pinch-cock may be employed for each burner. The sheet steel plate F, at the height of the laboratory table, is perforated at desired points with holes over which the Bunsen burners are placed in position to be readily warmed by small flames from the alcohol lamps B.

The chief advantage of the apparatus for laboratories remote from city supplies of gas is: The almost immediate availability of an unlimited, cheap supply of gas, capable of producing any desired degree of heat in the combustion furnace or in isolated Bunsen burners.

My students find no difficulty or danger in employing the apparatus for all work requiring the combustion furnace.

I have Mr. C. W. Beaver to thank for assistance in the preliminary experimentation.

OREGON AGRICULTURAL COLLEGE,
CORVALLIS, OREGON,
April 11, 1904.

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.

(SECOND PAPER.)

BY E. E. SOMERMEIER.

Received April 5, 1904.

OXIDATION OF PYRITES: PRODUCTS FORMED, THEIR CALORIFIC VALUES AND THEIR EFFECTS UPON THE HEATING VALUE OF COAL.

UPON exposure to air and moisture the pyrites in coal gradually oxidizes, the main product of oxidation being ferrous sulphate, together with smaller and variable amounts of free sulphur, free sulphuric acid, ferric sulphate and sulphur dioxide.

To obtain quantitative values for the products resulting from oxidation, tests were made upon a number of different samples of coal and pyrites.

The first tests were made upon an old sample of finely ground coal pyrites which had been kept around the laboratory for several years in a bottle closed with an ordinary cork. When opened, this sample gave off a strong odor of sulphur dioxide and even after the sample had been spread upon paper and exposed to air for some hours a slight odor of sulphur dioxide could still be detected.

The tests upon the sample after this preliminary exposure to air and the results obtained are as follows: (*a*) Ten to twenty grams were mixed in a 500 cc. flask with 500 cc. of water, recently boiled and cooled. After standing five minutes, the liquid was thoroughly mixed and aliquot parts filtered off and tested for ferrous iron, total iron, sulphur dioxide, free acid and total sulphuric acid. (*b*) Ten grams were mixed with 500 cc. of water, recently boiled and cooled, and containing 5 cc. of concentrated hydrochloric acid. After five minutes, aliquot parts were filtered off and tested for ferrous iron, total iron, sulphur dioxide and total sulphuric acid. (*c*) Ten grams were mixed with boiled and cooled water, containing 0.5 per cent. of sodium carbonate. After five minutes an aliquot part was filtered off and tested for total sulphuric acid. (*d*) Ten grams were extracted with carbon disulphide in a Soxhlet apparatus and the free sulphur extracted, oxidized with nitric acid and potassium chlorate and determined as barium sulphate.

One hundred cc. portions of the solutions from (*a*), (*b*) and (*c*) were tested for sulphur dioxide by addition of a standard solution of iodine, 1 cc. = 0.0005 gram of sulphur as SO_2, the portion from (*c*) being acidified with hydrochloric acid before titration. The amounts of iodine required to produce a blue color with starch varied from 0.1 to 0.3 cc. After allowing for a blank of 0.1 cc., these amounts correspond to 0.0 to 0.2 cc. of iodine required by the sulphur dioxide from the pyrites. These values, expressed in per cent., give 0.0 to 0.005 per cent. of sulphur as sulphur dioxide, which indicates that most of that present when the sample was first opened had escaped during the preliminary exposure to air before testing.

The results from the other tests in per cent. are as follows:

	Soluble ferrous iron.	Total soluble iron.	Ferric iron by difference.	Total sulphur present as soluble sulphate and as free H_2SO_4.	Sulphur as free H_2SO_4.	Estimated sulphur present as $FeSO_4$.	Estimated sulphur present as $Fe_2(SO_4)_3$.	Estimated sulphur present as free H_2SO_4.	Sulphur present as free sulphur.
(*a*)	1.77	2.50	0.73	2.38	0.50	1.01	0.83	0.54	...
	1.87	2.60	0.73	2.40	0.59	1.07	0.83	0.50	...
	1.91	2.67	0.76	2.49	0.60	1.09	0.87	0.53	...
(*b*)	1.80	2.50	0.70	2.40	...	1.03	0.80	...	...
	1.83	2.60	0.76	2.46	...	1.05	0.87	...	...
(*c*)	...	...	...	2.43	...	...	...	...	...
	...	...	...	2.50	...	...	...	...	...
(*d*)	...	...	...	...	...	...	...	...	0.06
	...	...	...	...	...	...	...	...	0.07
Average,	1.84	2.57	0.74	2.44	0.56	1.05	0.84	0.55	0.065

The total soluble sulphates obtained by the three methods of treatment differ but little in amount, as is also true of the results obtained for ferrous and total iron by the different methods of treatment. The free sulphuric acid was determined by titration with standard ammonia, using methyl orange as an indicator. The average of the results obtained agrees closely with the average calculated amount of free sulphuric acid present, which amount is obtained by subtracting the sulphur present as ferrous and ferric sulphate from the total sulphur present as soluble SO_4. The average of the results for total sulphur as soluble SO_4 is 2.44 per cent. The average for the results for total iron is 2.57 per cent. 2.57 per cent. of iron, if present as the result of oxidation of FeS_2, corresponds to 2.94 per cent. of sulphur in that form, or 0.50 per cent. more than the average of the results obtained for total sulphur as soluble SO_4. Deducting from this amount the free sulphur present, 0.065 per cent. leaves 0.43 per cent. unaccounted for, or about $^1/_7$ of the total sulphur from the FeS_2 oxidized.

