FORMS IN WHICH SULPHUR OCCURS IN COAL; THEIR CALORIFIC VALUES AND THEIR EFFECTS UPON THE ACCURACY OF THE HEATING POWERS, CALCULATED BY DULONG'S FORMULA.

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THE estimation of the calorific value of coal from the ultimate analysis, involves the calorific value of the sulphur present. There is much difference of opinion among authorities as to what this value is, and where the amount of sulphur is large, as is often the case, the question becomes of importance, especially as to how the heating value is affected by the different forms in which sulphur may occur. The investigation of this question, some of the results of which are given in this paper, was undertaken at the suggestion of Professor N. W. Lord, to whom the writer wishes to acknowledge his indebtedness for valuable advice and suggestions.

Of the various formulas for determining the calorific value from the ultimate analysis, that of Dulong, $8080C + 34460(H - \frac{1}{8}O) + 2250S$ is, perhaps, the one most generally used. The calorific value of amorphous sulphur burned to sulphur dioxide is 2250 calories, that of the ordinary rhombic form is 2220 calories, but, as free sulphur of any kind occurs but rarely in unweathered coal in any considerable amounts, the value given for sulphur in this formula is necessarily only an approximation.

Sulphur occurs in coal in the form of pyrites, sulphates, organic sulphur and as free sulphur, but in all samples of coal tested in this investigation, pyrites and organic sulphur represented most of the sulphur present. Very little free sulphur was found and only small amounts of sulphates. One of the purposes of this investigation is to determine how closely the calorific values of the different forms of sulphur agree with the value, 2250 calories, given in Dulong's formula.

CALORIFIC VALUE OF PYRITES.

Pyrites is rarely or never entirely absent from coal, the amount present varying from a fraction of a per cent. up to 8 or 10 per cent., or even more. In most bituminous coals probably the greater part of the sulphur present in the coal is there in the form of pyrites. That the presence of the pyrites has an important effect upon the heating power of the coal is a fact generally recognized, but authorities upon the calorific value of fuels are far from agreeing as to just what this effect is. Some apparently assume the heating power of pyrites to be merely that of an equivalent amount of free sulphur and neglect the iron entirely. Others apparently assume its heating power to be the same as that of equivalent amounts of free iron and sulphur. Both assumptions are arbitrary, and, as is shown by actual experiments, neither is true.

In order to investigate the actual heating value of pyrites, the following experiments were performed. A well crystallized specimen of pyrites, apparently free from oxidation or admixed impurities, was selected for the tests. This was finely powdered and thoroughly mixed. By analysis, it had the following composition: Fe, 46.50 per cent.; S, 53.2 per cent.; SiO_2, 0.45 per cent., = 100.15 per cent., which shows the sample to be very nearly pure FeS_2, the theoretical composition of which is Fe, 46.6 per cent.; S, 53.4 per cent.

Pyrites by itself does not burn completely in a calorimeter; in order to secure combustion it must be mixed and burned with some other substance having a high calorific intensity. Naphthalene and coal are two such substances. Coal was chosen, since pyrites can be more easily and thoroughly mixed with powdered coal than with naphthalene, and also, because the question to be investigated is the calorific value of pyrites in coal. The sample of coal selected was low in moisture, sulphur and ash. Analysis showed: Moisture 1.05 per cent., volatile matter 17.20 per cent., fixed carbon 75.70 per cent., ash 6.05 per cent., sulphur 0.54 per cent., nitrogen 1.38 per cent.

