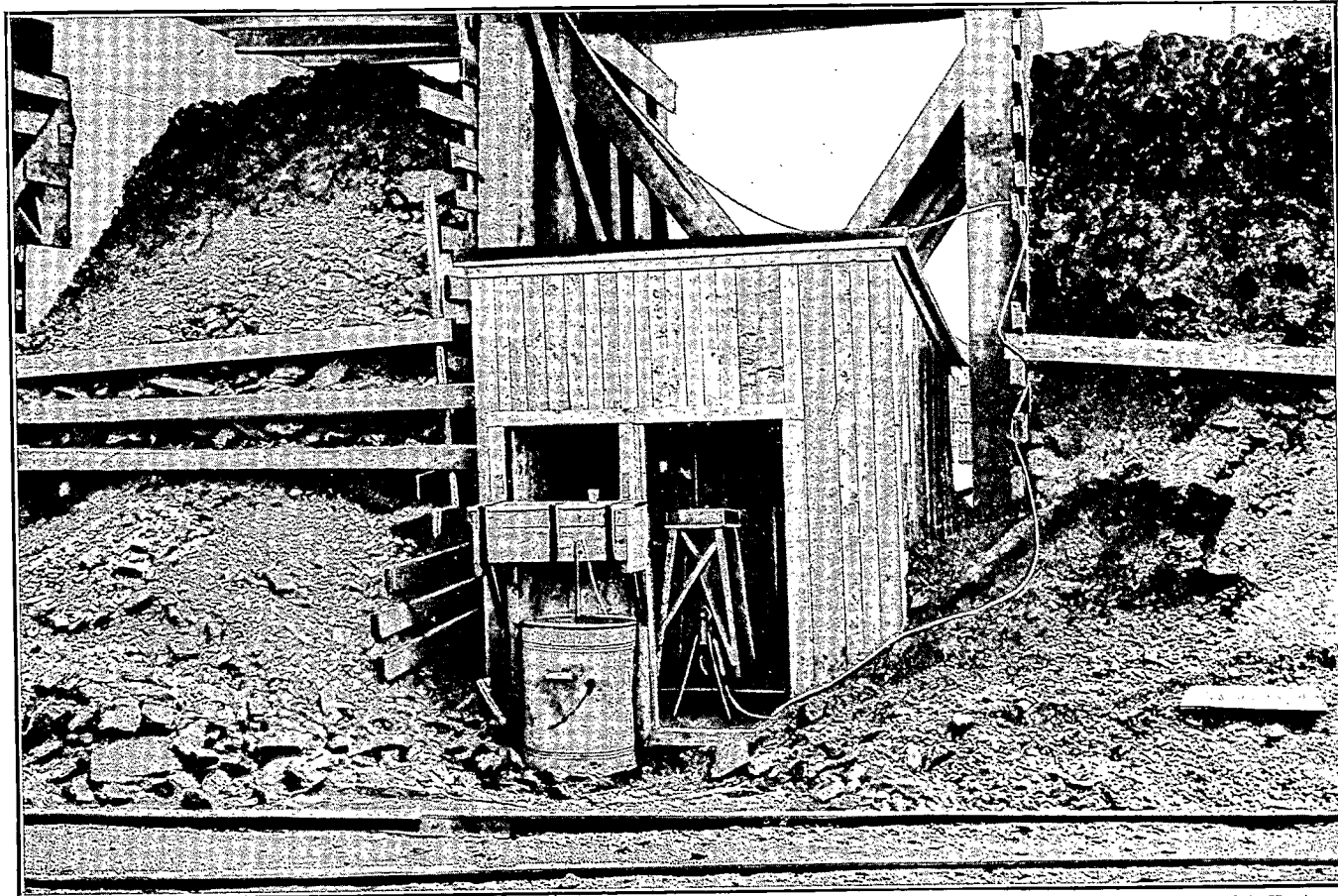
(Porter and de Hart)

Detailed view of pile observation station at Glace Bay.

and commenced a series of observations similar to theirs. Owing, however, to the fact that the coal was piled in comparatively cool weather no very great amount of heating took place. The observations, however, confirm in every respect the results previously obtained by Porter and Brunton as set forth in the following pages.

Porter and Brunton Experiments at Angus.

In the winter of 1910-11, J. B. Porter and J. S. L. Brunton carried out an extended series of observations on a very large storage pile, which had been built by the Canadian Pacific Railway between June and October, 1910, at Angus, Montreal, in accordance with their standard method, which has already been described on page 152. This investigation, although made before the Sydney experiments already outlined, is described after them for obvious reasons. The pile which was roughly triangular in shape was approximately two hundred yards long, eighty-five yards wide, and fifteen feet high; it contained approximately fifty-eight thousand tons. The underlying ground was the natural soil of the location—a firm sandy clay—levelled off and covered with a layer of about 1 ft. of roundhouse cinders.

The purpose of the investigation was (1) to study the temperature changes, and (2) to investigate the "breathing" of the pile, that is to say, to determine where and how air entered and escaped and whether barometric changes had any important effect upon ventilation.

A rectangular plot, 80 ft. by 90 ft. was laid out, one end of which was the northern edge of the pile. In one half of this experimental area all of the ventilation holes were filled up with fine coal, thus forming an unventilated block 90 ft. by 40 ft. An instrument house and six observation stations were located in the plot, three stations being in the unventilated area and three in the ventilated portion, as shown in Fig. 62, and in Plates I, II, and VI. Each station comprised a group of three one-inch pipes of varying lengths, each pointed and drilled with some $\frac{1}{4}''$ holes near the bottom to permit the entrance or escape of gas, and closed at the upper end with a threaded cap with a hose connexion. In each group pipe No. 1 was driven 9 ft. down into the coal, No. 2, 14 ft., and No. 3, 16 ft., i.e., just into the cinders below the pile. A small building to house the instruments was erected upon the pile in the position M as shown in the sketch. The instruments themselves were as follows:—

1. A standard thermometer, graduated in degrees Centigrade.
2. 2 doz. maximum recording thermometers, graduated from 0°—300°C. for measuring the temperature in the pipes.
3. A Richard thermograph reading to one degree Fahrenheit. This instrument was checked against a standard thermometer and was found very reliable. It and the thermometer were kept in a small latticed box fixed to the outside of the house on the northern side.

4. Two barographs, one being kept in the house and the other being in a constant temperature room at McGill University about a mile and one-half distant.

5. A Shaw-Dines microbarograph which was kept in the constant temperature room at the University.

6. A kathetometer, fitted with a micrometer eyepiece, capable of reading 1/100th of 1 millimetre.

7. A standard anemometer for noting wind velocities.

8. A delicate pressure gauge in the form of a U tube with the necessary connexions and stopcocks for adjustment. Toluol was the liquid employed as it combined extreme lightness with low viscosity even at very low temperatures. This gauge was suspended on the wall of the house.

9. Rubber hose 200 ft. long and iron gas pipe connexions for attaching the pipes to the pressure gauge.

The temperatures were obtained easily and accurately by lowering the recording thermometers inside the pipes to the required distance and allowing them to remain in position for some minutes, after which they were withdrawn and the temperatures read.

To obtain trustworthy pressure readings was a much more difficult matter. The method adopted was to remove the cap from the top of the pipe to be tested and in its place screw on a coupling which connected by means of very heavy rubber hose with a system of piping leading to one leg of the pressure gauge.

In the preliminary tests the other leg was left open, but it was found that under these circumstances the gauge sometimes showed pressures in the pipe, and at other times slight vacua, and whenever there was any wind the liquid surged more or less constantly, the fluctuation sometimes amounting to 10 or 15 millimetres. Various experiments were next made to eliminate the effect of the wind on the open leg of the gauge. Fairly satisfactory results were got by connecting this leg with a pipe which terminated in a barrel of crushed coal equally exposed on all sides to the wind, but finally it was discovered that pipes 2 and 3 at Station A made even more satisfactory dampers. These pipes were close to the edge of the pile and an exhaustive series of tests under all sorts of weather conditions failed to show any sign either of pressure or vacuum in them. At the same time the bottoms of the pipes were deep enough in the coal to be perfectly protected from gusts of wind. In all of the later and more trustworthy determinations of pressure, the "open" end of the U gauge was connected with one of these two pipes, and the other end was connected with whatever pipe was at the moment under observation.