A number of samples of coal high in pyrites were selected for a second series of tests. These samples, after having been crushed to finer than ¼ mesh, had been kept in sealed Mason jars for about a year and a half. The tests were made in essentially the same way as those upon pyrites, except that larger amounts of coal, 15 to 45 grams, were taken. The averages of the results in per cent. for each sample are as follows:

No.	Soluble ferrous iron.	Total soluble iron.	Ferric iron.	Total sulphur present as soluble sulphate and as free H_2SO_4.	Sulphur present as free H_2SO_4.	Sulphur present as free sulphur.
27 ...	0.40	0.44	0.04	0.30	0.03	0.08
38 ...	0.31	0.35	0.04	0.26	0.03	0.09
48 ...	0.39	0.44	0.05	0.33	0.04	0.08
50 ...	0.58	0.62	0.04	0.42	0.05	0.13
60 ...	0.10	0.12	0.02	0.09	0.01	0.03
48*a* ..	0.42	0.49	0.07	0.33	0.04	...

Practically the only soluble sulphate present is ferrous sulphate, the small amounts of ferric iron found being partially accounted for by slight oxidation during the carrying on of the tests. The values for free sulphur, as given, are probably too high, as the residue obtained by the extraction of the coal with carbon disulphide consisted of free sulphur plus a considerable amount of tarry matter. This free sulphur and tarry matter were oxidized by means of nitric acid and potassium chlorate, and the total sulphur present determined. Any combined sulphur present in the residue is, accordingly, included in the values given for free sulphur; however, the total amounts of sulphur obtained are so small that the error is of little importance. The average of the results for total sulphur soluble as SO_4 is 0.28 per cent. The average for total soluble iron is 0.40 per cent. 0.40 per cent. of iron calculated as FeS_2 corresponds to 0.46 per cent. of sulphur, which is 0.18 per cent. more than the total soluble SO_4 obtained. Deducting from this amount the free sulphur present (0.08 per cent.) leaves 0.10 per cent. unaccounted for, or $^1/_5$ of the total sulphur in the FeS_2 oxidized.

The results given under No. 48*a* were obtained on a portion of sample No. 48, which had been kept in an open sack. These results agree very closely with the results obtained on the sample which had been kept in a Mason jar. This indicates that the keeping of the sample in a sealed jar has little effect upon the rate of oxidation. However, no definite conclusions can be drawn from this one test, as the original sample, 100 to 200 pounds, taken from the mine, had been kept for about a month before crushing and sampling, and a considerable portion of the oxidation may have occurred before the sample was put into the jar.

A third series of tests was made upon a fresh unoxidized sample of coal pyrites which, after crushing to between 40 and 100 mesh, was partially freed from admixed coal and slate by washing with a solution of zinc chloride (sp. gr. 1.75). In a solution of this specific gravity the pyrites sinks while the free coal and lighter slaty material float and may either be removed by skimming or floated off by decantation. The pyrites, after washing with the zinc chloride solution, was thoroughly washed with water, then with alcohol and dried, after which it was very finely powdered. By analysis it contained 48.5 per cent. sulphur and 43.1 per cent. iron, which indicates the sample to be over 90 per cent. pure FeS_2.

To obtain quantitative values for the oxidation changes, 37 grams of this sample, spread on watch-glasses, were placed under an 8-liter bell jar. To absorb any sulphur dioxide, resulting from the oxidation, a beaker containing a 5 per cent. solution of sodium carbonate was placed under the bell jar with the pyrites, the jar being lifted once a week to renew the supply of air. After two weeks the sample was examined with the following results: Increase in the weight of the sample, 2.64 grams, or 7.1 per cent.; free sulphur, by extraction of 5 grams with carbon disulphide in a Soxhlet apparatus and oxidation of the residue with nitric acid and potassium chlorate, 0.34 per cent.; total sulphur as soluble sulphates and as free sulphuric acid, 0.87 per cent.; sulphur as free sulphuric acid, 0.05 per cent.; soluble ferrous iron, 1.35 per cent.: soluble ferric iron, none. The solution of sodium carbonate, after oxidation with bromine water, was tested for sulphate, but none was found, showing that no sulphur dioxide had had been given off during the oxidation.

The 1.35 per cent. iron, calculated as FeS_2, corresponds to 1.54 per cent. sulphur, or 0.33 per cent. more than the sum of the soluble sulphates, the free sulphuric acid and the free sulphur found.

