

Taking the results as a whole and in spite of the fact that the quantity of material in each case is small, and the liability to error, consequently great, the average results show a surprising constancy and justify the conclusion that in the analysis of clay by the method outlined above, the silica so separated is contaminated to some degree by the main constituents of the clay. The amount of contamination by substances other than Fe_2O_3 and Al_2O_3 is however, except in extreme cases, so small that it may be neglected unless extreme accuracy is required.

W. F. Hillebrand¹ states as follows: "Quite as rarely (as barium) is calcium or magnesium ever a component of the residue, if the decomposition of the rock powder was complete at the outset." Since the results obtained differ almost entirely from this statement, it was thought well to consider some of the possibilities of error in the experiment. The main ones may be summed up as follows: (1) insufficient washing of the separated silica; (2) incomplete decomposition of the clay at the outset; (3) evaporation in porcelain may have induced contamination; (4) different action of clay and rock powder in fusion or subsequent treatment. The first two may be dismissed as following in the main the general usage in silicate analysis. The third possibility was made the subject of a second series of experiments. A sample of ordinary clay was taken and prepared very carefully. After fusion in the regular way duplicate samples were evaporated in porcelain (Royal Berlin) and in platinum dishes, the silica volatilized and the residues analyzed as before. The results as yet are not sufficiently definite to throw any light on the point in question.

PULLMAN, WASH.

THE CONSTANTS AND VARIABLES OF THE PARR CALORIMETER.

By S. W. PARR.

Received July 5, 1907.

The calorimeter using sodium peroxide as a medium of combustion was first described in the October number of this Journal², 1900.

The chief element in the process as outlined at that time was the establishment of the ratio between the true heat of combustion of the fuel used and the total heat of the reaction developed by the process. For example, if the total indicated heat of a hydrocarbon, burning in a closed chamber by means of sodium peroxide were found to be 10,000 calories, then the true heat of combustion would be 7300 calories, and the other 2700 units would represent the heat of combination of the carbon dioxide and water with the chemical employed. The constant, therefore, representing the part of the reaction which was to be credited to combustion, was 73 per cent. This factor was determined empirically

¹ Bull., 305, U. S. Geol. Survey, 80.

² This Journal, 22, 646.

by comparison with results on the same material under the same conditions as obtained by means of the Mahler-Atwater apparatus. Moreover, as the ratio seemed to hold good for semibituminous coals as well as for coals of the highly bituminous type, it was assumed that this ratio was the correct one whether the excess of heat was due to the absorption of carbon dioxide or of water, and that fuels varying in the relative amounts of hydrogen and carbon were adapted for use by this process. Here, again, the basis for the conclusion was empirical.

In subsequent experiments, where a wider range of fuels was available, more especially such coals as were common to the continent of Europe, a lack as to the completeness of combustion was noted, and it was sought by means of the addition of other chemicals to increase the oxidizing effect of the sodium peroxide in order to insure a uniform and complete reaction. The materials tested were of two types: first, other organic substances of constant composition, such as sugar, tartaric acid, etc., which were added on the principle that kindling wood added to a fire helps to consume the more refractory material, and second, superoxidized compounds like barium peroxide, niter, potassium persulphate, etc., which were added to test the effect of substances more ready to part with their oxygen than does the sodium peroxide, and perhaps establish a condition where nascent oxygen might be present. Both of these ideas seemed to have some proper basis, and application was made of the same by proposing a mixture of tartaric acid one part, and potassium persulphate two parts, as an intensifier or accelerator of combustion.

On the basis of this second series of experiments upon European coals which were carried on in Dr. Lunge's laboratory at Zürich, a number of articles have appeared more or less critical of the process. Dr. Lunge, the first¹ and the last² to contribute to this discussion, has defended it as being well adapted to technical work. Langbein³ bases his criticism on the results obtained by Lunge and Offerhaus⁴ on the theory that variable temperatures gave varying degrees of completeness of combustion, and hence an inherent unreliability would attach to the values.

Further experiments by Lunge and Grossman⁵ and by Constam and Rougeot⁶ were mainly devoted to the influence of varying qualities of the sodium peroxide and to the fineness of division of that material.

While the specific answer to these criticisms is to be found in the presentation of facts and the discussion which follows, it may be said as a general proposition, first, that any results based upon the use of sodium

¹ *Z. angew. Chem.*, **14**, 800 (1901).

² *Ibid.*, **19**, 1963 (1906).

³ *Ibid.*, **16**, 1073.

⁴ *Ibid.*, **16**, 911.

⁵ *Ibid.*, **18**, 1250.

⁶ *Ibid.*, **19**, 1796.

peroxide which has been sifted or ground or otherwise handled in any manner to permit of the absorption of moisture from the atmosphere, are open to question. The slow absorption of moisture by sodium peroxide results in the formation of $\text{Na}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ ¹, and this compound at the higher temperature of fusion forms sodium hydroxide with evolution of heat.

