THE ANALYST.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

CORRECTIONS IN BOMB CALORIMETRY.

By G. NEVILL HUNTLY.

(Read at the Meeting, December 2, 1914.)

THIS present note is supplementary to a paper previously published (*J. Soc. Chem. Ind.*, 1910, 29, 917; *ANALYST*, 1910, 35, 444).

In a determination of the calorific value of a fuel with the bomb calorimeter, corrections are required for—(1) Errors of the thermometer tube (calibration); (2) heat given out by the fuse; (3) cooling (radiation); (4) change in water equivalent with temperature; (5) sulphuric acid formed; (6) nitric acid formed; (7) heat loss by evaporation; (8) heat gained from stirrer; (9) incomplete combustion.

Many instruments are used in a more or less empirical manner, especially by engineers, and it appears to be customary to make a rough allowance for cooling and to neglect the other corrections. Among chemists, in addition to the cooling correction, an allowance is generally made for the sulphuric acid and nitric acid formed by the combustion. For some purposes the neglect of small corrections may be justified by the nature of the sampling; but it seems worth while to estimate the magnitude and direction of all sources of error, so that their possible cumulative effect in the most unfavourable case may be known, and the number of significant figures given in the final calorific value made to correspond.

Thermometer Tube Errors (Calibration).—This question is discussed in a previous paper (*loc. cit.*). If a good thermometer is used without a calibration table—and this must not be confused with a table of corrections obtained by comparison with a standard, which is not good enough for the present purpose—the errors will not exceed, but may amount to, one unit of division; that is, 0.02° on a thermometer divided into fiftieths (8 per thousand),* 0.01° (4 per thousand) if the divisions are in 0.01° .

Fuse.—This may be iron, nickel, or platinum wire, either embedded in the briquette or resting on it, or the wire may be arranged not to touch the fuel, the flame being led down by a cotton thread or collodion wool. The cotton thread used with fine platinum wire is convenient, and rarely fails to ignite. The wire should be very fine (0.002 inch), and unnecessarily high battery voltage avoided. The heat of

* The figures in brackets represent throughout the error in parts per 1,000 on an assumed average rise of 2.5°C .

fusion even of this fine wire is just measurable, amounting to about 5 calories, to which is added about 20 calories for the cotton. The use of thick wires and high voltages will lead to an error which only vanishes when the rise of temperature for the fuel happens to coincide with the rise obtained during the calibration with a standard substance.

Cooling Correction.—This has been dealt with in detail in the earlier paper, in which the meaning of each of the terms in the Regnault-Pfaundler expression is discussed. The author is of opinion that this formula should always be applied in work of any pretensions to accuracy, and its application is much facilitated by the use of the form given below :

Date : November 23, 1914. Capsule + fuel = 7.8750. Thermometer : No. 1.
 Number : 585B. Capsule = 7.0200. Temperature (final) : 15.0.
 Substance : Oil. Water : 2,160.
 Ash : —. Weight = 0.8550. W.E. : 2,500.

Preliminary Period.		Chief Period.		After Period.	
Time.	Temperature.	Time.	Temperature.	Time.	Temperature.
0	0.026	6 θ_1	2.00	10 θ_5	3.598
1	0.030	7 θ_2	3.47	11	3.594
2	0.033	8 θ_3	3.60	12	3.590
3	0.037	9 θ_4	3.599	13	3.586
4	0.041			14	3.583
5 θ_0	0.045			15	3.578
		$\Sigma_1^*(\theta)$	= 12.67		
θ	0.035	$\frac{1}{2} (\theta_0 + \theta_5)$	= 1.82	$\theta' = 3.588$	
v	- 0.0038	$- n\theta$	= - 0.17	$v' = + 0.0040$	
nv	- 0.019	S	= 14.32	$k = \frac{v' - v}{\theta' - \theta} = \frac{+ 0.0078}{+ 3.55} = + 0.0022$	
Cooling correction = $nv + kS = - 0.019 + 0.0314 = + 0.0124$.					

