A NEW COAL CALORIMETER.

By S. W. Parr.

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IN the study of combustibles and in all tests connected with fuels no data is of any value that does not go back to the thermal units involved. This fact itself is not new but its application, especially in technical work, has had a marked increase in recent years. This increase has come about in spite of, rather than because of, the instruments available for the determination of heat units. It is not necessary here to describe the difficulties and defects connected with existing calorimeters, more than to note perhaps the two extremes; *viz.*, the L. Thompson calorimeter on the one hand which admits of results varying by 15 per cent. from the truth, and the high pressure bomb on the other which, while accurate, requires an elaboration of apparatus and skill in manipulation not conducive to the wide use it deserves.

The calorimeter here described has the advantage of operating without an oxygen gas supply ; its manipulation is simple and the extraction of the heat rapid, owing to the compact mass in which the heat is generated. It is especially adapted to soft coal and while designed for technical purposes its factor of error is well within 0.5 per cent., making its results, therefore, easily comparable with those obtained by the Berthelot or Mahler bombs. The principle involved in the process depends upon the liberation of oxygen from such a compound or chemical as shall in turn absorb the products of combustion thereby avoiding the necessity of providing conduits for the gases. A chemical which admirably meets these requirements is sodium peroxide. Its operation may be illustrated by the following experiment which was one of the first used to determine the adaptability of this chemical. A sample of combustible and sodium peroxide in suitable proportion were placed in a short, heavy, copper tube with close-fitting screw plugs at each end and the contents thoroughly mixed by shaking. The bomb was then held in the flame of a Bunsen burner till ignition was effected. Upon cooling and opening it was found that no pressure of gas was present and on dissolving out the fused mass the combustion was shown to be complete. The instrument ultimately employed for utilizing these conditions may be best shown by an outline sketch.

A (Fig. 1) is a copper vessel of a little over two liters' capacity insulated by two outer vessels of indurated fiber, B and C, so

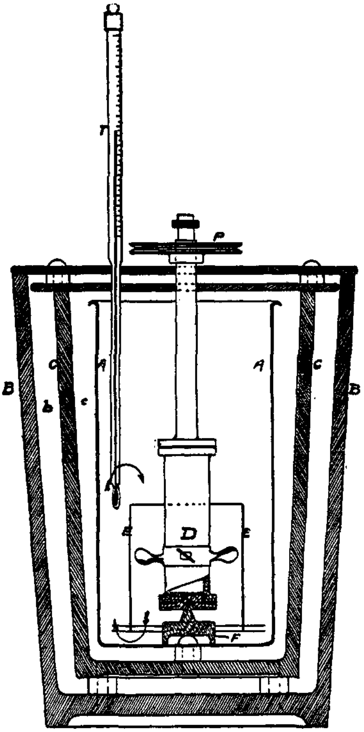

Fig. 1.

placed as to provide further insulation by the air spaces *b* and *c*. The cover is double to correspond with an air space between, the two parts being connected for convenience in handling. The cartridge D has an inside capacity of about 25 cc. It rests on a pivot below and extends through the covers above and has a small removable pulley at the end. Turbine wings fastened to spring clips are placed on the cartridge, and a short cylinder E, open at both ends, is provided for directing the current set up by rotation of the vanes attached to the cartridge. The vanes are so set as to deflect the currents downward first along the cartridge and then up along the outside of the cylinder. The stem G of the cartridge is so arranged as to permit the passage of a short piece of No. 12 copper wire (Fig. 2). It is, moreover, provided with a valve D at the lower end which prevents the escape of the enclosed air when heated by the combustion of the charge. The two ends B and C of the cartridge screw on. The process then is as follows: 1 gram of coal ground to pass through a 100-mesh sieve and dried in the oven as usual at 105°-110° is put into the cartridge, 16 to 18 grams of sodium peroxide are added, the top screwed on and the whole shaken to thoroughly mix the contents. The peroxide varies somewhat in fineness. It should practically all pass through a 25-mesh or 1 mm. sieve. After tapping the cartridge to settle the charge in the bottom, it is placed in the can and 2 liters of water added, the temperature of the water being 3° or 4° lower than the temperature of the work room. The pulley is connected by string to a small water or electrical motor giving about 50 to 100 revolutions per minute to the cartridge. When constant temperature is reached, the reading of the thermometer is taken and the hot wire is dropped through the valve into the charge which is at once ignited and burns completely in two or three seconds. The extraction of the heat is effected in about five minutes. The reading of the maximum temperature is taken and the calculations made as follows:

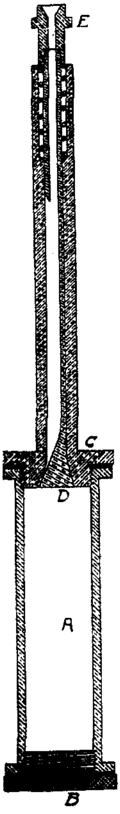

Fig. 2.

First.—A correction factor is needed for the hot wire. The average of many determinations on various lengths up to 2 inches establishes a fairly uniform factor of 0.012° C. or 0.021° F. per $\frac{1}{2}$ inch of No. 12 copper wire. In this work the lengths used have been $\frac{1}{4}$ inch and $\frac{3}{8}$ inch and the correction factor for the wire has been 0.006° and 0.009°.

Second.—A correction is made necessary by reason of the heat resulting from the combination of the products of combustion, carbon dioxide and water, with the chemical employed. This heat of combination causes an excess over and above the actual heat of combustion, amounting to 27 per cent. of the total indicated heat. Hence, this correction must also be applied in the calculation. The method then of calculation will be as follows: Supposing a centigrade scale to have been used, if C′ represents the total indicated calories, C the actual calories due to combustion, t the rise in temperature, and w the water employed,

then
$$C' = (t - 0.012^\circ) \times w,$$
and
$$C = C' - \frac{C' \times 27}{100},$$
or
$$C = (t - 0.012^\circ) \times w \times 0.73.$$

In case a Fahrenheit thermometer is used the temperature of correction for ½ inch of wire is 0.021° instead of 0.012° and the final result is B. T. U. per pound of coal instead of calories. Of course with a centigrade thermometer the ultimate reading is changed from calories to B. T. U. by multiplying the calories obtained by 1.8.

A word of explanation is necessary as to the method of arriving at the factor for the heat of absorption of the products of combustion. The two elements concerned are carbon and hydrogen. For the carbon dioxide resulting from the combustion of the former, the correction factor is easily determined. Pure sugar carbon is prepared and run in the calorimeter as above described. The average of a number of such determinations gave a total calorific result of 11,084. Now taking as the accepted figure for the heat of combustion of carbon in calories, 8,080, we have therefore an increase of 3,004 calories due to the heat of absorption of the carbon dioxide by the chemical. By computation this is found to be 27.1 per cent. of the total indicated heat. Now as to the heat due to the absorption of water from the combustion of hydrogen the problem is not so simple. The burning of sugar affords no indication, for seemingly other compounds than water are formed and as in the case of sugar burned in the bomb calorimeter, while the results are constant and repeat themselves with exactness, they vary so widely from the theoretical data as to make it evident that the combinations do not proceed in a simple manner. Naphthalene does not afford a factor, chiefly owing to its volatility and consequent faulty combustion. The liberation of a known weight of water in the interior of the cartridge gave very indifferent results, the water not disseminating throughout the peroxide but incrusting itself in a moist mass. Many other methods were tried with the result that so far at least it has been necessary to fall back on empirical data obtained from burning widely different varieties of coals and checking the same coals by combustion in standard bomb calorimeters. The following table gives the results thus obtained, using coals varying in their ash content from 3 to 32 per cent., and in water from 1 to 14 per cent. Also as wide a variation in the character of their hydrocarbons as possible, using a cannel coal,—Pennsylvania gas coal, a lignite and soft coals from widely separated districts in Illinois. Supposing the factor for absorption of water formed from a given weight of hydrogen to be approximately the same per cent. of total heat evolved as in the case of carbon dioxide, *viz.*, 27 per cent. and applying this factor throughout, we have the following results obtained by running parallel combustions in a standard Atwater or Mahler bomb calorimeter and the sodium peroxide apparatus. In a number of samples the process was conducted in both the Atwater and Mahler bombs. The instruments, however, checked so closely that this practice was not continued throughout the tests. The proximate analysis is included in the table in order that the wide variations in the character of the coals may be indicated (see table).