Each leg of the gauge had a by-pass to the air controlled by well ground glass stopcocks. After the connexion had been made these stopcocks were both opened and the toluol permitted to come to a level. The kathetometer was then sighted first on one leg and then on the other and adjusted

TABLE XLIX.

General Observations at Angus Storage Pile.
(Porter and Brunton)

Date.	Jan. 10.	Jan. 12.	Jan. 16.	Jan. 19.	Jan. 23.	Jan. 26.	Jan. 30.	Feb. 6.	Feb. 9.	Feb. 13.	Feb. 15.	Feb. 20.	Feb. 27.	Mar. 6.	Mar. 9.	Mar. 15.	Mar. 23.	Mar. 27.	April 6.	April 10.
Temperature	−7	−16	−19	−4	−5	−11	−15	−20	−1	−11	−18	−11	−11	−8	+2	+1	−5	+9		
Rising +, Falling −,		−			−	=	−	−	−	−	−	−		−	=	=	−			
Average for 24 hours		−15			−10	−12			−5	−15		−13		−11	−4	−1	−7		+4	+2
Barometer	29·58	30·15		29·45	30·10	29·90	29·05	30·17	29·70	29·70	30·10	29·60	29·60	30·15	29·80	29·20	29·70	29·35		
Rising +, Falling −,		+		−	+	−	+	+	=	−	+	−	−	+	−	+	+			
Average for 24 hours		30·44			30·45	30·35			30·05	30·25		30·01		30·44	30·07	29·57	29·90		29·61	30·43
Wind		N.			S.W.	N.	N.W.		S.W.	N.		N.W.		N.	S.E.	S.W.	W.		S.W.	W.
Velocity m. p. h.		10			11	14	35		4	12		9		11	10	17	23		20	14
Station A. Pipe 1 Temp.		4	5		5	5		5		5				※						
" 2 "		2	0−		0−	0−		0												
" 3 "		0−			0−	0−		0												
Station B. Pipe 1 Temp.		13	13	14	14	15		16	16			19	19	15	14		13	13	13	10
Press.									0	12						3				
Pipe 2 Temp.		6	8	7	7	7		7	7						9					
Press.									0	14							5			
Pipe 3 Temp.		7	7	7	6	7		5	6	7					9	7				
Press.																				
Station C. Pipe 1 Temp.		35	36	37	39	38		39	39	37	36	30			16	10	9	10	6	0
Press.					26†	9			28			0			5					
Pipe 2 Temp.		17	18	19	17	17		16	17							18				
Press.									28			7				15				
Pipe 3 Temp.		15	18	23	27	25		22	18											
Press.									26			13				10				
Pipe 4 Temp.									*	*	*	*	*	*	*	*				
Press.												0			0					6
Pipe 5 Temp.									*	*	*	*	*	*	*	*				
Press.										35		7		0	0	8	10		11	17
Pipe 6 Temp.									*	*	*	*	*	*	*	*				
Press.												0			12				15	11
Station D. Pipe 1 Temp.		2	2		2	2			2											
Press.						15†			0											
Pipe 2 Temp.		0−	0−		0−	0−			0											
Press.																				
Pipe 3 Temp.		0−	0		0−	0−			0											
Press.																				
Station E. Pipe 1 Temp.		10	11	11	11	12		12	13			14					16	17		
Press.						0			0							4				
Pipe 2 Temp.		5	5	6	5	5		6	6								14	12		
Press.														0	7	10				
Pipe 3 Temp.		5	4	5	5	5		6	6							15		15		
Press.															0	5				
Station F. Pipe 1 Temp.		17	13	15	15	16		18	18			18					19			
Press.									0										−11	21
Pipe 2 Temp.		12	13	14	14	14		13	14											6
Press.										19										
Pipe 3 Temp.		15	14	13	13	14		13	13											
Press.										19										

* For temperatures of the C. group of pipes, Feb. 10—March 16. See Table LI.
† Two of these determinations are less trustworthy than the others.

NOTE.—Barometer readings in inches. Thermometer in Centigrade degrees. Pressures in 1/100 millimetres of water gauge approximately

PLATE VI.

(Porter and Brunton)

Experimental area at Angus.

to a zero reading; both stopcocks were then closed and the difference in height of the two legs read. It was discovered, rather to the surprise of the observers, that the change in level reached its maximum in a few moments and thereafter the pressure did not increase, and that in no case did this pressure amount to more than a millimetre or two of toluol, equivalent to less than 1 millimetre of water. It was also noted that while the pipes frequently showed no differences of pressure from the outside air, yet when there was any difference the pressure in the pipe was always greater than that of the atmosphere although the difference as stated above was minute.

Table XLIX gives a long series of observations of temperatures and barometric pressures both at the surface and in the pipes. It records all observations of pipe pressures which were considered at all trustworthy. In general this pressure was highest in the portions of the pile which heated, but in no case did it exceed a minute amount and the only conclusion which can safely be drawn from these observations is that the interior of the pile could not at any time, even on a rising barometer, have drawn in any appreciable amount of air through its top surface.

In this connexion careful experiments were made to see whether any air was sucked in through the ventilation holes, but the most delicate apparatus which could be devised failed to show an entering current in any case, whereas in a number of cases a slight outward current was observed.

It should be noted that in extremely cold and quiet weather the ventilation holes over the whole surface of the pile were always observed to be giving off small amounts of vapour, which often showed as little columns of steam. Much of this exhalation was no doubt aqueous vapour from the moisture contained in the coal and from melted snow, but undoubtedly some air was also exhaled, and it must therefore be assumed that fresh air entered the pile, chiefly no doubt by diffusion but also, probably, around the sides.

Samples of the atmosphere or gas contained in the pile were drawn on February 13 from three pipes which showed unusually high temperatures and pressures. These samples were analysed by Mr. Edgar Stansfield, M.Sc., Chief Chemist of the Fuel Testing Division of the Mines Branch, Department of Mines, Ottawa, and the results are shown in Table L.

TABLE L.

Analyses of Gas Samples from Angus Storage Pile.

(Porter and Brunton)

Pipe.	Depth.	Temperature.	Pressure.[1]	CO_2	O_2
				%	%
C 5	7	—	35	0·5	16·8
C 6	14	—	—	0·3	18·8
F 2......	14	13	19	0·1	20·0

[1] Pressures in $1/100$ millimetres of water.

PLAN

ANGUS PILE ON REDUCED SCALE

PLAN OF EXPERIMENTAL AREA

SECTION OF EXPERIMENTAL AREA
ON LINE FROM A TO C
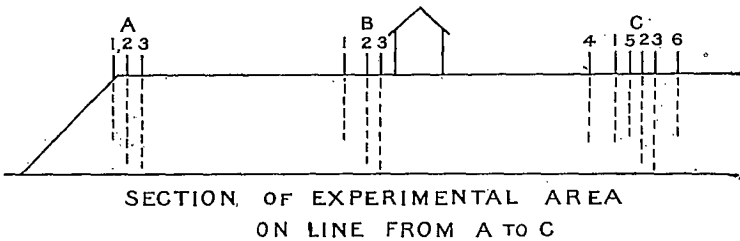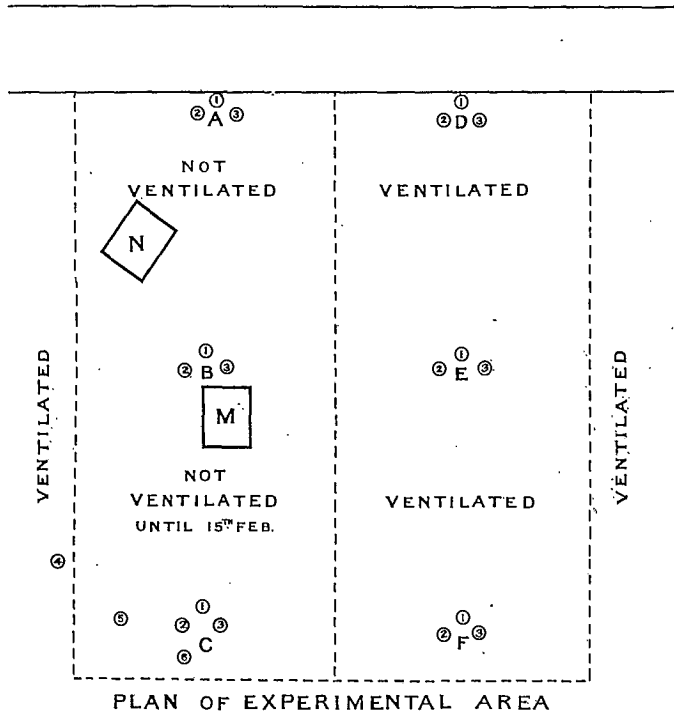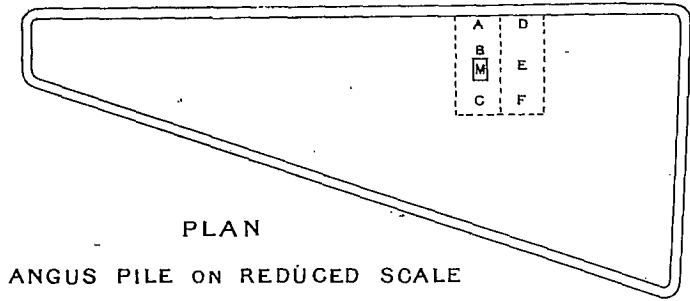
(*Porter and Brunton.*)

FIG. 62. Plans and elevation of Angus pile, Montreal.