The following mixtures of the finely powdered coal and pyrites were made:

	(1)	(2)	(3)	(4)	(5)	(6)
Percentage of coal...........	90	85	80	60	50	50
" " pyrites......	10	15	20	40	50	50

Accurately weighed briquettes of these were then burned in a Mahler calorimeter and the heat of the combustion of the mixtures determined. From the total heat developed in the calorimeter, the heat due to the combustion of the iron wire used as a fuse was deducted, and also 10 calories for the combustion of atmospheric nitrogen present in the calorimeter. This latter correction was found necessary, as will be shown later in this paper. The corrected results are as follows:

No.	Actual weight taken.		
(1)	0.8760 gm. of coal	+ 0.0973 gm. of pyrites	= 7509 calories
(2)	0.8273 “ “ “	+ 0.1460 “ “ “	= 7227 “
(3)	0.7825 “ “ “	+ 0.1956 “ “ “	= 6996 “
(4)	0.5895 “ “ “	+ 0.3930 “ “ “	= 5888 “
(5)	0.4876 “ “ “	+ 0.4876 “ “ “	= 5262 “
(6)	0.4870 “ “ “	+ 0.4870 “ “ “	= 5155 “

Reducing these values to a basis of 1 gram of coal which, determined in the same way, has a calorific value of 8275 calories, we have:

1 gm. of coal	+ 0.1111 gm. of pyrites	= 8572 cal. or	1 gm. of pyrites = 2673 cal.
1 “ “ “	+ 0.1765 “ “ “	= 8736 “	1 “ “ “ = 2612 “
1 “ “ “	+ 0.2500 “ “ “	= 8940 “	1 “ “ “ = 2660 “
1 “ “ “	+ 0.6666 “ “ “	= 9990 “	1 “ “ “ = 2573 “
1 “ “ “	+ 1.0000 “ “ “	= 10790 “	1 “ “ “ = 2515 “
1 “ “ “	+ 1.0000 “ “ “	= 10586 “	1 “ “ “ = 2311 “

As Nos. 4 and 5 gave results lower than those from 1, 2 and 3, formation of SO_2 was suspected, but a slow evolution of the gases of combustion from No. 6, through an alkaline solution of bromine, showed no sulphur, while at the same time the result obtained is much lower than Nos. 4 and 5, which themselves were suspected to be low. However, an examination of the magnetic residue, remaining after the combustion, showed the presence of a considerable amount of sulphur, and the quantitative results of later experiments justify discarding 4, 5 and 6 as being low on account of unburned ferrous sulphide in the residues, not, however, quantitatively determined. The average value for 1, 2 and 3 is 2648 calories.

To determine some of the reactions of the combustion the calorimeter, after a determination, was rinsed out six or eight times with water and the collected washings examined for total free acid, sulphuric acid and iron. The determination of the total free acid was made by titration with a standard solution of ammonia, using methyl orange as an indicator, the ammonia being added rather slowly and with constant stirring of the solution. The presence of ferric sulphate made the end-point somewhat indistinct as the color developed by that salt, as the solution approached neutrality masked the end-point and rendered it less sharp and well marked. The formation of a very slight permanent precipitate of ferric hydroxide was taken as the final end-point as titrations of standard acid solutions, containing approximately the same amounts of ferric sulphate, showed that working in this way results accurate to 0.1 cc. of standard ammonia could be obtained. A standard solution of ammonia, already made up in the laboratory for other purposes, was used. One cc. contained 0.005 gram of ammonia, equivalent to 0.0047 gram of sulphur as sulphuric acid, and to 0.0041 gram of nitrogen as nitric acid. The results of the tests upon the calorimeter washings are as follows:

	Gram of sulphur after deducting that in coal.	Gram of iron.	Gram of sulphur estimated as combined as $Fe_2(SO_4)_3$.	Gram of sulphur as free H_2SO_4 from pyrites.	Cc. of standard ammonia required to neutralize washings.	Estimated cc. of standard ammonia to neutralize free H_2SO_4 from pyrites.	Estimated cc. of standard ammonia to neutralize $H_2SO_4 + HNO_3$ from coal.	Cc. of standard ammonia to neutralize the HNO_3 from nitrogen of air.
(1)	0.0492	0.0030	0.0025	0.0467	16.0	10.0	3.9	2.1
(2)	0.0703	0.0045	0.0037	0.0666	20.0	14.2	3.7	2.1
(3)	0.0972	0.0065	0.0056	0.0916	26.0	19.5	3.5	3.0
(4)	0.1858	0.0095	0.0081	0.1777	42.0	37.8	2.7	1.5