Second, the adverse conclusions are all based upon combustions in which an indefinite amount of unburned carbon remained from the reaction. The extra chemicals used to accentuate the oxidizing effect of the sodium peroxide were tartaric acid and potassium persulphate, either separately or in conjunction. The fact that unburned carbon remained in small amounts from the use of this material, and further that the variables under discussion ranged within narrow limits, approximately from one to three per cent., would seem to indicate that the first essential in any critical study of the process would be to first eliminate or account for the unburned portion of the charge.

Under the first proposition, that of the effect of absorbed moisture, an easy verification of the fact of an increase of temperature is shown as follows: Ten g. of sodium peroxide were poured upon a watch glass and exposed to the air of the laboratory for about one hour. The amount of moisture taken up as shown by increase of weight was approximately 0.5 g. This material was then employed in a combustion under standard conditions, so that comparison could be made with the rise in temperature where the sodium peroxide had not been exposed to moist air. The following results were obtained:

TABLE I.
EFFECT OF ABSORBED MOISTURE.

Sodium Peroxide used.	Combustible.	Total rise in Temperature.	Average rise.
10 g. Na_2O_2 + 0.45 gram H_2O	0.5 g. Benzoic acid.	2.377	} 2.374
10 g. Na_2O_2 + 0.44 gram H_2O	0.5 g. Benzoic acid.	2.370	
10 g. Na_2O_2 without H_2O	Average of 8 tests.	2.180	2.180

Excess of temperature due to absorbed H_2O , 0.5 g. 0.194

Concerning the higher values resulting from the use of sifted material, it was suspected that either in the process of manufacture or in sifting the peroxide, the finer portions would absorb relatively more than the coarse, and it was a direct result of this behavior of the finer material that the tests recorded in the above table were made. Further experience in this same line demonstrated the fact that a certain procedure was necessary in the manufacture and handling of the sodium peroxide. By arrangement, therefore, with the manufacturers, a special burning of sodium is made to produce a peroxide which shall be as nearly as possible free from absorption of both water and carbon dioxide. This product is hermetically sealed in tins of such a size that the entire contents of a tin may be emptied at once into the glass container from which it is to

¹ J. Chem. Soc., 14, 267.

be used. By a process of manufacture, therefore, conducted with special care to accomplish a prescribed end, and by bringing this material to the laboratory in unbroken packages, it has been possible to readily provide a product of remarkable uniformity as has been shown by a continuous series of tests, extending through the last four years, since such material was available.

One thing further should be noted in this connection. A very important feature of the case is the kind of retainer in which the user keeps his current supply of sodium peroxide and from which he measures his portions for the tests. The avidity of the material for moisture requires a container with perfect seal. The best obtainable ground glass stoppered bottles were found altogether useless for this purpose. Various types of jars were tried, but none have served the purpose in a satisfactory manner, except one having a lever clamp known as the "lightning" or "Putnam" jar.

In this connection a comparison was made between the material as above prepared and some peroxide prepared without such definite specification, bearing the label of Dr. Heinr, Koenig & Company, Leipzig, Germany.

TABLE 2.

COMPARISON OF AMERICAN AND GERMAN SODIUM PEROXIDE.

Material	Rise in temperature
Na ₂ O ₂ from Standard Calorimeter Co.	Average of 8 tests.....2.180
Na ₂ O ₂ from Koenig & Co., Germany.	Same.....2.223
	2.213 Average 2.218
Higher reading of German peroxide	0.038°

For variable or unknown sodium peroxide there is indicated, therefore, the necessity of standardizing the material in order to determine its quality and effect when used in combustions. This, of course, necessitates a definiteness in all the other conditions and the elimination of any variable which might arise from incomplete combustion, etc. This, as will be shown in what follows, is a comparatively simple proposition and brings us to a discussion of the second topic, *viz.* :

The Use of Intensifiers for Producing Completeness of Combustion.

Reference has been made above to the use of additional chemicals to produce a more complete combustion than could take place with sodium peroxide alone. It must be apparent that a complete combustion of material is necessary before any exact study of the process could be undertaken. While tartaric acid and potassium persulphate made the best mixture of any substance studied up to that time, further improvement was possible and upon this part of the work much time and experiment has been spent.

Accelerators.—The accelerators employed have covered a very wide range of material. They naturally fall into certain groups, as, for ex-

ample, those producing additional heat by reason of their own fuel value, such as organic acids, sugar, powdered magnesium, etc. In this class also might be placed ammonium salts, for in these compounds the hydrogen burns, liberating nitrogen. Ammonium chloride and ammonium phosphate were quite extensively tried. Among these also may be mentioned ammonium persulphate which, in addition to furnishing heat from its own reactions with sodium peroxide, liberated also considerable oxygen. A number of other substances furnishing practically nothing but easily accessible oxygen were niter, potassium chlorate, peroxides of barium, calcium, zinc, lead, etc. There was also tried sodium perborate, but as the same effect could be accomplished by means of boric acid, that material was used instead.