Table XLIX, p. 160, records not only the temperature observations at the bottom of the pipes, but also the surface temperature at the central station, observed at the same time. It will be noted that groups A and D did not heat appreciably. This might have been expected as they were very close to the edge of the pile and the external temperature was almost constantly below zero. On the other hand the inner groups and particularly group C in the unventilated portion heated very decidedly. The temperatures shown in the table are only those observed at the bottom of the pipes, and considerably higher records were observed at depths of from six to eight feet in spite of the fact that the pile was at this time covered with a foot or two of snow.

Early in February a number of iron observation rods were driven into the unventilated portion of the pile particularly in the neighbourhood of group C, and on February 10 some of these were found to be hotter than any of the group C pipes; therefore additional pipes were driven to a depth of about ten feet at these points and daily observations were made until February 15 when the owners of the pile concluded that the heating was approaching the danger point, and the pile must be ventilated. On that day, therefore, the observation hut was moved from its original position M, to N, Fig. 62, and the whole of the heated portion of the pile was opened up by the usual method of driving two inch bars to the bottom and withdrawing them as explained on page 153.

TABLE LI.

Detailed Observations of Heating in Angus Pile.

(Porter and Brunton)

	Date	Feb. 10	12	13	14	15	16	20	27	Mar. 6	9	16
Pipe C1	6 ft.............	....	....	....	44	44	42	33	....	....	16	....
"	7 ft...........	42	43	....	....	....	....	....	....	....	....	....
"	8 ft..........	38	37	....	....	36	....	30	25	18	....	....
Pipe C2	6 ft...........	....	43	....	....	....	....	....	....	....	....	18
"	10 ft...........	....	38	....	....	....	....	....	....	....	....	....
Pipe C4	6 ft..........	....	24	29	34	34	33	29	20	18	19	....
"	8 ft..........	....	25	....	....	26	31	28	....	....	....	....
"	10 ft..........	....	19	....	....	14	....	....	....	....	....	....
Pipe C5	6 ft..........	....	56	56	55	55	50	41	....	....	....	....
"	8 ft..........	....	47	....	....	55	48	39	30	23	22	19
"	10 ft..........	....	....	....	....	55?	....	....	....	....	....	....
Pipe C6	6 ft..........	....	50	48	....	45	49	42	31	26	19	....
"	8 ft..........	....	....	....	....	45	43	42	....	....	....	....
"	9 ft..........	....	46	....	....	....	....	....	....	....	....	....
"	10 ft..........	....	....	....	....	17	....	....	....	....	....	....

NOTE.—This portion of the pile was unventilated from December 10 until February 15, by which time it had heated to such an extent that it was considered necessary to ventilate it in order to avoid fire. The ventilation holes were driven in the usual way on February 15, and the pile immediately began to cool off.

Table LI, p. 163, which gives a detailed record of the temperature at different depths in the group C pipes, shows that the result of this ventilation was an immediate and comparatively rapid cooling of the coal.

From a scientific point of view it is to be regretted that the heating could not have been permitted to proceed further, if possible even to actual ignition, but the action of the owners of the coal was of course perfectly reasonable, particularly as the heating was in a part of the pile which would have been very expensive to dig out or flood.

It is interesting to note that the above series of observations prove very clearly that the maximum heating was comparatively near the surface of the pile. As a matter of fact the hottest points were apparently not more than five or six feet from the surface, although the weather at the time was extremely severe. The common opinion of practical men in charge of coal storage is that fires usually occur close to the bottom, but in this case it is almost certain that had the pile been left unventilated it would have ignited within a week or two at a depth of not over six feet, and in certain other cases which the author has observed, fires in large piles have actually originated at this depth. The probable reason is that in a pile of great extent and depth, the coal in the lower portions is so heavily compressed and so isolated from supplies of fresh air that it does not receive sufficient oxygen. It must be confessed, however, that the persons responsible for coal storage are not willing to act upon this theory, which, if followed to a logical conclusion, would lead to the storage of coal in very deep piles on ground impermeable to air.

General Conclusions and Recommendations.

It is clear from what has been said in the preceding pages that there is an enormous difference in the liability of coals to weather. This explains the fact that in spite of the very large amount of experimental work which has been done on the subject, authorities still differ considerably as to the causes and prevention of deterioriation. Almost every piece of experimental work which has been done has been upon specific coals, usually from a single district, and the conclusions arrived at have naturally referred primarily to these coals and only in a lesser way to coals in general. It is therefore still impossible to formulate any comprehensive rules for the prevention of weathering, but nevertheless it is desirable to attempt to close this section of the report with a summary statement of the opinions of the most competent authorities.

The subject may be considered under two heads: first, mere deterioration or loss of calorific value; second, spontaneous combustion resulting in the actual destruction of the coal.

As to deterioration due to exposure irrespective of fire, it is a very serious matter with lignite, as has already been pointed out on pages 26, and 151, and lignites and lignitic coals cannot be stored more than a few weeks or months at the most without becoming almost valueless. Bituminous coals suffer less, but gas coals deteriorate sufficiently in respect of their gas producing qualities to make the question of long storage a serious

one in many cases. Exposure also rapidly decreases the coking qualities of many coals; this subject is considered again on page 172 and is discussed at length in the author's "Coals of Canada," but it is not a matter of very great commercial importance as it is rarely if ever desirable to store coal for any length of time before coking.

All coals but anthracite thus lose some of their calorific value on weathering, but with the exception of lignite and the lignitic coals above referred to, this loss rarely amounts to more than a few per cent of the total theoretical value, and fortunately the actual loss in service is usually even less, as the most easily weathered constituents are generally speaking those which are largely lost as smoke in ordinary use.

The most serious commercial damage which coal suffers in storage is due to the disintegration which results chiefly from the extra handling involved, but also in part from weathering proper, and in part from the crushing due to the weight of the superincumbent coal in storage piles. The total loss from these causes is usually very considerable, and as different coals differ greatly in strength, it is very well worth while for persons who have to store fuel, to experiment with the several coals available with a view to securing the one least liable to break up into slack.

In the matter of actual prevention of fires it may be concluded that all coals except the true anthracites are liable to spontaneous combustion under very unfavourable conditions, but with the exception of the lignites and lignitic coals, storage of most coals is practicable in a commercial sense in temperate countries provided reasonable precautions be taken. These precautions may be briefly stated in order as follows:—

1. Any coal can be safely stored under water, and if silt, etc., be excluded little or no deterioration takes place. This method of storage is very costly, and it is, therefore, not practicable except as a last resort.

2. Lump or screened coal except of the lignitic varieties can usually be stored with little or no danger. The size of the lumps is not ordinarily a matter of great importance so long as the screening devices ensure the complete removal of slack and dust. It must be noted, however, that unless lump coal is piled carefully and to small height a sufficient amount of crushing takes place to produce dust in the bottom of the pile. Owing to the cost of screening and the difficulty of disposing of the resultant slack this method is not generally practicable, and the following notes apply to where it is necessary to store run-of-mine coal or its practical equivalent in respect of fines due to secondary crushing, caused by rehandling.

3. Coal stored in cold weather is much less likely to give trouble than that which is stored in summer, and in cases where summer storage is necessary, risk of heating is much less if the pile is built during cloudy or cool weather. In very hot climates, or with very susceptible coal, covered storage may be justified as a means of protecting the coal from the sun not only during piling, but afterwards, although the later exposure is less serious.