The amounts of sulphur obtained from the calorimeter washings, after correcting for that present in the coal (0.54 per cent.), are given in the first column. These values run from 1 to 4 per cent. lower than the amount present in the pyrites (53.2 per cent.), but subsequent tests showed that more thorough washing of the calorimeter was necessary to obtain all the sulphuric acid present, while the presence of sulphur as ferrous sulphide in the magnetic residue, as is shown later, also accounts for a portion. The amounts of iron present in the washings are given in the second column. Calculating the iron present as ferric sulphate, the amounts of sulphur, so combined, are given in the third column.

The results given in the fourth column show the amounts of free sulphuric acid from the pyrites. They are obtained by deducting the sulphuric acid present as ferric sulphate from the total sulphuric acid, calculated from the first column. The total acidity is shown in the fifth column by the amount of standard ammonia required for neutralization. The sixth column represents the estimated amount of the standard ammonia required to neutralize the amounts of free acid given in the fourth column. The coal used in the combustions contained 1.38 per cent. nitrogen and 0.54 per cent. sulphur, which, during the combustion, were burned to nitric and sulphuric acids. The amounts of acid formed from the nitrogen and sulphur present in 1 gram of coal would require 4.5 cc. of standard ammonia for neutralization. The estimated amounts, corresponding to the amounts of coal taken, are given in the seventh column. Subtracting the sum of the amounts given in 6 and 7 from the amount required to neutralize the total free acid, gives the values in the last column, which represent the amount of standard ammonia required to neutralize the nitric acid formed from the nitrogen of the air present during the combustion. These values indicate some oxidation of this nitrogen to nitric acid, the average of the four being 2.2 cc. of standard ammonia. Tests on the washings of the calorimeter, after the combustion of the coal alone, gave an average titration of 5.8 cc. of standard ammonia; deducting 4.5 cc., accounted for by the nitrogen and sulphur present in the coal, leaves only 1.3 cc. of ammonia required to neutralize the nitric acid formed by oxidation of nitrogen from the air in this case. This value is, however, too low, as no allowance was made for the acid, combined with the iron, as was done in the first case, the iron not having been determined. This correction would be small because it appears from the table that the amount of iron in solution increases with the amount of free acid present, and in those cases where the amounts of free acid were three to ten times as great as from the coal alone the corrections would be equivalent to only 0.5 to 1.8 cc. of the standard ammonia.

One cc. of standard ammonia equals 0.005 gram of NH_3 = 0.0041 gram of nitrogen as nitric acid. The heat of formation of N_2O_5Aq, calculated from the value given by Ostwald,[1] is 29650 calories. Reduced to calories per gram of nitrogen to N_2O_5Aq; this gives 1058 calories; or 0.0041 gram of nitrogen gives 4.4 calories as the correction for each cubic centimeter of ammonia required from neutralization of nitric acid. The average titration value obtained for oxidation of nitrogen of the air during the combustion of coal and pyrites is 2.2 cc., which corresponds

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[1] All values of heats of formation, unless otherwise stated, are calculated from values given in Ostwald's "Grundriss der Algemeinen Chemie," 3rd edition.

to 10 calories of heat produced. The calorific values given have been corrected by this amount.

Failure to quantitatively determine the sulphur retained in the magnetic residue made the calorific values so far obtained for pyrites, uncertain, and after a lapse of several months the investigation was renewed with a view of eliminating this cause of error. As the sample of pyrites used in the first tests showed some oxidation into sulphate, due to standing, a new specimen was obtained from the Foote Mineral Co., and a second crystal selected for the later tests. This specimen was somewhat harder and lighter in color than the first, but contained, by analysis, the same percentage of sulphur, 53.2 per cent. The finely ground sample was mixed with coal in the following proportions and the weighed briquettes then burned in the calorimeter.