The portion of the sample not required for the foregoing tests weighed 20.4 grams, which is equivalent to 19 grams of the original sample. This was replaced under the bell jar together with another solution of sodium carbonate and allowed to remain for another period of two weeks. When removed from the bell jar the sample weighed 21.4765 grams, or a gain over the weight of the original sample of 13.03 per cent. The sample was then allowed to remain over night exposed to the rather dry air of a cool basement room. It then weighed 21.2360 grams or a loss of 1.28 per cent. of the original weight, the net increase in weight over the original sample being 11.75 per cent. Tests for the products of oxidation gave: Ferrous iron, 2.90 per cent.; total iron, 2.95 per cent.; total sulphur as soluble SO_4, 1.88 per cent.; sulphur as free sulphuric acid, 0.09 per cent.; free sulphur, 0.48 per cent. The solution of sodium carbonate, oxidized with bromine water and tested for sulphur, yielded 0.0035 gram of barium sulphate. A blank on the sodium carbonate showed no sulphur. This indicates the formation of a small amount of sulphur dioxide, being, however, only 0.003 per cent. of the original sample. 2.95 per cent. iron, calculated to FeS_2, gives 3.37 per cent. sulphur, as against $1.88 + 0.48$, or 2.36 per cent. found, 1 per cent. of sulphur being unaccounted for.[1] The $FeSO_4$, $7H_2O + H_2SO_4Aq.$ present in the oxidized sample represents an increase in weight, due to water and oxygen, of about 10.5 per cent. The increase actually found is 11.75 per cent., which leaves about 1.25 per cent. to be accounted for by additional moisture or other causes.

The calorific values of these oxidation products will now be considered.

Calorific Value of Ferrous Sulphate.—The products resulting from the decomposition of $2FeSO_4.7H_2O$, by burning with coal in air, are $Fe_2O_3 + 2SO_2 + O +$ aqua, heat being absorbed during the reaction. The heat of formation given by Thomsen[2] for $FeSO_4.7H_2O$ is 240,100 calories. Ledebur[3] gives 1,796 calories, the average of several authorities, as the calorific value of 1 gram of iron burned to Fe_2O_3, which, expressed in calories per gram-molecule, equals 201,200 calories as the heat of formation of Fe_2O_3. The heat of formation of SO_2 equals 71,000 calories.[4] From these values the heat equation for the transformation of

---

[1] Destruction by fire of samples, apparatus and laboratory in which the writer was working necessitates a temporary discontinuance of further investigations for the purpose of locating this unaccounted-for sulphur. However, this does not greatly affect the general conclusions arrived at in this paper, as the foregoing results suffice to show that the products resulting from oxidation of pyrites are quite variable in their quantitative relations to each other.

[2] "Thermochemical Untersuchung."

[3] "Eisenhüttenkunde," 3rd edition.

[4] All values for heat of formation, unless otherwise stated, are based upon values given in Ostwald's "Grundriss der allgemeinen Chemie," 3rd edition.

$2FeSO_4.7H_2O$ into $Fe_2O_3 + 2SO_2 + O$ + aqua, is $2(240,100) = 201,200 + 2(71,000) + x$, in which x is the heat absorbed in the decomposition. $x = 137,000$ calories. Reducing to a basis of 1 gram of sulphur gives 2,140 calories of heat absorbed, whereas in the form of pyrites burning to $Fe_2O_3 + 4SO_2$ it has a calorific value of 2,915 calories.[1]

Dulong's formula for calculating the calorific value of fuel from the ultimate analysis is $8,080C + 34,460(H - 1/8O) + 2,250S$.

It follows that in ascribing to sulphur a value of 2,250 calories the formula gives results too high by 2,250 + 2,140 or 4,390 calories, for all sulphur present as ferrous sulphate, as such sulphur represents heat absorption, not production. The error thus introduced is, however, partially corrected by another of opposite effect The application of the formula considers all of the oxygen in the coal as united with hydrogen and determines the available hydrogen on this assumption, but as part of the oxygen is united with sulphur, the value obtained for available hydrogen will be too small in the presence of sulphates, calculating the effect of 1 per cent. of sulphur as ferrous sulphate gives 1.25 per cent. oxygen as $2SO_2 + O$. 1/8 of 1.25 per cent. is 0.156 per cent. The available hydrogen value is therefore too small by this amount. 0.156 per cent. hydrogen represents a heat value of (0.00156 × 34,460) or 54 calories. Comparing the foregoing results it appears that where the sulphur occurs as ferrous sulphate the application of Dulong's formula gives, for sulphur 44 calories too high, for hydrogen 54 calories too low, or a net result of 10 calories too low for each per cent. of sulphur as ferrous sulphate.