4. Shallow piles are much less likely to give trouble than deep ones owing to their ample ventilation and the readiness with which they give

off any excess of heat. The critical depth depends upon the coal and the conditions at the time of its storage; some coals will fire if,piled even 4 feet deep, but ordinarily from 8-10 feet is safe and many coals may be stored to much greater depth.

5. Some coals, particularly those high in sulphur, undoubtedly heat more readily if damp, and in such cases exposure to rain and particularly to alternate wetting and drying is probably harmful. In some cases covered sheds are considered justifiable on this ground. In other cases piles have been protected by covering them with a layer of slack or coal dust.

In connexion with this question of rain it should be noted that the New South Wales Commission advocates wetting the coal thoroughly at the time of storage, the reference being particularly to ships' cargoes, and while this is contrary to ordinary practice it is extremely probable that many coals would stand more safely if treated in this way.

6. Ventilation either by the means described on page 152, or by the insertion of numerous perforated pipes is no doubt the most practical method of preventing fires, and by its use storage piles can be made larger and higher than otherwise. This method has been so fully discussed that it need not be further dealt with here.

7. Chemical treatment has proved successful in some cases. The material used is commonly either a solution of calcium chloride or of some other cheap hydroscopic salt. Several experimenters and commercial concerns state that they have found it effective to sprinkle the coal pile freely with a 10 per cent solution of calcium chloride. The cost of this treatment is possibly less than that of ventilation by the method referred to, but whether it is equally effective remains to be determined for each particular case.

8. Whatever method is used, and particularly in cases where no method of prevention is employed, a storage pile should be watched carefully, particularly for the first few weeks after it is built. Probably the simplest way of doing this is to have a large number of sharp pointed iron rods about one inch in diameter driven into different parts of the pile and left for a few hours, and then to shift them to other parts. An experienced man can very easily judge by handling the rods whether there is any undue heating, and a comparatively small amount of labour suffices for the observation of a large storage pile. If heating is observed it can be watched by driving pipes into the heated spots and using thermometers as already described. If the heating increases to a point approaching that of "autogenous oxidation" the pile should be ventilated or if necessary dug out or flooded. Among practical men there is a very strong prejudice against flooding, but probably this is not often justified. In place of flooding the use of sulphur dioxide gas or carbonic acid gas has been advocated. These gases are purchasable under high compression, and can be forced into the body of the pile by means of pipes driven down into the heated portion. Coal mine fires have been extinguished by this means, and it has also been used on board ship, and it undoubtedly would be effective in ordinary storage if the gas were used freely.

CHAPTER VII.

THE EFFECT OF SLOW WEATHERING ON THE COMPOSITION AND CALORIFIC VALUE OF COAL, WITH ESPECIAL REFERENCE TO CERTAIN CANADIAN CRETACEOUS COALS.

Under ordinary present day conditions very little time is lost between the mine and the furnace. Circumstances which have already been discussed of course necessitate the storage of reserve supplies, etc., and the aggregate amount of such supplies is very great, but a far greater part of the world's coal is now mined by quick recovery methods and once mined it is hurried to the consumer to be burned and "turned into power." Even the stored coal is rarely kept more than a few months or at the utmost a year, and on the whole, therefore, coal has not time to weather to any great extent, and if we omit the lignites we may say that in a commercial sense coal does not suffer much loss from such weathering as it ordinarily gets, and that our great concern with the matter is due to the risk of fire and total destruction rather than to mere calorific deterioration, etc.

The problem of slow weathering is, however, of considerable scientific interest, and is also of some practical importance as a means of enabling us to predicate the character of the deeper parts of a coal seam from the samples of weathered coal discovered at the outcrop.

In 1865 Fleck[1] investigated the nature of the changes which occur when coal is weathered. In 1856 a large quantity of each of six kinds of Saxon coal had been sampled and analysed. The remainder of the samples in lumps were kept until 1865 in a case at the Polytechnic Institute in Dresden, where they were again sampled and analysed by Fleck. The results of these analyses are shown in table LII.

It will be seen that the percentage of ash is very much larger in the samples which had been stored for nine years. The matter constituting the ash could not have increased by oxidation to any such extent, (in some cases about 18 per cent), it must therefore be inferred that the samples analysed in 1865 did not contain the same proportion of inorganic matter respectively as those analysed in 1856, and while weathering undoubtedly caused part of this change, bad sampling must be responsible for the rest. It is therefore impossible to draw any trustworthy conclusions from the analyses as they stand. There is very good reason to believe, however, that while inorganic matter is frequently unequally distributed through a seam of coal, the organic matter in that seam is much less subject to variation in chemical composition. If this be so, conclusions may safely be drawn from Fleck's figures recalculated to show the percentage composition exclusive of ash, that is carbon, hydrogen, oxygen and nitrogen,

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[1] Die Steinkohlen Deutschlands, etc. Vol., 2, 1865, p. 221. *Quoted* Percy Metallurgy-Fuels, 1875, pp. 290-2.

TABLE LII.

Analyses of Fresh and Stored Coal.

(Recalculated from Fleck)

Kinds of coal.	Year in which the analysis was made.	Percentage composition of the coal. Dried at 105°C.				Percentage composition exclusive of ash.			Hydrogen per 1000 parts of carbon.	
All from Carboniferous System.		Carbon.	Hydrogen.	Oxygen and nitrogen.	Ash.	Carbon.	Hydrogen.	Oxygen and nitrogen.	Disposable.	Non-disposable.
1 Hard shaly coal from the Oppelt pit in Zaukeroda............	1856	67·173	4·630	11·456	16·739	80·768	5·567	12·965	48·856	20·069
	1865	47·219	2·814	14·979	34·988	72·632	4·398	22·970	21·024	39·528
2 Soft coal from the third seam of the Oppelt pit.................	1856	26·544	1·904	7·320	64·232	74·230	5·325	20·445	37·303	34·434
	1865	32·779	1·756	11·132	53·333	70·241	3·764	25·995	7·331	46·255
3 Coal from the second seam of a colliery (des Gühneschen Werkes) in Niederwürschnitz.	1856	81·573	4·477	9·473	4·477	85·396	4·687	9·917	40·365	14·520
	1865	80·300	4·650	13·569	1·481	81·510	4·720	13·770	36·793	21·114
4 Soft shaly coal from the Gückelsberg pit.....	1856	87·825	2·663	4·670	4·842	92·295	2·798	4·907	23·669·	6·646
	1865	86·217	2·653	5·160	5·970	91·434	2·822	5·744	23·010	7·853
5 Coal (Pechkohle) from Helbigs & Co.'s pit in Oberhohndorf.......	1856	80·963	5·518	12·081	1·498	82·113	5·602	12·285	49·518	18·705
	1865	73·472	4·645	19·728	2·155	75·972	4·747	19·281	30·761	31·722
6 Coal from the upper seam of the Segen Gottes pit in Zwickau.	1856	75·747	4·881	15·570	3·802	78·740	5·074	16·186	38·748	25·692
	1865	76·363	4·166	16·555	2·916	78·658	4·272	17·070	27·168	27·131

disposable hydrogen and non-disposable hydrogen. This has been done and the figures show that in every instance the proportion of disposable hydrogen had decreased, while the proportion of the non-disposable hydrogen had increased relative to the amount of carbon. His analyses do not give the amount of oxygen in the samples, but it is clear that weathering must have increased the percentage of this element very materially, the coals must, therefore, have suffered a considerable loss of calorific value during the nine years which elapsed between the two series of analyses.

Parr and Wheeler whose work on the oxidation of coal in storage has been described at considerable length on page 69 et seq., secured samples of old outcrop coal, pillar coal, and storage piles of unusual age, and determined the loss in calorific power. Their results are set forth in Tables LIII and LIV.

TABLE LIII.

Analyses of Pillar Coal and Outcrop Coal compared with Fresh Coal.