Coal	80	75	70	60	50
Pyrites	20	25	30	40	50

The determinations were conducted in the same manner as the first series, except that the calorimeter in this series was filled with 10 atmospheres of oxygen, then emptied and refilled to 18 atmospheres, while in the first series this was not done. As the oxygen used contained only about 5 per cent. nitrogen, this emptying and refilling reduced the quantity of nitrogen, present during the combustion, to about half that present during combustion in the first series, and this would tend to reduce the amount of nitric acid formed from the air. Five cc. of water were placed in the calorimeter in each experiment to dilute the sulphuric acid formed. The following are the results obtained, after correcting for the wire fuse:

No.
(1) 0.7883 gm. of coal + 0.1971 gm. of pyrites = 7043 calories
(2) 0.6967 " " " + 0.2986 " " " = 6538 "
(3) 0.7956 " " " + 0.1989 " " " = 7101 "
(4) 0.6952 " " " + 0.2979 " " " = 6526 "
(5) 0.7441 " " " + 0.2480 " " " = 6801 "
(6) 0.4939 " " " + 0.4939 " " " = 5230 "
(7) 0.4878 " " " + 0.4878 " " " = 5104 "
(8) 0.5971 " " " + 0.3981 " " " = 5946 "

Tests on the washings from the calorimeter gave the following results:

Gram of sulphur after deducting that of coal.	Gram of iron.	Gram of sulphur estimated as $Fe_2(SO_4)_3$.	Gram of sulphur as free H_2SO_4 from pyrites.	Cc. of standard ammonia to neutralize washings.	Estimated cc. of standard ammonia to neutralize free H_2SO_4 from pyrites.	Estimated cc. of standard ammonia to neutralize $H_2SO_4 + HNO_3$ from coal.	Cc. of standard ammonia to neutralize HNO_3 from nitrogen of air.	Gram of sulphur found per gram of pyrites.
0.1028	0.006	.....	.....	...	...	..	..	0.5217
0.1545	0.008	.....	.....	...	...	..	..	0.5172
0.1048	0.007	.....	.....	...	...	..	..	0.5272
0.1552	0.009	.....	.....	...	...	..	..	0.5206
0.1290	0.0065	0.0056	0.1234	29.5	26.2	3.3	0.0	0.5200
0.2411	0.015	0.0130	0.2281	51.0	48.5	2.2	0.3	0.4883
0.2207	0.007	0.0060	0.2147	45.5	45.0	2.2	—1.7	0.4526
0.1998	0.013	0.0111	0.1887	42.5	40.2	2.7	—0.4	0.5020

An inspection of the results for oxidation of nitrogen from the air shows no oxidation, two results being negative, but as the repeated washings necessary to get all of the sulphuric acid out of the calorimeter, necessitated the use of considerable quantities of wash-water, the titrations for acidity were made on a large volume of solution, 300 to 400 cc. This large volume, combined with the effect of the presence of the ferric sulphate, made the exact end-point uncertain. Titrations on washings, after combustion of the coal alone, showed 4.4 cc., as against 4.5 cc. calculated, which also indicates no oxidation of atmospheric nitrogen to nitric acid.

Some tests on former determinations indicated that the probability of formation of sulphur dioxide increased with the amount of pyrites taken; on this account the gases of combustion from 6, 7 and 8 were passed through an alkaline solution of bromine and the amounts of sulphur determined, with the following results:

No.
(6) 0.0035 gram of sulphur = 0.0071 gram of sulphur per gram of pyrites
(7) 0.0149 " " " = 0.0302 " " " " " " "
(8) 0.0010 " " " = 0.0025 " " " " " " "

Sulphur in the Magnetic Residue.—The magnetic residues left in the platinum cup, in which the combustion took place, were ground and portions tested for sulphur, with results as follows:

No.	Gram of residue estimated from ash of coal + Fe_3O_4 from pyrites.	Gram of residue taken for the determination of sulphur.	Gram of sulphur obtained by evolution as H_2S.	Gram of sulphur obtained by oxidation and determination as $BaSO_4$.	Gram of sulphur obtained per gram of pyrites taken.
(1)	0.1790	0.0670	0.0001	.....	0.0014
(2)	0.2370	0.1250	0.00044	.....	0.0029
(3)	0.1800	0.1050	.....	0.0004	0.0034
(4)	0.2370	0.1300	.....	0.0008	0.0050
(5)	Lost.	.....	.....	.....	.....
(6)	0.3500	0.2310	0.0059	.....	0.0175
(7)	0.3450	0.0750	0.0031	.....	0.0289
		0.0750	.....	0.0038	0.0359
(8)	0.2900	0.1500	.....	0.0053	0.0259

The residues from 1 and 3, 2 and 4, and 6 and 7 are from the combustions of identical mixtures of coal and pyrites. A comparison of No.1 with its duplicate No. 3, and of No. 2 with its duplicate No. 4, indicates that all of the sulphur in the residue was not obtained by evolution as hydrogen sulphide. In the process as conducted, 1 gram of granulated zinc was placed in the evolution flask with the residue to be tested, which was then treated with 50 cc. of hydrochloric acid (five parts concentrated hydrochloric acid and one part water), and after solution, boiled till all of the gases were expelled, the hydrogen sulphide being absorbed in an ammoniacal solution of cadmium chloride and, after acidifying, titrated with standard iodine solution. Some of the magnetic residue was somewhat slower to dissolve than the zinc, and the ferric iron produced probably oxidized a portion of the hydrogen sulphide, accounting for No. 1 and No. 2 running lower than the gravimetric results for No. 3 and No. 4.

In order to make certain of this, equal portions of the residue from No. 7 were tested for sulphur. The portion tested by evolution of hydrogen sulphide yielded sulphur equivalent to 2.89 per cent. sulphur per gram of pyrites, and the acid solution left in the evolution flask yielded 0.73 per cent., or a total of 3.62 per cent. sulphur per gram of pyrites. Two similar portions, treated for sulphur with hydrochloric acid and potassium chlorate and by fusion with sodium carbonate and nitrate, yielded an average of 3.59 per cent. sulphur, showing conclusively that all of the sulphur present was not obtained by the evolution process.

A measure of the nature and completeness of the combustion is afforded by the total sulphur accounted for in each sample, which is as follows:

No.	Sulphur as H_2SO_4 in washings from calorimeter. Per cent.	Sulphur as FeS in magnetic residue. Per cent.	Sulphur in gases of combustion. Per cent.	Total sulphur found. Per cent.
(1)	52.17	0.14[1]	...	52.31[1]
(2)	51.72	0.29[1]	...	52.01[1]
(3)	52.72	0.34	...	53.06
(4)	52.06	0.50	...	52.58
(5)	52.00	...	...	52.00
(6)	48.83	1.75[1]	0.71	51.29[1]
(7)	45.26	3.59	3.02	51.87
(8)	50.20	2.59	0.25	53.04

The total sulphur obtained is a little lower than the amount present in the pyrites, 53.2 per cent. These results are, however, very satisfactory, considering the difficulty of obtaining all of it without mechanical losses. In those determinations, from relatively small amounts of pyrites, where no tests were made for sulphur dioxide in the gases of combustion, there is a possibility of some sulphur escaping in that way, but the writer's experience is that with a large excess of coal and plenty of oxygen the sulphur burns entirely to sulphuric acid. There is, however, always a chance of sulphuric acid being mechanically carried out with the gases from the combustion, especially where the calorimeter is allowed to empty rapidly. Several tests, by passing the escaping gases through plugs of cotton to catch any mechanically carried globules of sulphuric acid, showed in each test traces of sulphur escaping in this way. On this account the values, given for sulphur escaping as sulphur dioxide, are probably slightly high.