Calorific Value of Sulphur as Ferrous Sulphate in a Mahler Calorimeter.—Any difference between the products of the decomposition of ferrous sulphate in air and in a calorimeter affects the calorific result obtained by the difference in the value of the heats of formation of the resultant products. To determine the products formed in a calorimeter, a mixture of 0.8 gram of coal and 0.6 gram of ferrous sulphate was burned in a Mahler calorimeter. The gases from the combustion showed no sulphur dioxide. and the resultant residue was strongly magnetic. This indicates the following reaction and the heat equation as occurring:

$$3FeSO_4.7H_2O + \text{oxygen} = Fe_3O_4 + 3SO_3Aq.$$

---

[1] This Journal, 26, 555.

$3(240{,}100) = 264{,}800 + 3(142{,}500) \times x$. $x = 28{,}000$ calories, which, reduced to a value for 1 gram of sulphur, gives 290 calories as the heat absorption. As has already been stated, the reaction for decomposition of ferrous sulphate, when it occurs in connection with the combustion of coal in air, is $2FeSO_4.7H_2O = Fe_2O_3 + 2SO_2 + O +$ aqua, which corresponds to a heat absorption of 2,140 calories per gram of sulphur, from which it appears that the combustion of ferrous sulphate and coal in a Mahler calorimeter gives results higher than where the combustion occurs in air, by the difference between 2,140 and 290 or 1,850 calories. Therefore to obtain the calorific value of ferrous sulphate and coal burned in air, the calorimeter values obtained should be corrected by subtracting 18.5 calories for each 0.01 gram of sulphur present as ferrous sulphate.

In the tabulated determinations of the calorific value of coals given in the latter portion of this paper, the nature of the occurrence of the sulphur is not taken into consideration, but the formation of sulphur trioxide in the calorimeter instead of sulphur dioxide is corrected for by corrections equivalent to subtracting 22.3 calories for each per cent. of sulphur present in the coal. Where any of it occurs as ferrous sulphate, the correction is accordingly too large by the difference between 22.3 and 18.5 or 3.8 calories, a negligible error for the small amounts of sulphates usually found in coal.[1]

---

[1] The correction for formation of sulphuric acid during combustion in a calorimeter differs with different writers, some of whom do not appear to have a clear conception of the actual calorific effects. In the calorimeter work for the Ohio Geological Survey, carried on in the Metallurgical Laboratory of the Ohio State University, the following method for correction is used. The total acidity of the washings from the calorimeter is determined by titration with standard ammonia, using methyl orange as an indicator. The acidity is assumed to be due to nitric acid and a heat correction is made corresponding to the number of cubic centimeters of standard ammonia required in the neutralization. By assuming the total acidity to be due to nitric acid and making the heat correction on this basis, any SO_3Aq formed during the combustion is only partially corrected for, and it is necessary to make an additional correction of 13 calories for each 0.01 gram of sulphur present. This may be shown as follows: The heat of formation of N_2O_5Aq is 1,058 calories. Hence the necessary correction for 0.01 gram of nitrogen to N_2O_3Aq is 10.6 calories. The heat of formation of SO_3Aq is 142,500 calories. The heat of formation of SO_2 is 71,000 calories. Reduced to a basis of 1 gram of sulphur the difference in heat of formation is 2,230 calories. The correction for each 0.01 gram of sulphur to SO_3Aq instead of SO_2 is accordingly 22.3 calories. In the titration H_2SO_4 equals $2HNO_3$. 32 parts of sulphur count as 28 parts of nitrogen, or ${}^{32}/_{28}$ of 0.01 gram of sulphur to SO_3Aq instead of SO_2, is corrected for by 10.6 calories, which for 0 01 gram of sulphur is ${}^{28}/_{32}$ of 10.6 calories or 9.3 calories. Of the necessary correction, 22.3 calories for formation of SO_3Aq, the correction considering the total acidity to be due to nitric acid, allows a correction of only 9.3 calories. Therefore to secure a proper correction an additional correction of 22 3 − 9.3 calories, or 13 calories is necessary for each 0.01 gram of sulphur present. The calorific values given later in this paper have all been corrected on this basis.

Calorific Values of Sulphur as Sulphuric Acid and as Ferric Sulphate.—The reaction and heat equation for the decomposition of sulphuric acid by combustion with coal in air are

$$H_2SO_4Aq. = H_2O + SO_2 + O + Aq.$$

$$210,900 = 68.400 + 71.000 + x. \quad x = 71.500 \text{ calories,}$$

which, reduced to 1 gram of sulphur, gives 2,230 calories of heat absorbed, as against 2.140 calories absorbed for 1 gram of sulphur as ferrous sulphate.

In a Mahler calorimeter the sulphuric acid is unchanged and no heat is absorbed, as against 290 calories absorbed for 1 gram of sulphur as ferrous sulphate.

The reaction affecting calculations by Dulong's formula is $H_2SO_4Aq. = H_2O + SO_2 + O + Aq.$ For 1 per cent. of sulphur the oxygen as $SO_2 + O$ is 1.5 per cent.; 1/8 of 1.5 per cent. is 0.1875 per cent., the amount that the available hydrogen is low. This in calories is 0.001875×34.460 or 64.8. By Dulong's formula the result for 1 per cent. of sulphur as H_2SO_4 is for sulphur 44.8 calories high, for hydrogen 64.8 calories low or a net result 20 calories low as against 10 calories low for sulphur as ferrous sulphate.