(Parr and Wheeler)

Description.	Total. mois- ture.	Dry coal.			B.Th.U. referred to actual or unit coal.	Decrease.	
		Ash.	Sulphur.	B.Th.U.		B.Th.U.	Per cent.
St. Clair County, Illinois.							
Fresh coal............	9·76	15·80	4·76	12,202	14,896	—	—
Pillar coal. (Exposed 22 years)..	10·18	16·21	5·01	11,797	14,482	414	2·78
Gallatin County, Illinois.							
Fresh coal............	4·47	10·85	3·72	13,235	15,133	—	—
Pillar coal.... (Exposed 27 years.)	4·76	1²·84	3·84	12,514	14,857	·276·	1·82
Peoria County, Illinois.							
Fresh coal............	13·86	16·25	3·91	12,044	14,757	— ·	—
Outcrop slightly cover- ed with soil.........	29·81	16·86	0·85	9,257	11,331	3,426	23·21

TABLE LIV.

Analyses of Fresh and Stored Coal.

(Parr and Wheeler)

Commonwealth Edison Company, Chicago.

Sample taken.	Dry coal.			B.Th.U. referred to actual or unit coal.	Decrease	
	Ash.	Sulphur.	B.Th.U.		B.Th.U.	Per cent.
FRANKLIN COUNTY, ILLINOIS. *Nut Coal.*						
April, 1908..................	10·16	1·81	13,021	14,688	—	—
July 14, 1909................	10·44	2·15	12,924	14,642	.46	0·31
WILLIAMSON COUNTY AND FRANKLIN COUNTY, ILLINOIS. *Egg Coal.*						
April, 1908..................	10·97	2·35	12,909	14,728	—	—
July 14, 1909................	11·49	1·84	12,697	14,559	169	1·15
WILLIAMSON COUNTY, ILLINOIS. *No. 1 Washed Nut.*						
April, 1908..................	9·21	1·82	13,205	14,726	—	—
July 14, 1909................	9·43	1·72	13,008	14,540	186	1·26

A number of experiments were made to determine the loss of calorific value of certain Illinois coals due to weathering. A table of analyses compiled from curves shown in a paper by **Parr and Hamilton**[1] is given below.

TABLE LV.

Analyses of Fresh and Stored Coal.

(From Parr and Hamilton)

Vermilion County No. "7" Coal—Oakwood Nut and Slack—Calorific Power 14,410 B.Th.U. one day after mining.

Time of exposure in months.	Outdoor exposure.	Dry storage at 85°–110°F.	Wet[2] storage at 85°–120°F.	Submerged at 70°F.
3.....................	14,200	14,050	14,150	14,400
5.....................	14,050	13,800	14,000	14,400
7.....................	14,150	13,875	13,950	14,400
9.....................	14,025	13,900	14,025	14,400

Christian County No. "5" Coal—Pana Nut and Slack—Calorific Power 14,220 B.Th.U. three weeks after mining.

3.....................	14,200	14,040	14,080	14,180
5.....................	14,190	13,920	13,990	14,150
7.....................	14,170	13,950	13,540	14,100
9.....................	13,990	14,080	13,880	14,130

Perry County No. "6" Coal—Du Quoin Lump broken to Nut—Calorific Power 14,930 B.Th.U. one week after mining.

3.....................	14,450	14,550	......	14,930
5.....................	14,130	14,300	......	14,930
7.....................	14,020	14,260	......	14,930
9.....................	14,080	14,320	......	14,920

[1] Univ. of Illinois. Eng. Expt. Station, Bull. 17, 1907.
[2] "Drenched with water two or three times a week."

These figures show that outdoor exposure involves a loss of calorific value of from 2% to 8%. Dry (i.e. covered) storage shows no advantage over storage in the open except in the case of high sulphur coals where the oxidation of the pyrite would cause a large disintegrating effect. In most cases the losses appear to be practically complete in five months. Submerged coals show practically no loss of calorific value.

Some figures are given in the Illinois State Geological Survey year book for 1907 showing the loss of calorific value of coal samples due to weathering. Some of the samples were analysed by the Illinois State Geological Survey and others by the United States Geological Survey, but the methods of analysis were the same in both cases.

Seventeen Illinois State samples which had been six months in the laboratory showed an average loss of 365 B.Th.U. or 2·5% of the calorific value as determined from 8 United States Geological Survey samples analysed soon after collection. Another lot of 17 samples analysed six months to one year after collection showed an average loss of 365 B.Th.U. or 2·4% of the calorific value as determined in the same laboratory from 16 samples analysed within two weeks of their collection.

White[1], in a very valuable critical study of the numerous and trustworthy ultimate analyses of coal made by the United States Geological Survey in connexion with their investigation of the fuels of the United States, proves conclusively that, "oxygen and ash are of very nearly equal anticalorific value," and that "the calorific value of coals in general is essentially indicated by the balance between the total carbon, on the one hand, and the sum of the two great impurities, oxygen and ash, on the other, the hydrogen, nitrogen, and sulphur being usually negligible, as constants."[2] In other words, that oxygen, even when an essential, i.e. original constituent of coal, is, in a practical sense, so much additional dead matter or ash, and should be so considered in estimating the usefulness of the coal as fuel.

He tabulates all trustworthy analyses from all parts of the United States, and from these figures draws a curve which has been reproduced as Fig. 63. In this diagram, the carbon and oxygen plus ash ratios form the horizontal, and the observed calorific values the vertical component, and of all of the 320 odd analyses tabulated, ranging from a sample of peat with 31% of oxygen, to some very high grade semi-bituminous coals and anthracites from West Virginia and Pennsylvania, none depart materially from a very clear and narrowly defined curve, and few, except weathered samples and cannels, depart by more than a fraction of one per cent. White further points out that if the analyses and calorific values are recalculated to a moisture free basis, the results again fall into a similar and equally clear curve.

The case of the cannel coals need not be discussed here; but White points out that the weathered coals invariably show marked calorific deficiencies, and low hydrogen-oxygen ratios.

[1]A "The effect of oxygen in coal." Bull. 29 U. S. Bureau of Mines 1911, pp. 1-80. Reprint from U. S. G. S. Bull. No. 382, 1909.
B "The Origin of Coal." Bull. 38, U. S. Bureau ot Mines, 1913, pp. 1-304.
[2] Variances "on account of the neglected constants—hydrogen, sulphur, and nitrogen—are rarely over 2 per cent, unless in cannels, anthracites and weathered coals." Ibid, p. 71.

White then studies the weathered samples by themselves, and finds that many of the more unstable coals weather quite appreciably, even in place underground if comparatively near the surface, and that even less susceptible coals begin to absorb oxygen as soon as opened up by mining operators, and he concludes that cases of absorption of from 10% to even 20% of oxygen may be considered "neither extraordinary nor even unusual" in semi-bituminous coals, and that lignites and peats may suffer still more. Table LVI shows two typical analyses selected by White, of cretaceous coal from near Fort Steel, Wyoming. Analysis A represents an unweathered sample from underground near the foot of a shaft; B the same sample recalculated to show the effect of the hypothetical addition of 10% of oxygen, and C the actual analysis of a weathered sample of the same coal from near the surface at an outcrop.

TABLE LVI.

Comparison of Fresh and Outcrop Coals to show Effect of Weathering.

(*White*)

No.	S	H	C	O	Ash	Mois-ture	F. C.	H. O.	Av.H.	Cal.	Curve Error
A	0·85	5·16	63·57	22·05	3·80	8·70	55·36	24·2	2·02	6310	+30·
B	0·77	4·70	57·80	29·14	3·46	7·91	—	—	—	5736	—
C	0·31	4·90	59·86	29·39	4·12	9·34	55·57	18·3	1·23	5636	−219

In connexion with his study of the effect of oxygen, White considers the matter of coking, and calls attention to the fact that nearly all coking coals have a dry basis hydrogen-oxygen ratio of at least 55 per cent, and good coking coals 59 per cent or over up to the beginning of anthracitization. This conclusion is of special interest in relation to the effect of weathering on coking qualities.[1] White has found as already stated that weathering materially lowers the hydrogen-oxygen ratio, and as suitability for coking decreases rapidly as this ratio falls below 59 per cent, it is easy to see that a relatively small amount of weathering may produce a profound effect on the coking qualities of a coal in which this ratio is close to this limit.