Correction for Formation of FeS and SO_2.—The heat of formation of FeS is 23900 calories, that of Fe_3O_4 is 264800 calories, that of SO_3Aq is 142500 calories, that of SO_2 is 71000 calories. The reaction and heat equation for the combustion of FeS to $Fe_3O_4 + SO_3Aq.$ are

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[1] These values are low, owing to the low results obtained by the evolution process in obtaining the values given. Taking the sulphur in the residues of No. 1 and No. 2, as the same as in their duplicates, No. 3 and 4, and that in No. 5, being intermediate in amount of pyrites, as intermediate in amount of sulphur in the residue between No. 3 and No. 4, the total sulphur results so corrected are as follows:

Per cent.	Per cent.
(1) 52.51	(5) 52.40
(2) 52.22	(6) not corrected
(3) 53.06	(7) 51.87
(4) 52.58	(8) 53.04

$$3\ \mathrm{FeS} + \text{oxygen} + \text{aqua} = \mathrm{Fe_3O_4} + 3\mathrm{SO_3Aq}.$$

$$3\ (23900) + x = 264800 + 3(142500). \qquad x = 620600 \text{ calories.}$$

This reduced to 1 gram of FeS becomes 2350 calories, or to 1 gram of sulphur as FeS, 6462 calories, or to 0.01 gram of sulphur as FeS, 65 calories.

The reaction and heat equation for the combustion of SO_2 and the formation of $SO_3Aq.$ are

$$\mathrm{SO_2} + \text{oxygen} + \text{aqua} = \mathrm{SO_3Aq}.$$

$$71000 + x = 142500, \qquad x = 71500 \text{ calories.}$$

This reduced to 1 gram of sulphur becomes 2234 calories, or to 0.01 gram of sulphur, 22 calories.

The calorimeter results, corrected for FeS and SO_2, are as follows:

	Gram of coal	+	gram of pyrites	=	calories	+	correction for FeS and SO_2	=	calories.
(1)	0.7883	+	0.1971	=	7043	+	4	=	7047
(2)	0.6967	+	0.2986	=	6538	+	10	=	6548
(3)	0.7956	+	0.1989	=	7101	+	4	=	7105
(4)	0.6952	+	0.2979	=	6526	+	10	=	6536
(5)	0.7441	+	0,2480	=	6801	+	7	=	6808
(6)	0.4939	+	0.4939	=	5230	+	..	=	....
(7)	0.4878	+	0.4878	=	5104	+	144	=	5248
(8)	0.5971	+	0.3981	=	5946	+	66	=	6012

Reducing the corrected values to a basis of 1 gram of coal, which, determined under similar conditions, has a calorific value of 8278 calories, the values obtained for 1 gram of pyrites in

(1) is 2648 calories.
(2) " 2618 "
(3) " 2608 "
(4) " 2622 "
(5) is 2616 calories.
(6) " .... "
(7) " 2480 "
(8) " 2686 "

No. 1 is suspected high, owing to the switch throwing in the electrical circuit remaining closed for a few seconds after combustion of the wire fuse. Nos. 7 and 8 are uncertain, owing to the large corrections for ferrous sulphide, also No. 8 was determined under rather unfavorable temperature conditions and at a different time from the remainder of the series. The average of 2, 3, 4 and 5 is 2616 calories. The calorific value obtained for pyrites in this way involves not only any errors of the individual determinations on coal and pyrites, but also any error in the determination of the calorific value of the coal. The error in the calorific value of a relatively large amount of coal is thrown upon a relatively small amount of pyrites and in obtaining the value for 1 gram of pyrites this error is, in these particular determinations, multiplied from two to five times.