The calorific value of sulphur as ferric sulphate does not differ greatly from that as ferrous sulphate. The heat absorption when burned with coal in air is about 2,100 calories per gram of sulphur. In a Mahler calorimeter the heat absorption is about 150 calories per gram of sulphur. The effects upon calculations by Dulong's formula is to cause results too low by about 21 calories for each per cent. of sulphur. The small amount of ferric sulphate usually found in coal renders a more detailed explanation unnecessary. The amount of free sulphuric acid usually found in coal is also too small to have an important effect upon the calorific value, and for practical purposes all of the SO_4 present in coal may be considered as occurring as ferrous sulphate and corrections made on that basis without materially affecting the accuracy of calorific results.[1]

---

[1] Any sulphur present in coal as gypsum, $CaSO_4.2H_2O$, has an effect on the calorific value, not widely different from that of sulphur present as ferrous sulphate. $CaSO_4.2H_2O$, if decomposed to $CaO + SO_2 + O + 2H_2O$, is accompanied by a heat absorption of 3.750 calories per gram of sulphur, but incomplete reduction to this form and the heat of combination of CaO with other constituents of the ash make the actual heat absorption considerably less than this. The heat absorption by the decomposition of ferrous sulphate when burned with coal is likewise modified by the heat of combination of any oxide of iron with other constituents of the ash. This effect is, however, neglected owing to the uncertainty as to the nature and extent of the reaction.

Reduction of Calorific Value of Coal by Oxidation of Pyrites.—The main product of the oxidation of pyrites is ferrous sulphate, the calorific value of which, when burned in air, is —2,140 calories. It has already been shown that corrections involved in the application of Dulong's formula and in the determination of the calorific value in a Mahler calorimeter give results very close to this actual value. In each case, however, the close agreement is a coincidence and not according to any law, but from a practical point of view the close agreement is the important fact.

The negative value of 2,140 calories for sulphur as ferrous sulphate, is not, however, the measure of its total influence on the calorific value of the coal.

One per cent. of sulphur as $FeSO_4.7H_2O$ represents a heat absorption of only 21.4 calories, but 1 per cent. of sulphur so combined represents 8.7 per cent. of $FeSO_4.7H_2O$ present. The exact reactions for oxidation of FeS_2, as has been shown, are uncertain and variable but for illustration we may consider the reaction for the oxidation of pyrites to be

$$FeS_2 + \text{water} + \text{oxygen} =$$

$$FeSO_4.7H_2O + \begin{cases} \text{S as free sulphur or} \\ H_2SO_4Aq \text{ (remaining with coal) or} \\ SO_2 \text{ (escaping as such).} \end{cases}$$

For 2 per cent. of sulphur originally in the coal as FeS_2 there is now present:

(*a*) 1 per cent. of sulphur as $FeSO_4.7H_2O$ + 1 per cent. of free sulphur.

(*b*) 1 per cent. of sulphur as $FeSO_4.7H_2O$ + 1 percent. of S as H_2SO_4Aq.

(*c*) 1 per cent. of sulphur as $FeSO_4.7H_2O$ + 0 per cent. of SO_2 (having escaped).

Two per cent. of sulphur as pyrites has a calorific value of 58.3 calories.

(*a*) 1 per cent. of sulphur as $FeSO_4.7H_2O$ + 1 per cent. of free sulphur has a calorific value of —21.6 calories + 22.2 calories = 0.6 calorie.

(*b*) 1 per cent. of sulphur as $FeSO_4.7H_2O$ + 1 per cent. of sulphur as H_2SO_4Aq. has a calorific value of —21.6 calories —22.3 calories = —43.9 calories.

(*c*) 1 per cent. of sulphur as $FeSO_4.7H_2O$ + 0 per cent. of sulphur as SO_2 has a calorific value of —21.6 calories.

From (*a*) the loss in calorific value is the difference between 58.3 calories and 0.6 calorie or 57.7 calories. From (*b*) the loss is the difference between 58.3 calories and —43.9 calories or 101.2 calories. From (*c*) the loss is the difference between 58.3 calories and —21.6 calories or 79.9 calories. At the same time the weight of the original sample has increased by the difference between the weight of FeS_2 origially present and the weight of the oxidation products now present. In (*a*), where the products are $FeSO_4.7H_2O + S$ this difference is 6 per cent. of the weight of the original sample. In (*b*), where the products are $FeSO_4.7H_2O + H_2SO_4Aq.$, this difference is 11 per cent.[1] In (*c*), where the product present in the coal is $FeSO_4.7H_2O$, this difference is 5 per cent.