Uncorrected rise	3.598°	Calibr.	- 0.0069°	Rise per grm. = $\frac{3.560^\circ}{0.855^\circ}$ R ... = 4.164° R × 2500 = 10,410 cal. per grm. R × 4500 = 18,740 B.T.U. per pound
	0.045°		- 0.0000°	
	3.553°		+ 0.0069°	
			- 0.0079°	
Thread ...			+ 0.0124°	
Cooling ...			- 0.0048°	
Nitric acid ...			—	
Sulphur ...				
Total correction	= + 0.007°			
Corrected rise ...	= 3.560°			

According to this the correction is—

$$nv + \frac{v' - v}{\theta' - \theta} \left\{ \Sigma_1^*(\theta) + \frac{1}{2} (\theta_0 + \theta_5) - n\theta \right\}.$$

The calculation of the correction should be obvious from the form. Sixteen readings are taken at intervals of one minute, and in the intervals between the

readings the values of θ , v , nv , $\Sigma_1^*(\theta)$, $\frac{1}{2}(\theta_0 + \theta_5)$, $n\theta$, S , (the large bracket) the thermometer calibration errors, and the uncorrected rise, are readily calculated and inserted, so that after the last thermometer reading only θ' , v' , k , and kS , have to be inserted, and the time required for this averages two minutes. At the risk of repetition, it may be emphasised that this is the only expression which takes into account errors due to evaporation from the calorimeter vessel and the heat evolved by the friction of the stirrer.

A Shortened Form of the Regnault-Pfaundler Formula.

The expression

$$\text{Correction} = nv + \frac{v' - v}{\theta' - \theta} \left\{ \Sigma_1^*(\theta) + \frac{1}{2}(\theta_0 + \theta_5) - n\theta \right\}$$

represents the approximate integration of the time-temperature curve, and if conditions are arranged so that the shape of this curve remains similar, the formula can be reduced to a very simple expression without loss of accuracy. The shape of this curve depends on the heat conductivity of the walls of the bomb, the rate of stirring, and the velocity of combustion of the fuel. The predominating factor is the rate of stirring. The first obviously remains constant for a given instrument, the second can be kept constant if the stirrer is driven by a suitable motor, and the third depends on the nature of the fuel burnt. From the examination of over 200 determinations, the author has found that for his own instrument (Kroeker, enamel-lined), with the stirrer working at 120 complete oscillations per minute, $\frac{S}{\theta' - \theta}$ is constant, and equals 4.2 ± 0.1 for coals (in briquettes), and 4.45 ± 0.05 for oils or pure organic substances. This leads to an expression of extreme simplicity, which for this instrument, working under these fixed conditions, retains the accuracy of the original lengthy formula. Numbering the temperature readings t_0 , t_1 , up to t_{15} , the formula may be written:

$$\text{Correction} = (t_0 - t_5) + \frac{S}{5(\theta' - \theta)} \left\{ (t_{10} - t_{15}) - (t_0 - t_5) \right\}$$

Taking the coal figure, $\frac{S}{5(\theta' - \theta)} = \frac{4.2}{5} = 0.84$, the correction reduces to $0.16(t_0 - t_5) + 0.84(t_{10} - t_{15})$, due regard being paid to the signs of the two temperature differences.

If a small table of two columns be made, giving the products $0.16(t_0 - t_5)$ and $0.84(t_{10} - t_{15})$ for such temperature differences as are found to occur in practice, the whole correction is complete within thirty seconds.

For oils or pure organic compounds, the corresponding expression is

$$0.11(t_0 - t_5) + 0.89(t_{10} - t_{15}).$$

The average error of this approximate method is under 0.001° , and rarely amounts to 0.002° . The saving of time over the full expression, if the form be used as above described, is not more than two minutes, but the liability to error is reduced; even if the full calculation be preferred, the shortened form is a valuable check on the calculation.

Two points of interest can be deduced from the above. If $-(t_0 - t_5) = +(t_{10} - t_{15})$

—that is, if the rate of gain of temperature during the preliminary period is exactly equal to the rate of cooling during the after-period—it has been assumed by many workers that the cooling correction is *nil*. In this case we get as the correction $(t_0 - t_5)$ (0.84 - 0.16). Taking the rise of temperature during the preliminary period as 0.020, the correction is +0.014° (5.6 per thousand) instead of 0.000°.