It is needless to go into the details of these very numerous and extended tests. In general, those compounds which contain in their structure or develop from the reaction any considerable amount of water are to be discarded, because the benefit derived is small, while the pressure developed from the liberated oxygen may make, with sufficiently high temperature, too great a strain upon the bomb.

Mixtures containing boric acid make a very satisfactory fusion with bituminous coals, but not with anthracites. Moreover, the avidity of the finely divided boric acid for moisture makes it variable, as to its own heat value, requiring standardization for each new lot of material.

The accelerators finally found to be of greatest efficiency were (a) a mixture of potassium and ammonium persulphates in the ratio of two to one, and (b) potassium chlorate alone. By use of these substances a uniformly complete combustion is attainable. This statement should be qualified only to this extent. Sugar-carbon, anthracite and similarly difficultly combustible substances should be ground to pass a 200-mesh sieve, or, what is quite as convenient, filter off on a Gooch crucible the unburned portion, weigh and deduct the same from the amount of the charge. Account can thus be made of particles that adhere to the surface of the chamber and about the terminals in the upper part of the bomb above the zone of fusion. Such material, while extremely minute in amount, should be taken account of in any investigation looking to the establishment of factors or evidence of accuracy of the process.

With these conditions established as a preliminary requisite, we may take up, first, the verification of the most important constant involved in the process, *viz.* : the *Ratio of 73 per cent.* as representing the part the heat of combustion is of the total heat evolved.

The Reaction Constant of 73 Per Cent.

The first essential in studying the adaptability of sodium peroxide as a medium of combustion is to determine the behavior of both carbon and hydrogen with respect to the heat evolved in combining their combustion products with the chemical employed. That is, if carbon dioxide in

uniting with sodium peroxide has a ratio of heat to the total heat evolved which is widely different from the ratio found where water is the uniting substance, then the process as a method for measuring heat values is without application except upon substances of known or constant composition with respect to their carbon and hydrogen content. On the other hand, if these respective heat ratios are identical or vary within sufficiently narrow limits, then all hydrocarbons, however, widely varying in their amounts of carbon and hydrogen, may indicate their heat of combustion by applying this constant to the total heat indicated in the reaction.

It may be well, first, to present some of the earlier data obtained in attempting to find these two ratios. The plan followed was to first determine the factor for carbon alone, by use of pure sugar-carbon, and for the hydrogen factor, make use of a pure hydrocarbon, as naphthalene, in which the carbon values having been determined, the factor for hydrogen could be directly deduced.

In some earlier experiments conducted in 1902 eight combustions of pure sugar-carbon gave an average for the total indicated heat of 11021 calories. If we accept 8080 as the correct factor for carbon, we have a ratio $\frac{8080}{11021}$ or expressed in per cent. of 73.3. The carbon employed was carefully prepared by finally heating in a current of chlorine gas with subsequent washing in alkaline and acid water, with final washing with pure water.

For the hydrogen factor, pure naphthalene was prepared by repeated crystallizations from alcohol. It was found impossible to burn this material satisfactorily without an additional chemical. For this, the mixture of ammonium and potassium persulphate was used, one of ammonium persulphate to two of potassium persulphate. It was necessary first to standardize the persulphates used in order to determine the heat correction that should be applied to these chemicals. This was accomplished by making a series of combustions with a given quantity of naphthalene (0.2 g.) and varying the persulphate as in the following table. The total rise in temperature is given in degrees centigrade.

TABLE 3.—STANDARDIZATION OF PERSULPHATE ACCELERATOR.

Chemical constants	1 gram persulphate	1.5 grams persulphate	2 grams persulphate	2.5 grams persulphate
		Total Rise in Temperature	Temperature	
Approximately	1.634	1.827	2.022	2.214
10 grams	1.635	1.828	2.022	2.220
(measured)	1.636	1.829	2.024	2.222
of Na ₂ O ₂ and	1.636	1.830	2.025	2.216
0.2 grams		1.837	2.028	2.229
pure naphthal-		1.838	2.030	2.231
ene, C ₁₀ H ₈ .		1.839	2.030	2.233
			2.032	2.241
Average	1.635	1.832	2.026	2.225
Difference		0.197	0.194	0.199
Average of Differences		0.197		

It would seem from the foregoing table that the proper correction for the persulphate mixture would be 0.197° per 0.5 g. By applying, therefore, this correction in the same series of readings, we have the indicated heat for naphthalene. The true combustion factor for naph-

TABLE 4.
COMBUSTION CONSTANT FOR NAPHTHALENE.

[illegible]

thalene has been taken as 9692, and the ratio is derived by dividing this number by the total indicated heat for the naphthalene. The results are serially arranged in order to show at a glance the highest and lowest results obtained in the various tests.