To illustrate the effect upon the calorific value, let the calorific value of the original sample be considered to be 8,000 calories. The calorific value per unit of sample after oxidation is for:

$$(a)\ \frac{100}{106} \text{ of } (8{,}000 - 58) = 7{,}493 \text{ calories.}$$

$$(b)\ \frac{100}{111} \text{ of } (8{,}000 - 101) = 7{,}117 \text{ ''}$$

$$(c)\ \frac{100}{105} \text{ of } (8{,}000 - 80) = 7{,}543 \text{ ''}$$

A decrease in calorific value of 457 to 883 calories for each per cent. of sulphur present in the form of ferrous sulphate as an oxidation product from pyrites. Whatever be the particular reaction,

---

[1] The increase of 11 per cent. for $FeSO_4.7H_2O + H_2SO_4Aq$ is obtained by arbitrarily assuming H_2SO_4Aq to consist of equal parts of acid and water. The amount of water that H_2SO_4 takes up is variable and the assumption of a definite amount taken up is merely to obtain a value for the increase in weight. The assumption of 100 per cent. is under ordinary atmospheric conditions, probably not far from the amount taken up. A sample of concentrated sulphuric acid exposed on a watch-glass to the air of a cool and rather dry basement room at the end of twenty hours had taken up 65 per cent. of its weight of water, at the end of forty-eight hours 87 per cent. After forty-eight hours the amount of water retained by the acid varied from day to day, being dependent upon the humidity of the air. At the end of ninety-six hours the amount of water held by the acid was 90 per cent., at the end of three hundred hours 78 per cent., and at the end of five hundred hours 85 per cent. The average amount for the twenty-one days that the experiment was carried on was about 85 per cent. In damp weather the amount of water that is taken up by sulphuric acid is much more than 100 per cent., several hundred per cent. being a conservative estimate. The increase in weight for reaction (*b*) on the assumption of 200 per cent. water taken up by H_2SO_4 is 14 per cent.; with 300 per cent. water taken up the increase is 17 per cent. These values correspond respectively to a decrease in the calorific value of 1,079 and 1,249 calories.

these values all show an important loss in the calorific value of the coal.

This loss in the calorific value and increase in weight of coal due to oxidation of pyrites is of both technical and commercial importance. For the analyst, it follows that samples of coal, containing considerable amounts of pyrites, should be analyzed as promptly as possible, if the results obtained are to be representative of the unweathered coal. For the consumer, it means that by purchasing weathered coal, he is made to assume the burden of a double loss, namely, the receiving of fewer calories of heat and the paying for more tons of coal.

The foregoing conclusions as to the effects of the oxidation of pyrites upon the calorific value of coal have been arrived at by considering the coal upon an air-dry basis, and without regard to effects due to other oxidation changes. Other oxidation changes and especially variations in the amount of moisture present may also have an important effect upon the calorific value. This is especially true of coals high in moisture and somewhat lignitic in character. A coal containing 10 to 20 per cent. of moisture may lose a considerable portion of this moisture within a few days or weeks after being mined, especially in dry weather. On the other hand, in wet or rainy weather, coal containing considerable slack may take up and mechanically hold 10 to 15 per cent. of its weight of water. The importance of the moisture variations in coal is well known to analysts and precautions against moisture changes and losses do not require elaboration here.

With coals high in both moisture and pyrites the problem as to when the consumer receives the best value for his money is complicated and somewhat indeterminate. The loss of moisture in a freshly mined coal, as already stated, is often very considerable, the rate and amount of loss being greatest in dry weather; however, this moisture change rapidly becomes less and less and within a few weeks is probably largely dependent upon variations in the temperature and humidity of the atmosphere. The oxidation of the pyrites, while gradual, is also influenced by atmospheric conditions. The rate of oxidation of the pyrites is, however, largely dependent upon several other conditions: First, the way in which it occurs, whether in relatively large masses which afford but little surface for oxidation, or in small particles which, having a relatively large surface, favor rapid oxidation. Second whether it is scattered irregularly through the coal or whether it occurs largely along regular seams or partings; this latter condition is particularly favorable to rapid oxidation, the effect of the oxidation of an exposed portion of pyrites being to open up the coal along the seam and thereby expose fresh pyrites to oxidizing influences. Third, the condition and nature of the coal with which the pyrites occurs. Coal which breaks up badly during mining and handling, exposes a greater per cent. of pyrites to oxidizing influences, than coal which mines largely in blocks and lumps. The texture and porosity of the coal and the extent to which it protects included pyrites from atmospheric influences is also an important factor.

Upon an unaltered sample of coal high in moisture and pyrites, the effects of the moisture changes and the oxidation of pyrites are, under ordinary conditions, during the first few days or weeks, a considerable decrease in weight due to loss in moisture, and a probably much smaller increase in weight, accompanied by a slight loss in calorific value due to oxidation of a portion of the pyrites. The net result is, in this case, an increase in calorific value per unit of coal. After the first few days or weeks the moisture changes are variable and the calorific value per unit of coal is increased or diminished according to whether moisture is given off or taken up, while the effect of the continual oxidation of the pyrites is to continually increase the weight of the coal and to lessen its calorific value.