Another interesting application is the deduction of the effects of thermometer errors (reading or calibration or both combined) on the final corrected rise. The latter is $(t_{10} - t_5) + 0.16(t_0 - t_5) + 0.84(t_{10} - t_{15})$, and this reduced to approximately $1.84t_{10} - 1.16t_5 + 0.16t_0 - 0.84t_{15}$, so that an assumed error of 0.001 on each reading will give the total error on the corrected rise. The *maximum* error will be obtained if the errors on the four readings— t_0 , t_5 , t_{10} , t_{15} —are alternately plus and minus, as shown below:

Reading.	Assumed Error.	Effect on the Corrected Rise.
t_0	+ .001°	+ .00016°
t_5	- .001°	+ .00116°
t_{10}	+ .001°	+ .00184°
t_{15}	- .001°	+ .00084°
		+ .004°

From this it appears that an error on the first reading is comparatively unimportant, but that an error on the first reading of the after period has double weight. Also the error on the corrected rise may be, as a maximum, four times the possible error of reading. This means 22 B.T.U. on a coal of 14,000 B.T.U. per pound, or 30 B.T.U. on an oil of 20,000 B.T.U. per pound. If readings are taken to 0.005° only, as appears to be frequently the case, the possible error due to this cause alone will be 110 B.T.U. on a coal of 14,000. This result is general, and is not limited by the particular method of applying the cooling correction.

Whilst dealing with the cooling correction, it may be of interest to compare the method used by Mahler with the Regnault-Pfaundler correction. Taking an example given by Mahler (*Bull. de la Société d'Encouragement pour l'Industrie Nationale*, 1892, 310), the corrected rise given in the paper is 3.615°; by the longer method, 3.598°. Mahler deduces a heating value of 9,691.8 calories, instead of 9,646, a difference of about 0.5 per cent. It is clear that, if a rough-and-ready cooling correction is deemed sufficient, the number of significant figures in the resulting calorific value must be limited to correspond.

J. A. Riche (*J. Amer. Chem. Soc.*, 1913, **35**, 1747) abolishes the cooling correction by the use of a glass Dewar tube. In the form proposed both the radiation and evaporation errors are abolished, the heat evolved by stirring still remains unaccounted for. From the description given, it would appear that the time required to fit the bomb into place would exceed that required for the full correction. This vacuum jacket method is to be preferred, in principle, to the method of adiabatic calorimetry proposed by T. W. Richards.

The Temperature Coefficient.—The water equivalent of the bomb, water and containing vessel, varies slightly with the temperature. Hence, unless the room in which the calorimetric determinations are carried out can be kept at a uniform

temperature throughout the year, this correction must be measured and allowed for. As regards the change in the specific heats, each 4° from 15° C. causes a variation of 1 part in 1,000 in the W.E. If a thermometer of the Beckmann type with variable zero is employed, the value of the degree varies with the temperature—that is, with the weight of mercury in the bulb. These two corrections are conveniently combined by determining the water equivalent at regular intervals by combustion of a pure substance, benzoic acid for preference. A set of figures obtained with such a thermometer is appended. The quantity of water taken was constant (2,160 grms.), and corresponded with a water equivalent of 2,500 grms. at 15° C. The variation was found to be linear, and could be expressed by the relation $W.E. = 2,500 + (T - 15^{\circ})$ where T was the final temperature of the water in the calorimeter :

Temperature : 0° C.	Water Equivalent.		Difference.	
	Calculated.	Found.	Grms. Water.	Parts per 1,000.
10	2,495	2,491	- 4	- 1.6
12	2,497	2,496	- 1	- 0.4
14	2,499	2,500	+ 1	+ 0.4
14	2,499	2,500	+ 1	+ 0.4
15	2,500	2,500	—	—
22	2,507	2,504	- 3	- 1.2
22	2,507	2,508	+ 1	+ 0.4
23	2,508	2,510	+ 2	+ 0.8
23	2,508	2,509	+ 1	+ 0.4

Average error from the mean, 0.6 per thousand, or 4 calories.