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[1] The Coals of Canada. J. B. Porter and others—Vol. I, pp. 220-1, and Vol. VI, pp. 26-7.
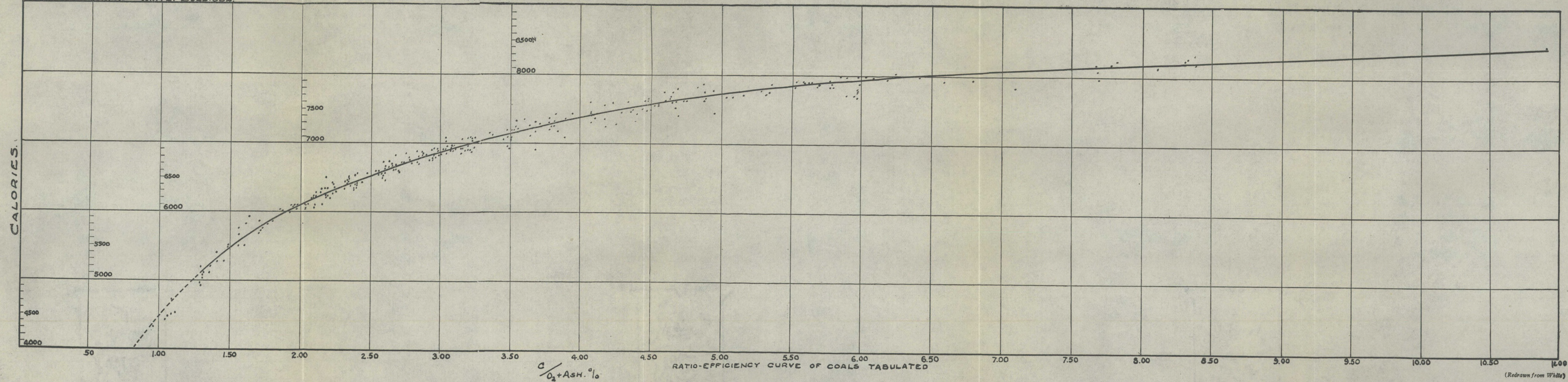
Fig. 63.   Graphic record of efficiency of coals in relation to oxygen content.

(Redrawn from White)

Porter, de Hart, and Billington's Studies of Old Samples of Canadian Coals.

In connexion with the author's investigation of Canadian coals it seemed desirable to carry out a series of analyses in parallel with those of Fleck and White just quoted, and thanks to the generosity of the Director of the Geological Survey, portions of nine official samples of western coals, chiefly from Alberta, were obtained from the Victoria Memorial Museum at Ottawa. Three of the samples, Nos. 7-9, were taken in 1910-11 in such a way as to represent weathered, slightly weathered, and unweathered coal from the same seam. The other samples Nos. 1-6 were much older and had been analysed and their calorific value determined thirty years ago by Dr. Hoffmann, at that time Chief Chemist to the Geological Survey. All nine samples were carefully analysed in 1912 by J. B. de Hart and E. E. Billington, research assistants of the author, and the following statement of results and conclusions is largely drawn from Mr. de Hart's report on this work.

Samples 1-6 were first studied. They were collected by members of the staff of the Geological Survey in 1881-1882 and portions were analysed at the first convenient opportunity, while other presumably similar portions were deposited in the Survey Museum. All were cretaceous coals from western Canada, one being a typical bituminous coal from Nanaimo, Vancouver Island, and the others lignitic coal, and bituminous coal proper from different parts of the Belly River and Eastern Crowsnest Pass coal fields of Southern Alberta.

Hoffmann gives detailed descriptions of the several coals, and tabulates the results of his analyses in detail in his report on the work of the Geological Survey laboratory.[1] He also gives details of his methods, and while more recent experiments have led chemists to adopt somewhat different methods as standard for coal analysis,[2] it is interesting and satisfactory to note that everything points to Hoffmann's great skill and to the substantial accuracy of his results.

The samples as obtained from Ottawa in 1912 by the author were as far as possible representative of the coals as they were exhibited in the museum, partly lump and partly fines. Each was ground to pass through 100-mesh and riffled down to about 10 grammes. The calorific values of all nine samples were determined and both proximate and ultimate analyses were made. All the determinations were made in duplicate.

The analyses were carried out in the Mining Department at McGill University exactly as described in "The Coals of Canada" volume II, page 133, et seq., except as noted below:—

Fixed Carbon and Volatile matter. The only difference between the method used and that given in the above mentioned report is that porcelain crucibles were used instead of platinum crucibles.

[1] Annual Report Geol. Survey of Canada 1882-4, part M. Coals and Lignites of the North West Territory by G. C. Hoffman, pp. 1-43 and 3 tables.
[2] The Coals of Canada, J. B. Porter and others—6 Vols. Dept. of Mines, Ottawa, 1912. Vol. II, p. 134.

Carbon and Hydrogen. For these determinations sulphuric acid absorption trains were used, the drying train comprising suitable vessels containing: (1) sulphuric acid, (2) soda lime and calcium chloride, (3) potassium hydroxide solution, (4) sulphuric acid (next the combustion tube), while the absorption train comprised: (1) sulphuric acid (next the combustion tube), (2) potassium hydroxide solution and calcium chloride, (3) sulphuric acid, (4) sulphuric acid. The last sulphuric acid bottle was used to prevent any moisture diffusing back from the aspirator bottles. In all other respects the method was similar to that given in the Coal Report.[1]

Nitrogen was determined by Kjeldahl's method. The only difference between the method used and that described in the Coal Report was that no mercury was added and consequently it was unnecessary to add sodium sulphide.[2]

The calorific value determinations were made with a Berthelot-Mahler calorimeter.[3] The temperatures were read as in the determinations made for the Coal Report[4] except that an ordinary thermometer graduated
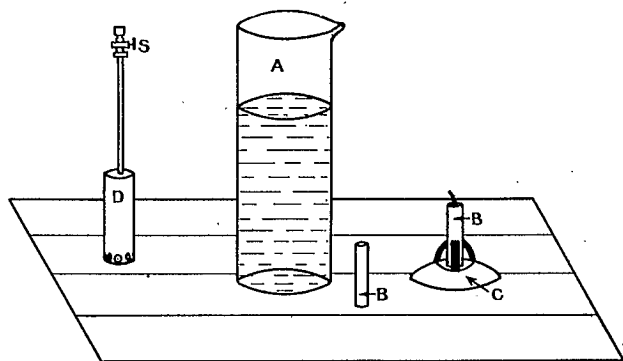
(Porter and de Hart.)

FIG. 64. Thompson calorimeter.

to $\frac{1}{50}$ of a degree was used instead of a Beckmann thermometer: this thermometer was read by means of a telescope. The calculations were made as in the Coal Report[5].

The water equivalent of the calorimeter was determined indirectly by testing a coal whose calorific value had already been determined on the Koehler calorimeter. The method used in determining the water equivalent of the latter and the method of making all calculations is described in the Coal Report[6] and need not be repeated.

[1] The Coals of Canada, J. B. Porter and others, 6 Vols., Dept. of Mines, Ottawa, 1912, Vol. II, p. 136.
[2] Ibid. p. 147.
[3] This apparatus which is described by Thwaite in Journ. Iron and Steel Institute for 1892 is substantially identical with the Koehler Calorimeter referred to in the report cited. The Koehler apparatus is, however, slightly better in some features of its design.
[4] Ibid. p. 143.
[5] Ibid. pp. 151-3.
[6] Ibid. pp. 151-4.

Hoffmann determined the calorific value of his coals in 1882-3 with the Thompson calorimeter. (See Fig. 64.) This apparatus consists of a glass vessel A, graduated to contain 2000 grammes of water, a copper cylinder B, capable of holding 2 grammes of coal and the necessary amount of fusion mixture, a brass base C, on which the cylinder is placed, and a copper cylinder D, with a row of holes round the bottom and a pipe with a stopcock S leading out of the top.

It is obviously impossible to determine the exact amounts of the errors in Hoffmann's determinations due to the use of this comparatively crude calorimeter, particularly as no figures are available as to the amount or composition of the fusion mixture used by him, or as to the exact correction which was made to compensate for "losses". In order, however, to get some
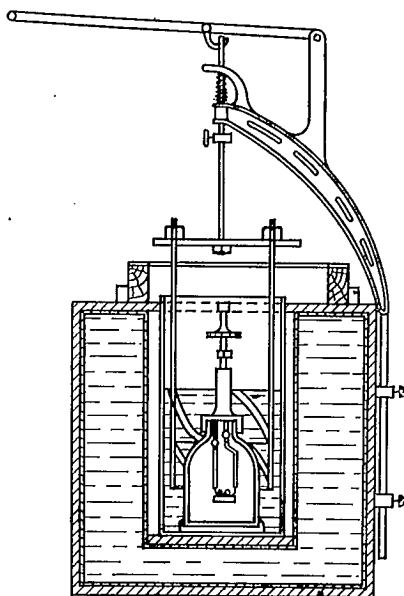
(Redrawn from Mahler.)