ORGANIC SULPHUR.

Wormley[1] has shown that considerable sulphur occurs in Ohio coals in some other form than in combination with iron. In order to determine the amounts of this so-called organic sulphur, and to determine whether the sulphur in Ohio coals, not combined with iron, is actually organic or whether it occurs in combination with some other bases, analyses were made of the ash of six coals having the following composition:

Sample No.	Moisture.	Volatile combustible matter.	Fixed carbon.	Ash.	Sulphur.	Carbon.	Hydrogen.	Nitrogen.	Oxygen.
27	5.05	39.75	47.43	7.77	4.80	68.07	5.37	1.18	12.81
38	5.32	40.93	47.45	6.30	4.22	69.29	5.50	1.24	13.45
48	4.44	40.71	50.40	4.45	3.54	72.65	5.53	1.35	12.48
50	4.72	40.30	49.51	5.47	4.05	71.08	5.53	1.32	12.55
69	3.18	43.56	46.33	6.93	4.12	71.13	5.50	1.28	11.04
38*a*	...	...	..	2.85	2.72	...	...	...	...

---

[1] Report of the Ohio Geological Survey, 1870, p. 412.

No. 38*a* was obtained by taking 100 grams of No. 38 and separating it by sifting into two portions: 57 grams between 20 and 40 mesh, and 43 grams finer than 40 mesh. The 57-gram portion was then washed on a $CaCl_2$ solution (sp. gr. 1.35) and yielded 45 grams of coal and 12 grams of slate and pyrites. Sample 38*a* is the 45 grams of washed coal.

The iron in the coal and the distribution of the sulphur are as follows:

Sample No.	Total iron.	Iron as $FeSO_4$ and $Fe_2(SO_4)_3$.	Total sulphur.	Sulphur as soluble sulphate.	Free sulphur.	Sulphur present as FeS_2.	Sulphur not combined with iron and not present as free sulphur.
27	2.80	0.44	4.80	0.30	0.08	2.70	1.72
38	1.90	0.35	4.22	0.26	0.09	1.77	2.10
48	1.93	0.44	3.54	0.33	0.08	1.70	1.43
50	2.27	0.62	4.05	0.42	0.13	1.89	1.61
69	1.70	0.12	4.12	0.09	0.03	1.81	2.19
38*a*	0.62	...	2.72	...	...	0.71	2.01

In obtaining the values given for sulphur as pyrites, the iron present as ferrous and ferric sulphate, was subtracted from the total iron and the remainder calculated to FeS_2. If any of the iron occurs in other forms, the values for sulphur as pyrites are accordingly too high. The differences between the total sulphur and that present as free sulphur, as sulphate and as pyrites, are given in the last column. If the values for sulphur as pyrites are too high, these values are correspondingly too low. The errors are, however, probably quite small.

The sulphur in No. 38*a*, 2.01 per cent. not there in combination with iron, shows that sulphur present in the sample in other forms than as pyrites or as soluble sulphate, can not be removed by washing, indicating either fine dissemination or existence in a compound having a specific gravity corresponding closely to that of the coal.

That no considerable quantities of sulphides or sulphates of the heavy metals or alkaline earths can be present in the coal is shown by inspection of the ashes, which have the following composition:

Sample No.	Total ash.	SiO_2 by HF	Insoluble residue from SiO_2.	Fe_2O_3.	Al_2O_3.	CaO.	MgO.	Difference.
27...	7.77	1.85	0.06	4.00	1.36	0.12	0.06	0.32
38...	6.30	1.68	0.07	2.71	1.50	0.12	0.05	0.17
48...	4.45	0.62	0.04	2.76	0 69	0.13	0.05	0.16
50...	5.47	0.78	0.05	3.24	0.77	0.12	0.06	0.45
69...	6.93	2.03	0.07	2.43	1.65	0.32	0.06	0.37
38*a* .	2.85	0.82	0.00	0.89	0.81	0.18	0.03	0.12

The only mineral compounds of sulphur and alumina, insoluble in water which probably may be present in coal, are those represented by alunite, $K_2O.3Al_2O_3.4SO_3.6H_2O$. Two per cent. of sulphur as alunite would, however, require the presence of 1.5 per cent. potassium oxide and 5 per cent. of aluminum trioxide. If the column of results marked "difference" be considered as all potassium oxide, inspection of the values for aluminum trioxide and potassium oxide shows that in none of the samples can much of the sulphur exist as alunite. That it does exist in combination with carbon or with carbon and hydrogen, seems by process of excluding its existence in other forms to be conclusively shown.