We have now two sets of results, one for carbon alone, showing an average constant of 73. per cent. for the heat of combustion and the other for naphthalene (composed of 93.75 per cent. carbon and 6.25 per cent. of hydrogen), showing a constant of 73.2 per cent. for the ratio between the actual heat of combustion and the indicated heat of the reaction.

The results of Table 4 were obtained in 1905 by Mr. C. H. McClure, and much credit is due him for the painstaking care with which he carried out that work. A room under temperature control was used and corrections for radiation were applied in all of the tests. There would seem to be from this data, therefore, a close agreement between the heat developed from absorption of carbon dioxide and of water.

To the above results should be added others obtained during the current year by Mr. W. F. Wheeler.

This additional series is given for the reason that in connection with the coal work for the Illinois State Geological Survey a careful examination of methods, appliances and material used in that work was made for the elimination of errors. Results obtained, therefore, in comparison with the Mahler-Atwater apparatus would have still greater value than any preceding.

It may be worth while to refer briefly to some of the points covered in attempting to arrive at correct standards. The oxygen bomb used was of the Atwater type with platinum lining. The water equivalent was sought by burning pure naphthalene. A new lot of this material with Merck's label, highest standard of purity, etc., was obtained. The water equivalent indicated by burning the material was higher than the factor previously established for the calorimeter. An examination of the naphthalene showed that it contained 0.16 per cent. of sulphur. A supply of Kahlbaum's naphthalene was then tested, and it was found to contain 0.13 per cent. of sulphur. After an extended series of crystallizations from alcohol, this difficulty was remedied. But the experience is worth noting, because of the statement occasionally met with recommending naphthalene for this purpose, because of the ease with which this material may be obtained in the pure state. Perhaps a more difficult problem is to decide upon an acceptable factor for naphthalene. Atwater¹ uses a value of 9628 calories. Prof Lord² uses 9692. Landolt and Bornstein (1905) gives 9701. Here is a difference of 74 calories in 9600 or over

¹ This Journal 25, 693.

² Report of Coal Testing Plant, U. S. Geol. Sur. Prof., Paper No. 48, 180.

0.70 per cent., sufficient to make a difference of approximately 20 cc. in the water equivalent of the apparatus. A greater variation exists in the values for sugar. The values for benzoic acid are less variable. By elaborating a series of tests with these three substances a water value was established of 445, as against an earlier value of 420, using for the smaller factor, however, a value of 9628 calories for naphthalene. The water equivalent of the other form of calorimeter was obtained first by calculation; all parts being of brass, having a constant composition of zinc, copper and two per cent. of lead, the specific heat of the alloy was taken as 0.092. The total weight of metal being 1470 grams, the calculated equivalent of the metal would be 135 cc. A second method was employed, using the electrical process of Magie-Pfaundler¹. Three results by this method gave values of 134.8, 135.4, and 135.2, with an average of 135.1. The accepted factor, therefore, was taken as 135, or a total water equivalent in operation of 2135 grams.

Concerning the preparation of pure carbon, crystals of rock sugar were used. As a means for fine grinding, a sample of 100 grams of the carbon was placed in an Abbé ball mill having a jar of Royal Berlin porcelain. After two hours running, the pulverized material was found to have an ash content of 3.16 per cent, indicating a serious wearing of the porcelain. A different method of grinding, was of course, necessary. It should, moreover, be noted that the avidity of sugar carbon for moisture makes it necessary that this constituent be removed or taken account of in standardization tests.

On account of the possible variables connected with sugar-carbon, it was deemed simpler to omit the treatment with chlorine gas and depend for a comparison upon the value as indicated by the Atwater bomb. Even if pure carbon were assumed to be obtained, it would still be an open question whether we should accept for comparison the calorific value by Thomsen of 8080 or that of Berthelot of 8137.5. In the table following, the accelerator employed in the combustion was chlorate of potash instead of the persulphate mixture. This has the advantage of being more easily prepared, more constant as to composition, non-hygroscopic and non-deteriorating. Moreover, it has even a higher oxidizing power than the persulphate mixture with a lower correction for its heat of decomposition, thus lessening the possible error in correcting for its own heat equivalent. Contrary to what might be expected, no oxygen is set free in its use, hence it has greater safety so far as danger of explosion is concerned than any other accelerator used. This will be more fully explained under the discussion of the heat equivalent of potassium chlorate. The correction factor employed for 0.5 g. of this accele-

¹ Phys. Rev., 1902.

rator was 0.040° and for 1. g. 0.108° . The obtaining of these values will also be taken up later in the discussion.

TABLE 5.

COMBUSTION OF SUGAR-CARBON, USING 10 GRAMS Na_2O_2 AND 0.5 GRAM KClO_3 .