FIG. 65. Berthelot-Mahler calorimeter.

idea of the value of his figures, the identical calorimeter used by him was obtained from Ottawa by the courtesy of Mr. F. G. Wait of the Mines Branch, and the calorific value of a coal which had already been determined by the Berthelot-Mahler calorimeter, (Fig. 65) was re-determined by means of this Thompson instrument.

The fusion mixture recommended for the Thompson calorimeter in the text books is 3 parts of potassium chlorate to 1 part of potassium nitrate, but this mixture was found to be so fusible, that a crust formed on the top and a portion of the mixture did not burn. Hence it was necessary to use less potassium nitrate, which is the more fusible of the two salts, and a mix-

ture of 17 parts of chlorate and 3 of nitrate was successfully employed. Two grammes of finely ground coal were mixed with 20 grammes of this fusion mixture and the whole transferred to the copper cylinder, a small amount at a time, the whole being packed down evenly. About half an inch of fuse was inserted in the top. This fuse was prepared by soaking a thread of ordinary cotton wick in a strong solution of potassium nitrate and then drying it. The copper cylinder was then placed in the stand and the large cylindrical copper cover put on. The whole was put into the glass vessel and moved up and down to thoroughly stir the water.

The temperature of the water was then taken and the cylinder and stand taken out. The outside cylinder was quickly removed, the fuse lighted, the cylinder replaced and the whole immersed in the water. When the combustion was complete the stopcock was opened, the water stirred, its temperature observed, and its maximum rise recorded.

All the copper parts of the apparatus were weighed and their water equivalent calculated. The calorific value was taken as being equal to:—

$$\frac{(W + w) \, t}{c} - w^1$$

W = weight of water taken in grammes.
w = weight of water equivalent to the copper parts.
c = weight of coal taken in grammes = 2 in this case.
t = observed rise in temperature in degrees Centigrade.
w^1 = theoretical heat evolved by the burning of the fusion mixture.

Two experiments with the Thompson calorimeter were run on the same coal; they checked fairly well and the mean of the results was near enough to the value as determined by the Berthelot-Mahler instrument to give satisfactory evidences as to the substantial accuracy of Hoffmann's work.

Table LVII, p. 179, gives the results of both Hoffmann's and de Hart's analyses and calorimetric determinations, and also the theoretical calorific powers as calculated from the ultimate analyses.

The analyses made by Hoffmann do not show oxygen and nitrogen separately, but give percentages of oxygen + nitrogen. In order to be able to compare these analyses with de Hart's results two assumptions have been made: (1) the nitrogen has been assumed to have remained constant in amount, and (2) the coal has been assumed to have remained constant in weight.

The first of these assumptions is probably not very far from the truth, and as the amount of nitrogen in the coal is small compared with the oxygen, very little error will be introduced by it. The second assumption is justifiable if an attempt is made to estimate the percentage of nitrogen in Hoffmann's analyses. Some experiments were made in 1907 at McGill University, by Edgar Stansfield, on changes in weight of laboratory samples.

These samples were ground to pass through 30-mesh and were spread out in trays and left exposed to the air in a dust proof case. The trays were weighed from time to time for three years and while appreciable changes were noted, they were all very small in amount. This experiment is taken as sufficient ground for the second assumption[1], which is further justified by the fact that the Museum samples were lumps over $\frac{3}{4}$ inch in diameter instead of dust, and would consequently change at a much slower rate.

The necessity of making somewhat questionable assumptions as above in comparing analyses would be overcome if some substance in coal were found to be absolutely unaffected by weathering. It is quite probable that nitrogen or phosphorus may remain almost absolutely constant, but this fact has not yet been positively determined. It has been suggested that when samples are to be tested for weathering a known weight of gold dust should be mixed with the coal. Analyses and assays made before and after could then be compared with perfect confidence. The fatal defect in this method is the fact that it would be impossible to mix the gold dust evenly through the material and, therefore, assays of the samples taken before and after the test would be misleading.

Descriptive list of samples analysed.

No. 1 Bituminous Coal—Newcastle seam Wellington mine, Nanaimo, Vancouver island, B.C.
Seam 6 to 10 ft. thick. Sampled 1875 by Dunsmuir and Co.
(Hoffmann, No. 33, p. M. 37, Ann. Rep. C. G. S. 1882-4.)

No. 2 Lignitic coal—main seam at Coal Banks, Belly river, Alberta. Now Sheran's mine, Lethbridge.
Seam 5½ ft. thick. Sampled 1881, G. M. Dawson.
(Hoffmann, No.26, p. M. 30, Ann. Rep. C. G. S. 1882-4.) (See also Dawson, Ibid, p. 70C).

No. 3 Bituminous coal—upper seam middle fork Oldman river, Alberta. Now Lundbreck mine.
Seam 3 ft. thick. Sampled 1881, G. M. Dawson.
(Hoffmann, No. 30, p. M 34, Ann. Rep. C. G. S. 1882-4.) (See also Dawson, Ibid, p. 101C).

No. 4 Bituminous coal—lower seam, middle fork Oldman river, Alberta, Now Lundbreck mine.
Seam 3 ft. thick. Sampled 1881, G. M. Dawson.
(Hoffmann, No. 31, p. M 35, Ann. Rep. C. G. S. 1882-4.) (See also Dawson Ibid, p. 101C).

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[1] This second assumption, although convenient for the reasons given above, is clearly wrong as Table LVIII shows the carbon to have remained surprisingly constant when calculated to oxygen free coal, and therefore the total weight including oxygen could not have remained constant. It would have been far better to have assumed the nitrogen to have remained constant in the oxygen-ash-sulphur-moisture free coal. In either case, however, any error introduced is trifling.

No. 5 Bituminous coal—Upper Belly river, 25½ miles above mouth of
Waterton river, Alberta.
Seam 1 foot thick.   Sampled 1881, R. G. McConnell.
(Hoffmann, No. 32, p. M 36, Ann. Rep. C. G. S. 1882-4.) (See also
McConnell, Ibid, p. 61C).

No. 6. Bituminous coal—Mill Creek, Alberta.   Outcrop 4 miles above
mill.   Seam 8 to 9 ft. thick.   Sampled 1882, G. M. Dawson.
Hoffmann, No. 35, p. M 40, Ann. Rep. C. G. S. 1882-4.) (See also
Dawson, Ibid, p. 99C).

No. 7 Bituminous coal—Tunnel seam Jasper Park colliery, Alberta.   Out-
crop one-half mile from tunnel.   Sampled 1910 D. B. Dowling.
(See C. G. S. Summary Reports 1910, pp. 163-4, and 1911, p. 218).

No. 8 As above, but sample taken in shaft 30 feet from surface.

No. 9 As above, but sample taken Sept. 1911, in tunnel at distance of 1900
feet from entrance.

TABLE LVII.

Old and Recent Analyses of Coals in Canadian Geological Survey Museum.

(*Hoffmann*)   (*Porter and de Hart*)

Coal No.	1		2		3		4		5		6	
Date of determination.......	1883	1912	1883	1912	1883	1912	1883	1912	1883	1912	1883	1912
Proximate analysis:—												
Moisture..............%	2·75	1·35	6·50	4·50	3·27	2·26	2·36	1·60	3·91	3·04	1·63	1·14
Volatile matter.........%	30·95	29·15	31·59	32·16	26·41	29·45	32·07	32·08	30·93	33·03	22·61	16·31
Fixed carbon...........%	59·72	58·85	54·36	56·94	50·50	53·09	56·37	53·07	53·83	54·58	63·39	73·89
Ash..................%	6·58	10·65	7·55	6·40	19·82	15·20	9·20	13·25	11·33	9·35	12·37	8·66
Ultimate analysis:—												
Carbon...............%	72·65	68·12	65·30	62·40	59·84	62·99	71·11	66·36	66·19	65·57	71·57	72·52
Hydrogen.............%	4·89	4·56	4·30	4·68	4·17	4·87	5·04	4·70	4·43	3·83	4·05	3·73
Oxygen...............%	11·73	13·43	14·18	19·66	11·05	12·66	10·13	11·70	10·51	14·56	9·07	12·45
Nitrogen.............%	1·04	1·04	1·47	1·47	1·30	1·30	1·50	1·50	1·45	1·45	0·87	0·87
(Oxygen and nitrogen)...%	12·77	14·47	15·65	21·13	12·35	13·96	11·63	13·20	11·96	16·01	9·94	13·32
Sulphur..............%	0·36	0·85	0·70	0·89	0·55	0·72	0·66	0·89	2·18	2·20	0·44	0·63
Ash..................%	6·58	10·65	7·55	6·40	19·82	15·20	9·20	13·25	11·33	9·35	12·37	8·66
Moisture.............%	2·75	1·35	6·50	4·50	3·27	2·26	2·36	1·60	3·91	3·04	1·63	1·14
Calorific value:												
Determined—B.Th.U. per lb..............	12963	11815	11133	11520	10762	11524	12635	11974	11885	11970	11885	12323
Calculated—B.Th.U. per lb.	12700	11727	11097	10490	10460	11235	12713	11692	11648	10868	12240	11918

TABLE LVIII.