The calorific value of pyrites may, however, be found directly from the determinations on coal and pyrites by elimination of the coal by addition or subtraction. Proceeding in this way

2 with 3 gives for 1 gram of pyrites 2632 calories.
3 " 4 " " 1 " " " 2643 "
2 " 5 " " 1 " " " 2623 "
3 " 5 " " 1 " " " 2641 "
4 " 5 " " 1 " " " 2644 "

The average obtained in this way is 2637 calories.
The average for both methods is 2627 calories.

These values are uncorrected for heat of formation of ferric sulphate. If $Fe_2(SO_4)_3Aq.$ is formed instead of $Fe_3O_4 + SO_3Aq.$ the equation for the difference in the heat production between the formation of

$$3Fe_2(SO_4)_3Aq. \qquad \text{and} \qquad 2Fe_3O_4 + 9SO_3Aq.$$

is

$$3(619000) = 2(264800) + 9(142500) + x.$$

$$x = 44900 \text{ calories,}$$

or per gram of iron equals a heat production of 134 calories if $Fe_2(SO_4)_3Aq.$ is formed instead of $Fe_3O_4 + SO_3Aq.$, a negligible amount for the formation of very small quantities of ferric sulphate.

If the ferric sulphate formed is due to the subsequent action of sulphuric acid and oxygen upon the exposed iron of the calorimeter, owing to cracking and chipping of the enamel lining, the heat production is expressed by

$$2Fe + 3H_2SO_4Aq. + \text{oxygen} = Fe_2(SO_4)_3Aq. + H_2O + 4H$$

$$3(210900) + x = 619000 + 68400$$

$x = 54700$ calories. Per gram of iron $= 490$ calories, or for the amounts of iron found in the washings from the calorimeter (0.006 to 0.015 gram) a minus correction of from 3 to 7 calories, if all of the production of heat due to this reaction occurs during the first few minutes following the combustion. It seems probable, however, that the extent of the action of the acid upon the calorimeter is more or less dependent upon the time that the acid remains in contact with the exposed iron. If such be the case, a considerable portion of the heat so produced is produced after the finishing of the temperature readings and therefore does not affect the value as determined.

In order to obtain information upon this question, mixtures of sulphur and naphthalene in the proportion of ten parts naphthalene to four parts sulphur were burned in the calorimeter, and the dilute sulphuric acid formed allowed to remain in the calorimeter for different periods of time. 0.62 gram of the mixture = 0.18 gram of sulphur, equivalent to 0.35 gram of pyrites was taken for each test. No. 1 was opened after about three minutes, No. 2 was opened after five minutes and No. 3 was opened after twenty minutes from the time of the burning of the wire fuse. The amounts of iron found in the washings are

In No. 1 = 0.004 gram Fe
" " 2 = 0.007 " "
" " 3 = 0.011 " "

In determination No. 6 of the coal and pyrites, which shows the largest amount of iron (0.015 gram), the calorimeter was not opened till over an hour after the time of combustion. These values indicate that time is an important factor in the extent of the reaction, and that the heat produced during the time of the determination is very small, so small as to be nearly negligible; furthermore, where the values are determined by elimination, any small errors of either nitrogen to nitric acid or iron to $Fe_2(SO_4)_3$, being partly eliminated along with the coal, have little effect upon the values obtained.

Conclusions.—The average of the results obtained in sample No. 1 is 2648 calories, the average of three determinations; in sample No. 2 the average of four determinations is 2627 calories; or an average for the two samples of 2637 calories. With 53.2 per cent. sulphur in the pyrites the calorific value per gram of sulphur as pyrites is 4957 calories.

In the calorimeter the products of combustion are $Fe_3O_4 + 6SO_3Aq.$, while in the ordinary combustion of pyrites with coal the products of combustion are $Fe_2O_3 + 4SO_2$. The equation for the difference in heat production of $2Fe_3O_4 + 12SO_3Aq.$ and $3Fe_2O_3 + 12SO_2$. is $2(264800) + 12(142500) = 3(201200)$[1] $+ 12(71000) + x$. $x = 784000$ calories. Hence, on a basis of 1 gram of sulphur 2042 calories are to be subtracted from the heat

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[1] Calculated from the calorific value of iron to Fe_2O_3, given by Ledebur as 1796 calories, see Eisenhüttenkunde, 3rd edition.

combustion in a Mahler calorimeter to obtain the calories of heat produced by combustion in the air.