The best known sulphur carbon compound, carbon disulphide, is endothermic and it seems probable that the sulphur carbon compounds present in coal may also have a higher calorific value than that of the elementary constituents. Carbon disulphide has a heat of formation of —28,700 calories. Reducing to a basis of 1 gram of sulphur its calorific value when burned is 448 calories greater than the combustion of equivalent amounts of free carbon and sulphur or 4.5 calories for each per cent. of sulphur. The nature of the combination of carbon and sulphur in coal has not been determined and that it is endothermic is merely assumed as probable, and not based upon any experimental tests.

The amount of organic sulphur occurring in Ohio coals makes the question of its probable endothermic combination of some importance and the writer hopes to be able some time to conduct some experimental investigations along this line.

Conclusions, Summary of the Effects of the Application of Dulong's Formula for Sulphur in Different Forms.—

(1) For sulphur present as ferrous sulphate, it gives results too low by 10 calories for each per cent. of sulphur so combined.

(2) For sulphur as pyrites it gives, on uncorrected ultimate analyses, results too high by about 9.6 calories for each per cent. of sulphur present as pyrites. On corrected ultimates[1] the results are too low by 6.6 calories.

(3) For sulphur as organic sulphur it gives results probably too low by about 4.5 calories for each per cent. of sulphur existing in this form.

The results for sulphur by Dulong's formula on the average of the five samples of coal are for:

	Per cent.	Uncorrected ultimate.	Corrected ultimate.
Sulphate	0.32	3 calories low.	3 calories low.
Pyrites	1.97	19 '' high.	13 '' ''
Organic sulphur ...	1.79	8 '' low.	8 '' ''
Free sulphur.......	0.08	..	..
Total sulphur.....	4.16	8 '' high.	24 '' ''

For these particular samples the results are, from the uncorrected ultimate, 2 calories high for each per cent. of sulphur present, and from the corrected ultimate, 6 calories low for each per cent. of sulphur present, from which it appears that Dulong's formula unmodified for sulphur applied to an uncorrected ultimate gives, in so far as it relates to sulphur, very satisfactory results.

SOME CALORIFIC VALUES OBTAINED BY APPLYING DULONG'S FORMULA.

To show the degree of accuracy obtainable by Dulong's formula, by permission of the Ohio Geological Survey, the average composition and calorific value of eighty-nine samples of Ohio coals are given as follows:[2]

COMPOSITION.

	No. samples tested.	Moisture.	Volatile combustible matter.	Fixed carbon.	Ash.	Sulphur.	Hydrogen.	Carbon.	Nitrogen.	Oxygen.
Limestone coal	17	5.33	39.07	44.95	10.76	4.33	5.30	65.04	1.25	13.32
No. 5 coal	3	6.21	37.34	48.10	8.35	4.03	5.37	67.07	1.21	13.97
No. 6 coal	57	5.46	38.30	48.90	7.34	3.38	5.43	68.96	1.26	13.63
No. 7 coal	4	5.28	39.81	47.13	7.78	3.80	5.47	68.38	1.25	13.32
Waterloo coal.	8	7.97	32.23	49.48	10.31	1.62	5.18	65.32	1.28	16.29

---

[1] Corrected ultimate analysis refers to correction for oxygen in the ash. See this Journal, **26**, 567.

[2] For complete analyses and description of the samples see Report of the Ohio Geological Survey, 1904, now in press.

CALORIFIC VALUES.

	No. samples tested.	Determined in a Mahler calorimeter.	Calculated by Dulong's formula.	Calculated by Dulong's formula, but using 8,140 as the value of carbon.
		Calories.	Calories.	Calories.
Limestone coal	17	6640	6609	6648
No. 5 coal	3	6820	6758	6798
No. 6 coal	57	6970	6931	6971
No. 7 coal	4	6968	6919	6959
Waterloo coal	8	6504	6398	6437
Average		6780	6723	6763

Dulong's formula gives results lower than the value as determined in the Mahler calorimeter, especially on the samples highest in moisture and oxygen, the Waterloo coal. By substituting Berthollet's value for amorphous carbon 8,140, the application of the formula gives a very close agreement with the calorimeter results on all of the samples except the Waterloo coal, the average of the results on this being still 1 per cent. low. On the No. 6 coal, which represents the average of 57 samples, the agreement of the calculated and determined value is almost perfect, the value being 6,970 calories as determined and 6,971 calories as calculated.

For some of the Ohio coals, at least, this modification of Dulong's formula gives a calculated calorific value agreeing very closely with the value actually determined, the average difference being within the limits of error of the individual determinations.

The writer again wishes to acknowledge his indebtedness to Professor N. W. Lord for valuable advice and suggestions.

METALLURGICAL LABORATORY,
OHIO STATE UNIVERSITY,
COLUMBUS, O.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 97].

A NEW SEPARATION OF THORIUM FROM CERIUM, LANTHANUM AND DIDYMIUM BY METANITROBENZOIC ACID.[1]

BY ARTHUR C. NEISH.

Received May 2, 1904.

THE work herein described was undertaken with the object of finding a shorter and more satisfactory method for the determination of thorium in monazite sands.

---

[1] Read at the meeting of the New York Section of the American Chemical Society, May 6, 1904.