Carbon, less Moisture & Ash	Un- burned carbon	Car- bon burned	Total Rise, Cor- rected for Radi- ation	Correction for Chlor- ate, Wire & Moisture $0.040 +$ $0.008 +$ 0.006	Cor- rected Rise	Total Heat per Kilo $\frac{\text{tx}2135}{\text{C. burned}}$	Ratio of Bomb value to total heat $\frac{8218}{\text{total ht.}}$
0.4856	0.0201	0.4655	2.515	0.054	2.461	11,280	72.8
0.4856	0.0159	0.4637	2.541	0.054	2.487	11,310	72.65
0.4856	0.0150	0.4706	2.538	0.054	2.484	11,265	72.95
0.4856	0.0138	0.4718	2.550	0.054	2.496	11,290	72.75
Average						11,286	72.8

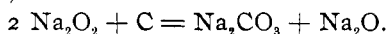
Under corresponding conditions by the same operator combustions of naphthalene were made. Potassium chlorate was used as the accelerator. Relatively more of the naphthalene could be burned than with the persulphate mixture, 0.3 g. giving a good combustion. The following results are tabulated with reference to the ratio of the true heat of combustion, to the total heat indicated for this material.

TABLE 6.

COMBUSTION OF NAPHTHALENE, USING 10 GRAMS Na_2O_2 AND ONE GRAM KClO_3 .

Naph- thalene used	Chlor- ate used	Total Rise Correct- ed for Radi- ation	Correc- tion for Chlor- ate and Wire $0.108 + 0.008$	Cor- rected Rise	Total Heat per Kilo: $\frac{\text{tx}2135}{\text{wt.}}$	Ratio of Naphthalene to total heat: $\frac{9692}{\text{total heat}}$
0.3	1.0	1.988	0.116	1.872	13,320	72.70 per cent.
0.3	1.0	1.986	0.116	1.870	13,310	72.80
0.3	1.0	1.987	0.116	1.871	13,315	72.75
0.3	1.0	1.967	0.116	1.851	13,160	73.50
0.3	1.0	1.970	0.116	1.854	13,190	73.40
0.3	1.0	1.972	0.116	1.866	13,220	73.30
Average						13,253 73.1 per cent.

It would seem from all the above results that empirically, at least, the ratio of the heat of absorption for carbon dioxide is the same as for water, that is, the water which forms as a result of the reaction. Reference has been made above to the empirical nature of this factor. This feature has also been made the basis for some of the criticisms concerning the process. At the time of developing the earlier results no factor was available for the heat of composition of sodium peroxide. A factor is now given by De Forcrand¹ of 119.8 per g. molecule. It is of interest, therefore, to calculate these two ratios, using the above factor. The reaction with carbon is,



From this we have, expressing the final factor in kilo-calories:—

¹ Compt. rend., 128, 1449.

$$\frac{(100.3 + 272.6) - 2(119.8)}{12} = 11.108.$$

The theoretical factor, therefore, for the total heat evolved in the reaction is 11.108 calories per kilo. The ratio of 8080, the combustion factor used for carbon to this value, would give a constant of 72.74 per cent.

Calculating in a similar manner for hydrogen, we would have



From this reaction we would have slightly varying results depending upon the factors employed. Using Thomsen's value of 101.9 for NaOH we would have

$$\frac{4(101.9) - (119.8 + 100.3)}{4} = 46.875.$$

Developing the ratio with 34460 as the factor for hydrogen, we have $\frac{34460}{46.875} = 73.5$. If instead of Thomsen's factor we use Berthelot's for NaOH, of 102.7, we shall have

$$\frac{4(102.7) - (119.8 + 100.3)}{4} = 47.675$$

and this referred to the hydrogen factor of 34460, gives a percentage for the latter 72.3.

It is no part of the purpose of the present paper to settle points of difference between Berthelot and Thomsen. If we may venture to average the two results, however, we would have 72.9 as the percentage factor for hydrogen. The experimental data, it may be noted, is not more widely at variance than the two authorities above quoted.

Benzoic Acid.—In all of the experimental work, it has been evident that a standard substance was very desirable which would give good fusions and serve as a basis of comparison. Naphthalene has some disadvantages, chiefly because only a small amount may be burned satisfactorily, and small errors are multiplied. Benzoic acid has many points of advantage, but a question arises as to how we shall account for the heat of the water formed from the oxygen of the benzoic acid when this water unites with the sodium peroxide. This heat, of course, can not be credited to combustion in the ordinary sense and hence must be corrected for in the temperature readings.¹ A correction factor of 0.097° is

¹ From tables 4 and 6 we may develop the expression $\frac{34460}{0.73} = 47205$ as representing the heat which would result from the combustion and absorption of water formed from one kilo of hydrogen. One-ninth therefore of 47205—34460 would represent the absorption value per kilo of water. The water equivalent of the system being 2135, it follows that the absorption value per kilo of water divided by 2135 would give the rise in temperature per g. in the apparatus used, that is 0.663°. The empirical factor 0.097° would represent a quantity of water equal to 29.5 per cent. of the benzoic acid used or the equivalent of two molecules.

used per 0.5 gram of the substance for the heat of this part of the reaction.