Analyses Recalculated to Basis of Ash, Sulphur, and Moisture Free Coal.

(Porter and de Hart)

Coal No...............	1		2		3		4		5		6	
Date of analysis............	1883	1912	1883	1912	1883	1912	1883	1912	1883	1912	1883	1912
Ultimate analysis:—												
Carbon................%	80·45	78·16	76·60	70·75	78·37	76·99	81·01	78·76	80·15	76·77	83·65	80·97
Carbon loss in 29 years..%		2·85		7·64		1·76		2·78		4·22		3·20
Oxygen................%	12·99	15·42	16·64	22·28	14·47	15·47	11·54	13·88	12·73	17·05	10·60	13·90
Oxygen gain in 29 years.%		18·7		33·9		6·9		20·3		33·9		31·1
Hydrogen.............%	5·41	5·23	5·04	5·30	5·46	5·95	5·74	5·58	5·37	4·48	4·73	4·16
Hydrogen available.....%	3·79	3·30	2·96	2·52	3·65	4·02	4·30	3·85	3·78	2·35	3·41	2·42
Hydrogen available, loss in 29 years...........%		12·9		14·9		−10·1		10·5		37·8		29·0
Nitrogen...............%	1·15	1·19	1·72	1·67	1·70	1·59	1·71	1·78	1·75	1·70	1·02	0·97
Calorific value, determined in B.Th.U. per lb............	14340	13520	13030	13020	14080	14050	14370	14170	14290	13910	13870	13730
Loss in 29 years........%		5·7		0·1		0·2		1·4		2·7		1·0

TABLE LIX.

Analyses Recalculated to Basis of Oxygen, Ash, Sulphur, and Moisture Free Coal.

(Porter and de Hart)

Coal No.	1		2		3		4		5		6	
Date of analysis	1883	1912	1883	1912	1883	1912	1883	1912	1883	1912	1883	1912
Ultimate analysis:—												
Carbon...............%	92·46	92·41	91·89	91·03	91·63	91·08	91·58	91·45	91·84	92·55	93·57	94·04
Hydrogen.............%	6·22	6·18	6·05	6·82	6·38	7·04	6·49	6·48	6·15	5·40	5·29	4·83
Nitrogen.............%	1·32	1·41	2·06	2·15	1·99	1·88	1·93	2·07	2·01	2·05	1·14	1·13

Summary and Conclusions.

A comparison of the ash determinations shows discrepancies which can only be explained by imperfect sampling. This was expected and was unavoidable as it was not permissible to destroy the whole of the Museum samples and therefore fragments had to be taken of which the best that can be said is that they were as nearly representative as possible. Fortunately, however, it has been proved by Lord that the organic constituents of any particular coal are very nearly constant throughout an extensive area, even where different samplings show large variations in the proportion of ash. If, therefore, we recalculate Table LVII on a pure coal basis, eliminating ash and moisture, or ash, moisture and oxygen, we have good ground for believing that comparison of Hoffmann's and de Hart's analyses will be much more trustworthy than if made directly on the original data. The result of this recalculation is shown in Table LVIII, but it should be noted that it has not been considered worth while to recalculate the proximate analyses.

A study of Tables LVII and LVIII shows, as might have been expected, that weathering has decreased the percentage of carbon in every case, while the percentage of oxygen has increased in every case. The question arises as to whether the decrease of carbon is due to actual loss of carbon in the form of carbon dioxide, etc., or merely to the greater weight of the sample because of its absorption of oxygen. If it were due to the latter cause alone the carbon would be constant when recalculated on an oxygen free basis. Table LIX was therefore calculated, and it shows rather surprising constancy in the carbon contents. It is true that some coals show increases and some decreases, but the variations are so small that they can easily be accounted for by the fact that, as above explained, the sampling was not above reproach. In view of this it is unsafe to draw any definite conclusions, particularly as the samples were few in number.

The available hydrogen like the carbon, shows changes varying from an increase of 0·71% to a decrease of 0·86. It is quite possible that the trouble again lies with the sampling, but these variations are interesting, and it is worthy of note that they are virtually nil when the carbon remains unchanged, but become considerable and always in a contrary sense where the carbon changes are at all considerable.

The losses in calorific power (Table LVIII) show variations from 5·7% down to almost nothing. Since the figures are on a basis of organic coal free from sulphur, ash, etc., the above loss must be an actual organic loss; in other words, a certain proportion of the carbon and hydrogen have actually disappeared in weathering as was to have been expected. In this connexion it should be noted that the largest decreases are in the mine sample No. 1, and the narrow seam No. 5; suggesting that the outcrop coal had already suffered the main part of all possible weathering before being sampled in 1882.

Table LX gives the results of a series of analyses of coals Nos. 7, 8, and 9, which were dealt with exactly as were coals Nos. 1 to 6. These

last three samples were all relatively recent, and we have no data to show what changes they have experienced since being taken, but when the samples were collected an especial attempt was made to secure three lots of material which would typify (a) natural outcrop, i.e., coal which had experienced full natural weathering for a very long period of time; (b) shallow coal, which while covered was yet within the zone of slight natural weathering, and (c) deep and hence unweathered coal.

Except as regards weathering the three samples were chosen to be as nearly as possible identical, and there is every reason to believe that they were originally virtually identical except in the matter of ash and moisture. In Table LXI, these constituents including also sulphur have been eliminated, and we thus have an apparently trustworthy indication of the effect of long continued weathering under natural conditions.

A study of these last tables, LX and LXI, and particularly the latter one, confirms the conclusion drawn from the three preceding tables, namely, that weathering, and especially natural weathering in place over very long periods of time, results in a marked decrease in carbon and available hydrogen and a corresponding decrease in calorific value, and that the change is accompanied by a large increase in the amount of oxygen.

TABLE LX.

Analyses and calorific values of samples from Jasper Park seam.

(*Porter and de Hart*)

Coal No.	7	8	9
Date of sampling at mine	1910	1910	1911
Proximate analysis			
Moisture.........................%	5·57	0·69	0·39
Volatile matter...................%	18·80	16·25	13·72
Fixed carbon.....................%	48·32	78·27	67·04
Ash..............................%	27·31	4·80	18·85
Ultimate analysis			
Carbon..........................%	50·26	83·84	72·03
Hydrogen........................%	2·56	4·77	3·81
Oxygen..........................%	13·09	4·06	3·13
Nitrogen.........................%	0·86	1·20	1·11
(Oxygen and nitrogen)............%	13·95	5·26	4·24
Sulphur..........................%	0·35	0·65	0·68
Ash..............................%	27·31	4·80	18·85
Moisture.........................%	5·57	0·68	0·39
Calorific value			
Determined—B.Th.U. per lb.... ...	8,332	14,465	12,447

TABLE LXI.

Analyses recalculated to ash, moisture and sulphur free basis.

(*Porter and de Hart*)

Coal No.	Carbon %	Hydrogen %	Oxygen %	Nitrogen %	Available hydrogen %	B.Th.U. per lb. "pure coal"
7	75·40	3·84	19·61	1·29	1·65	12,414
8	89·37	5·08	4·32	1·28	4·60	15,390
9	89·90	4·75	3·90	1·39	4·31	15,735

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[Owing to the character of this book it is impossible to index it thoroughly without including a very large number of items, many of them of relatively small importance, and it is doubtful whether such an elaborate index would be of use: the following index therefore has been pre-prepared with a view to covering the main references only and seekers for specific items are strongly recommended to make careful use of the Table of Contents as well as the Index]