Greatest error between extreme results, 2.4 per thousand, or 15 calories.

Maximum error due to assumed error of 0.001° on the four critical thermometer readings, 0.004° , or 10 calories.

The Corrections for Sulphur and Nitric Acid.—For the determination of this correction it is usual to place 10 c.c. of water in the bomb, and, after allowing time for the fog to settle (thirty minutes from the time of firing), estimate the nitric and sulphuric acids formed, either by a volumetric method (baryta and sodium carbonate) or by a titration of the total acidity followed by a gravimetric estimation of the sulphuric acid. In the latter method, preferred by the author, there are two sources of error to be noted. In a bomb lined with enamel, minute transparent particles of the enamel are apt to be detached, and if these are weighed as barium sulphate the result will be high. With a leaden washer, appreciable quantities of lead nitrate and sulphate are formed. If a measured excess of $\frac{N}{10}$ sodium carbonate is added to the bomb washings, the liquid boiled and filtered, the excess of alkali can be accurately determined by back titration with acid, with a sharp end-point. Direct titration with alkali gives a rather indefinite end-point in presence of the lead salt, and the total acidity will be too low, this error falling on the nitric acid. The filtration also removes any particles of enamel, and the filtrate serves for the

precipitation with barium chloride. Direct experiment shows that no sulphate has been carried down by the lead carbonate.

The correction for nitric acid is fairly constant for a given bomb, and rarely exceeds 10 to 12 calories. One c.c. $\frac{N}{10}$ sodium carbonate = 0.143 calorie, or 0.00057° for a water equivalent of 2,500.

As regards the sulphur, it is usual to subtract 22.5 calories for each 1 per cent. present, or, as an alternative, 0.00144° for each c.c. of $\frac{N}{10}$ alkali used by the sulphuric acid (W.E. 2,500). This is based on two assumptions: that the sulphur is completely oxidised to sulphuric acid in the bomb, and that in practical use of the fuel the sulphur is burnt entirely to sulphur dioxide. The first of these assumptions is substantially accurate, the second is not. In a paper* on the influence of the volatile constituents of solid fuel on the efficiency of internally-fired boilers, Constam and Schläpfer have investigated the question of the distribution of sulphur in fuel between the ash and the flue gas, and the proportion of sulphur dioxide in the latter. In one set of four experiments, after deducting the sulphur found in the ash, the amounts of SO₂ found in the flue gas only amounted to from 15 to 25 per cent. of that calculated on the assumption that all the volatile sulphur was burnt to SO₂. Another set of four experiments by the same authors gave an average of 40 per cent. of the expected sulphur dioxide, and this would be still lower if calculated on the total sulphur in the coal. Some sulphur trioxide is well known to be formed during the combustion of sulphur compounds in air, and it is probable that under the catalytic action of traces of oxides of nitrogen, always present in a flame, and of ferric oxide on the boiler tubes, a further conversion into SO₃ takes place. In internal combustion engines of the Diesel type the conditions of combustion approach those obtaining in the bomb, and consequently for fuel oils this correction may become misleading. Thus, direct analysis of the exhaust gas from a Diesel engine burning a fuel oil containing 3.6 per cent. of sulphur showed that only 5 per cent. of the total sulphur was given off as SO₂. Here the same set of experimental figures could be interpreted to give a gross calorific value of 18,445 or 18,300 B.T.U. per pound, depending on the omission or application of the sulphur correction. In this case the omission of the sulphur correction would correspond nearer to the facts, although there is still uncertainty, as 90 per cent. of the sulphur of the fuel remained in the cylinder, and only a small proportion of this was present as sulphuric acid. To avoid dispute, therefore, a certificate of analysis should state whether the sulphur correction has been applied or not, together with a statement of the assumptions upon which the difference is based.