Applying this correction, therefore, in a series of combustions of benzoic acid, using $\frac{1}{2}$ g. with $\frac{1}{2}$ g. of potassium chlorate as in Table 5, we have the results as given in Table 7. In selecting a factor for benzoic acid with which to compare the results, it should be noted that Stohman gives one factor of 6281, another of 6360. Stohman and Langbein give 6322. Berthelot and Luginni give 6335. The latter factor has been taken for comparison.

TABLE 7.
COMBUSTION OF BENZOIC ACID, USING ONE-HALF GRAM WITH ONE-HALF GRAM KClO_3 .

Total rise cor- rected for radiation	Correction for water formed, reaction-accele- rator and wire	Correct- ed temp- erature	Total indicated heat $\frac{\text{tx}2135}{0.5}$	Indi- cated calories	Compared with 6335
2.176	0.097 0.040 0.008	2.031	8675	6330	- 5 cal.
2.180	0.145	2.035	8690	6340	+ 5
2.180	0.145	2.035	8690	6340	+ 5
2.185	0.145	2.040	8715	6360	+25
2.170	0.145	2.025	8645	6315	-20
2.198	0.145	2.053	8780	6410	+75
2.162	0.145	2.017	8610	6280	-55
2.186	0.145	2.041	8720	6365	+30
Average			6330	6330	-5

Combustion of Other Organic Compounds.—Before leaving the subject of benzoic acid reference should be made to other organic compounds, containing oxygen. In the case of sugar, for example, it is evident that Dulong's formula does not apply. By that procedure the value for sugar would be only 3402 calories instead of 3962 calories, the observed value. By the same argument, the amount of water of composition suggested by the Dulong formula would be inadmissible as a basis for correcting for that constituent. In the following tests, the empirical correction used for this part of the reaction is 0.139° when the amount of sugar is 0.5 g. and 0.167° with 0.6 g.

TABLE 8.
COMBUSTION OF CANE SUGAR WITH 10 GRAMS Na_2O_2 AND ONE GRAM KClO_3 .

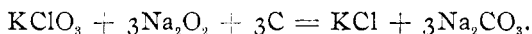
Amount of sugar taken	Correc- tion for hydroxyl reac- tion	Total correc- tion includ- ing chlorate and wire	Total Rise	Corrected Rise	Indi- cated calories $\frac{\text{tx}2135 \times .73}{\text{weight}}$	Compare Factors: Berthe- lot 3962
0.5	0.139	0.255	1.535	1.280	3989	+27
0.5	0.139	0.255	1.516	1.261	3929	-33
0.5	0.139	0.255	1.518	1.261	3929	-33
0.6	0.167	0.283	1.783	1.500	3895	-67
0.6	0.167	0.283	1.798	1.515	3935	-27
0.6	0.167	0.283	1.801	1.518	3943	-19
Average					3937	-25

It is interesting to compare these results with the nine authorities quoted by Fries¹. In that list the factors for sugar range between 3866 by Stohman and 4173 by Rechenberg with an extreme variation of 6.42 per cent.

It is not possible here to touch upon other experiments in this line which already indicate equally interesting features along the lines above indicated.

Heat Value of KClO₃.—In studying the heat value of potassium chlorate, it is manifestly different from a simple decomposition. The heat value in passing from KClO₃ to KCl + O₂ would be 105.6 — 95.8, or 9.8 calories per g. molecule, which calculated to the water equivalent of the instrument would call for a correction of 0.023° per one-half g.

Mention has already been made of the fact that, as used in fusion with carbonaceous material, no oxygen pressure is evident upon opening the bomb. This suggests either the use of the oxygen in reaction with the carbon, or the uniting of the same with the oxides of sodium. Probably both combinations occur. In studying the behavior of the chlorate, it was found that by increasing the quantity used, with a constant amount (1/2 g.) of pure carbon, no pressure of free oxygen could be detected until approximately two g. of chlorate had been employed. This suggests the following equations expressing the possible reactions:



Under the conditions indicated by this equation, we might expect to find no free oxygen liberated. Beyond this ratio of chlorate to carbon, however, we would expect to note a pressure of gas, and this conforms to our experience. That is in the ratio of 122.5: 36 or 1.7 g. of chlorate to 0.5 g. of carbon, no pressure is in evidence, but a slight pressure is found when a ratio of two g. of chlorate are used with 0.5 g. of carbon. This fact seems to prove further that part of the oxygen from the chlorate combines with the carbon and part with the Na₂O. It is this latter combination which adds to the heat value of the chlorate above its heat of simple decomposition. If we take such an equation as the following for the probable reaction and calculate the heat due the chlorate under this hypothesis, we shall have

$$\begin{aligned} &\text{KClO}_3 + \text{Na}_2\text{O} = \text{KCl} + \text{Na}_2\text{O}_2 + \text{O}_2. \\ &\frac{(105. + 119.8) - (95.8 + 100.3)}{122.5} \times 1000 = 235 \text{ cal.} \end{aligned}$$

By dividing this number of calories per g. of KClO₃ by the water

¹ Investigations in the Use of the Bomb Calorimeter. Bull. No. 94 U. S. Dept. Agr. (1907).

equivalent of the apparatus (2135), we have 0.108 as the rise in temperature for one g. of chlorate when used in combustions. This factor, therefore, has been used in the preceding tables where one g. was the quantity employed.