A few facts should be noted :

(*a*) It has been discovered after most tedious experience that a comparison of calorimeters should be made at approximately the same time. For example a series of calorific determinations made on finely ground samples on May 12, 1900, were found to give a reading 2.4 per cent. less on July 12, 1900. It was necessary to repeat practically all the above determinations on this account, all results showing a slow deterioration in the finely ground samples. This subject will receive further attention later.

(*b*) In the table it should be noted that the first five samples are from the same mine and vary but slightly in composition. The particular purpose in introducing this series was to note if

Kind of coal.	Proximate analysis. Moisture.	Volatile combustible.	Fixed carbon.	Ash.	Sulphur.	B. T. U. per pound air-dried coal. Bomb calorimeter.	New method.	Variation from standard bomb in per cent.
216 Carterville, Ill., mine run	4.87	34.11	52.17	8.85	0.85	12,205	12,214	+0.07
217 " " washed No. 1	4.66	33.99	54.21	7.14	0.74	12,289	12,286	0.00
218 " " " " 2	4.31	35.12	55.01	5.56	0.87	12,914	12,934	+0.08
220 " " " " 4	4.86	33.26	55.29	6.59	1.15	12,355	12,345	—0.08
221 " " dust from washer	5.50	32.97	53.01	8.52	1.16	12,384	12,336	—0.39
226 Odin, Ill., pea coal	7.27	35.76	42.96	14.01	3.89	11,025	11,064	+0.35
227 Farmington, Ill., mine run	11.22	35.93	36.60	16.25	3.98	9,986	10,018	+0.32
228 Pennsylvania gas coal	0.92	36.66	58.94	3.46	1.40	14,270	14,275	0.00
229 Kentucky cannel coal	0.99	32.33	34.35	32.33	1.07	10,313	10,328	+0.14
230 Mississippi lignite	14.56	43.82	29.30	12.32	...	8,316	8,378	+0.74

the calorimeter would differentiate between such small variations in the inert material, the ash and water.

Tabulating the results with reference to these inert materials and giving simply the calorimetric reading for each we have :

No.	Total of water and ash. Per cent.	B. T. U.
216	13.79	12,214
217	11.80	12,286
218	9.87	12,924
220	11.45	12,345
221	14.02	12,056

(*c*) It has already been mentioned but attention should again be called to the fact that with the calorimeter it is necessary to operate on the oven-dried sample for the reason that the water, if left in the sample, gives off heat in combining with the chemical; hence, a gram sample is weighed and dried in the oven or if the per cent. of moisture is known, an oven-dried sample may be weighed out, making allowance for the water. No other conditions vary the results. About 17 times the weight of coal is the best amount of peroxide to insure complete combustion but variations from 16 to 20 times the amount do not appreciably vary the results. Indeed with careful work and a good thermometer the instrument repeats its own results fully as closely as the bomb calorimeters. The usual practice, moreover, has been to work with half-gram samples, using a measured quantity,—8 to 9 grams of peroxide. With a suitable room and reasonable precautions as to temperature of both room and water employed, exceedingly constant and satisfactory results may be obtained which should vary less than 0.5 per cent. from the best figure obtainable with a standard instrument.

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ON THE DETERMINATION OF PHOSPHORIC ACID AS PHOSPHOMOLYBDIC ANHYDRIDE.

BY H. C. SHERMAN AND HENRY ST. JOHN HYDE.

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ALTHOUGH a great amount of work has been done in this country upon the subject of phosphorus determination, practically no attention seems to have been given to methods