4957 calories — 2042 calories, or 2915 calories is the heat of combustion of 1 gram of sulphur as pyrites under ordinary conditions of combustion. Owing to the small amounts of pyrites necessarily taken for a determination and the resultant multiplication of any errors, this value cannot be considered as exact, but as a close approximation to the actual calorific value.

Where the sulphur is present in the coal as pyrites the value 2250 for sulphur in Dulong's formula is accordingly too low by approximately 2915 — 2250, or 665 calories, and the result obtained by the application of the formula will be too low by 6.6 calories for each per cent. of sulphur present as pyrites.

It should be noted in this connection that the oxygen in the ultimate analysis being determined by difference, if no allowance is made for the oxygen taken from the air to form Fe_2O_3 with the iron in the pyrites, the results for hydrogen by Dulong's formula will be too high by 16.2 calories for each per cent. of sulphur present as pyrites.

This may be shown as follows: As the sulphur is replaced by three-eighths of its weight of oxygen from the air, the sum of the components, including the ash, will exceed the weight of the coal taken by this amount, if the weight of the ash as found be used. The weight of the oxygen determined by difference from the amount taken will be low by a corresponding amount, and the available hydrogen (H — one-eighth O) will be high by an equivalent quantity. On the basis of 1 per cent. of sulphur the oxygen will be three-eighths of a per cent. low and the available hydrogen will be one-eighth of three-eighths, or 0.047 of a per cent. high. The heating power of this is 0.00047×34460, or 16.2 calories. As the usual value for sulphur gives for sulphur as pyrites a result too low by 6.6 calories, the net result when applying the formula in its ordinary form to an uncorrected ultimate analysis is the difference of these, or 9.6 calories too high. Obviously, the sum of the errors involved by omitting the oxygen correction in the ultimate analysis is but very little larger than the error due to the difference between the heating value of sulphur, as given in the ordinary formula, and the heating value of sulphur as pyrites, being for each per cent. of sulphur present as pyrites, plus 9.6 calories in one case and minus 6.6 calories in the other.

Some of the products resulting from the oxidation of pyrites and the occurrence of organic sulphur in coal will be considered in another paper.

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THE RAPID DETERMINATION OF FAT BY MEANS OF CARBON TETRACHLORIDE.

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THE number of solvents which have been proposed for use in determining the fat in animal and vegetable tissues is considerable, including ether, petroleum ether, alcohol, carbon bisulphide, acetone, chloroform and carbon tetrachloride. Of these the most generally accepted is ether. This may, in fact, be considered as the official solvent in all cases of dispute or comparison. Petroleum ether is, however, preferred by many who consider the results obtained with this solvent as rather more trustworthy than those with ether.

It is not the purpose of this paper to enter into any historical resumé of the subject of the determination of fat, either as regards kinds of solvents or methods of manipulation; but rather to indicate the reasons which have led up to the adoption of carbon tetrachloride by the writer as a rapid and accurate reagent in the commercial determination of fat. In factory control work it becomes necessary to determine the proportion of fat in different products within a comparatively few hours. The usual duration of extraction with ether is about sixteen hours, although essentially all of the fat can be extracted in much less time. Petroleum ether is said to require about the same length of time as ether, although approximate results can usually be obtained in from four to six hours' extraction. Carbon bisulphide extracts to practical completion inside of four hours, and has been used quite frequently in the rapid determination of fat, giving quite satisfactory results as a rule. It has the advantage that it can be used on materials containing not more than 10 per cent. moisture without previous removal of the water. As just stated, extraction appears to be com-