Whether the oxygen unaccounted for unites directly with carbon or is dissolved in the fusion, or unites to form intermediate or different oxides as suggested by De Forcrand,¹ cannot be affirmed. One further point is to be noted: In use of one g. and also one and one-half g. of chlorate the correction per half g. as above indicated is 0.054° . Of this 0.023° are considered to be the theoretical heat of dissociation of the potassium chlorate. The excess of 0.031° is considered as resulting from some recombination of the liberated oxygen. This reaches its normal height at one g. of chlorate. With less of chlorate this extra heat diminishes. If this extra heat is represented by a rise of 0.031° for one g. and $.000^{\circ}$ for no chlorate, it would be 0.016° for one-half g. which added to the normal heat of decomposition (0.023), would equal 0.039° as the correction factor to be used when one-half g. of chlorate is employed in combustions. In the calculations and tables thus far, the factor used has been 0.040° , and this also agrees with the experimental data.

Variables.—From the preceding discussion, it would appear that for materials of definite composition the empirical nature of the process has given place to a more nearly theoretical basis. We have been discussing thus far what may be properly termed the constants involved. Coal is not a substance of uniform composition, and it is upon fuels that the use of the method mainly centers. It is in this connection, therefore, that we would expect to find the variables.

Nitrogen.—Probably the most troublesome constituent to correct for in the Mahler type of calorimeter is the nitrogen. In the instrument under discussion, this element does not enter into the case, because in contrast to combustions with compressed oxygen there is no appreciable oxidation of nitrogen where sodium peroxide is the oxidizing medium.²

Sulphur.—First on the list of real variables is sulphur. It is now comparatively simple to adopt standard conditions, as for example, by using benzoic acid and potassium chlorate, we can add to such a charge a given weight of the substance to be examined. This has been done with powdered sulphur and also with iron pyrites. Since the conditions with sulphur alone are not widely different from those attending the combustion of iron pyrites, and since it is in the latter form that the sulphur of coal mainly occurs, we will give attention only to this material.

The average of a number of combustions using $\frac{1}{4}$ g. of carefully

¹Compt. rend., 128, 1519.

²Z. angew. Chem., 17, 1454.

selected iron pyrites gave an increase in temperature of 0.362° . The relation this reading bears to a correct value is derived as follows:—If we apply the same constants for calculating sulphur as for carbon or hydrogen, the rise in temperature per $\frac{1}{2}$ g. of sulphur would be $\frac{2250}{3117}$ or 0.7225° . The 0.362° rise, found as above indicated, would represent for the corresponding $\frac{1}{2}$ g. of contained sulphur in pyritic form $\frac{0.362}{0.1333 \times 2}$ or 1.356° . From this it appears that the indicated rise per 0.5 g. of sulphur content is too high by $1.356^{\circ} - 0.7225^{\circ}$ or 0.634° , and for 0.005 g. of sulphur which would be the equivalent of one per cent. in the usual $\frac{1}{2}$ g. taken, the error would be 0.00634° . It appears from this, therefore, that sulphur, while a variable, can be easily corrected for, by subtracting from the indicated rise in temperature, 0.006° for each per cent. of sulphur in the sample. This is a matter of considerable importance in coals with four or five per cent. of sulphur.

Ash.—The effect of silicious matter in fusion with sodium peroxide should be taken account of, and its determination has been made possible by the same development of standard conditions for testing. The following tests were made: Sample (a) was shale, free from carbonaceous matter, taken immediately above a coal seam; (b) nearly pure amorphous silica which had been previously ignited; (c) finely pulverized glass; (d) a composite ash; (e) dark red ash, high in iron; (f) and (g) were gray ashes low in iron. The last four samples were obtained by burning off a quantity of coal as in the usual ash determination. One-half g. was taken for each test and run in duplicate with the standard charge of 0.5 g. of benzoic acid and 0.5 g. of potassium chlorate. The results are given in Table 9.

TABLE 9.
FUSION OF SILICIOUS MATERIAL WITH SODIUM PEROXIDE.

Substance	Total Rise: (standard + $\frac{1}{2}$ g. si- licious matter)	Rise for standard $\frac{1}{2}$ g. Ben- zoic acid, $\frac{1}{2}$ g. KClO_3)	Rise in de- grees centi- grade for equivalent of 1% ash i.e. 0.005 grams
(a) Kaolin.....	2.288	2.180	0.0011
(b) Shale.....	2.320	2.180	0.0014
.....	2.336	2.180	0.0015
(c) Silica.....	2.357	2.180	0.0017
.....	2.359	2.180	0.0018
(d) Glass.....	2.275	2.180	0.0009
(e) Composite Ash from Ill. coals.....	2.279	2.180	0.0010
(f) Ash from Sangamon Co., Ill. coals.....	2.278	2.180	0.0010
(g) Ash from Vermillion Co., Ill. coals.....	2.297	2.180	0.0012
(h) Ash from Williamson Co., Ill., coals.....	2.279	2.180	0.0010

From this it appears that a very fair uniformity exists with regard to

the heating effect of silicious material and a correction of 0.001° is indicated for each per cent. of ash content in the material to be tested.

One other variable is met with, and this is the oxygen compounds or hydroxyl constituents which in coal are sufficiently definite in the different types to make a correction easily applicable. In anthracites and semi-anthracites, of course, there is nothing of this element, at least not in sufficient amount to be taken account of. It is even a question whether it should be corrected for in semi-bituminous coals. In bituminous coals and lignites, however, it should enter into the final correction. The amount of the correction is readily arrived at as follows. We have already observed in connection with benzoic acid and sugar that the hydroxyl constituents when referred to the percentage basis of the water formed in their decomposition, represent a heat value as shown in a rise of temperature equal to 0.0033° for the equivalent of one per cent. of water so combined. In bituminous coals this constituent varies so slightly from 10 per cent. in amount that the corresponding correction of 0.033° is practically a constant component of the correction called for in coals of the bituminous type. In lignites a similar condition exists in that black lignites have a content of this material sufficient to require a correction of 0.056° for each $\frac{1}{2}$ g. used and brown lignites require a correction of 0.111 per $\frac{1}{2}$ g.

Ignition wire.—The value of the fine wire used for ignition by the electric method was determined by fusing a number of wires with a coal of known value as shown in the table.

TABLE 10.

FUSION OF IRON WIRE WITH SODIUM PEROXIDE AND STANDARD COAL.				
Weight of iron wire burned	Total Rise	Correction for standard material used	Rise for wire	Rise for 1. gram iron
0.2951	2.840	2.591	0.249	0.844
0.3100	2.856	2.591	0.265	0.855
0.4860	2.990	2.591	0.399	0.821

The wire used in these tests had an average weight of 0.010 g. per 10 centimeters. As the wire was practically all consumed, the correction factor indicated was 0.008° for each length of 10 mm. used.

If we list, therefore, the component parts of the correction factors that enter into the various types of coal, we would have for average conditions the following :

(a) CORRECTION COMPONENTS FOR AVERAGE ANTHRACITE COAL, USING 10 GRAMS Na_2O_2 AND $\frac{1}{2}$ GRAM KClO_3 .

$\frac{1}{2}$ gram KClO_3	0.040°
1 per cent. Sulphur.....	0.006
7 " " Ash.....	0.007
Fuse Wire.....	0.008

Total..... 0.061° C.
or, 0.110° F.

(b) AVERAGE SEMI-BITUMINOUS COAL (NOT OVER 25 % VOLATILE MATTER.)

½ gram KClO ₃	0.040°
1 per cent. Sulphur	0.006
7 " " Ash	0.007
4 " " Hydroxyl	0.013
Fuse Wire	0.008
Total	0.074° C.
	or, 0.123° F.

(c) AVERAGE BITUMINOUS COAL (OVER 25 % VOLATILE MATTER).

½ gram KClO ₃	0.040°
2 per cent. Sulphur	0.012
10 " " Ash	0.010
10 " " Combined Water	0.033
Fuse Wire	0.008
	0.103° C.
	0.185° F.

Where the component parts vary widely from these average conditions the ultimate correction factor may readily be made up from the schedule of units as listed under No. 6 of the Summary, below.

Summary.

1. The heat of combustion of carbon is 73 per cent. of the heat of the reaction of the carbon with sodium peroxide.
2. The heat of combustion of hydrogen (to liquid water) is 73 per cent. of the heat of the reaction of hydrogen with sodium peroxide.
3. The sodium peroxide used must be free from absorbed moisture or the correction value of the same must be determined.
4. Standard conditions based upon theoretical data are available for checking material and apparatus.
5. The constants are the large elements in the case and practically govern the accuracy of the process.
6. The correction components may be readily reduced to a unit basis; thus,--

Sulphur	0.006°	for 1% in 0.5 g. of material
Ash	0.001°	" " " " " "
Combined Water	0.0033°	" " " " " "
KClO ₃	0.040°	" 0.5 g. used
Fuse Wire	0.008°	" 10 mg. burned

UNIVERSITY OF ILLINOIS, URBANA.

THE ANALYSIS OF ICE CREAM.

BY CHARLES D. HOWARD.

Received September 5, 1907.

With the recent enactment of standards for ice cream by several of the states, the analysis of this substance is just beginning to receive attention on the part of food inspection chemists. As the literature seems to contain no specific methods, the following (in part simple modifications of