Heat Loss by Evaporation.—Mahler (*loc. cit.*) gives the loss by evaporation as 1 gm. per hour. This will obviously vary with the instrument, but, accepting this figure as an approximation, the heat loss will be about 10 calories per minute, or 0.004° per minute for a calorimeter with water equivalent 2,500. This is in the same direction as the cooling correction. This error is eliminated by the Regnault-Pfaundler formula, but is not eliminated in methods of adiabatic calorimetry unless the calorimeter vessel is enclosed in an air-tight manner. The heat developed by

* "Mittellungen über Forschungsarbeiten auf dem Gebiete des Ingenieurwesens," *Verein deutschen Ingenieure*, Heft 103. Berlin, 1911.

the stirrer acts in the opposite direction. Richards and Burgess (*J. Amer. Chem. Soc.*, 1910, **32**, 448) give some data on this point, and show that with 110 oscillations per minute the temperature rise is of the order of 0.006° for five minutes. The importance of efficient stirring does not always appear to be realised. Inefficient stirring magnifies the errors due to the lag of the bomb and thermometer, and vitiates the radiation correction, as the latter is based on the assumption that the reading of the thermometer represents the temperature of the outer wall of the calorimeter vessel. The only drawback of rapid stirring is the development of heat by the friction, and this is eliminated completely by the full correction, provided the rate of stirring is uniform throughout, a condition which can only be fulfilled by using a motor. One hundred and twenty oscillations per minute is a convenient rate.

Incomplete Combustion.—Ash-free solids, or liquids with low vapour pressures, are burnt completely without difficulty in the bomb. Volatile liquids are also completely burnt, provided the precautions indicated by Berthelot are followed. With coals the combustion is not always complete, and these cases may be conveniently classified under three heads: (1) Fuels with low hydrogen content, such as anthracite, coke, graphite; (2) fuels with high, non-fusible ash; and (3) coals with fusible ash.

For substances such as anthracite and coke briquettes cannot be formed, and the substance must be burned as a fine powder. Various methods may be adopted. The use of a sheet of mica or a pad of asbestos or other non-conducting material prevents the ash from being prematurely cooled by the platinum capsule, and this device, together with a higher oxygen pressure (40 atmospheres instead of 25) has given satisfactory results with several workers. Another device, which gives very good results, is to moisten the coal, after weighing out, with a few drops of a high boiling oil (B.P. paraffin oil does well) of known calorific value. The oil is weighed and its heat of combustion deducted. Another device which the author has proved to be satisfactory is to weigh out the coal in a small square of dry, ash-free filter-paper, the calorific value of the paper being determined in a separate experiment, and of course deducted as before. This works better than the oil when the coal ash happens to be fusible.

For bituminous or semi-bituminous coals (over 15 per cent. volatile matter) with high non-fusible ash, combustion is complete if a mica plate is inserted under the briquette. With clinker, flue dust, or similar products, the addition of oil is necessary for satisfactory combustion.

The third class is the most difficult to handle, coals giving fused globules in the platinum capsule. These almost invariably contain enclosed particles of unburnt carbon. The error can be reduced by using a mica plate, or, better, ignited quartz sand, as numerous small globules are thus obtained instead of two or three large ones. Breaking up the briquette into six or eight pieces also reduces the size of the globules, and using 0.5 gm. instead of 1 gm., with a lower oxygen pressure, also gives higher results. But the only really satisfactory method of dealing with such cases is the determination of the unburnt carbon in the ash. The use of quartz sand facilitates removal of the ash from the capsule, and also renders its pulverisation in a steel mortar more complete.

A combustion of this is made in a miniature closed tube after mixing with lead chromate and potassium dichromate, the CO_2 being either weighed or, more conveniently, caught in baryta solution and titrated. For a given coal of this class, the amount unburnt is curiously constant, so that two or three consecutive determinations of calorific value may agree well, and yet be from 1 to 4 per cent. low. One Scotch coal gave results 8 per cent. low when burnt in platinum; with quartz sand this error was reduced to between 1 and 3 per cent. This was exceptional, but deficiencies up to 3 per cent. may be expected whenever large globules of ash are found. This is the most serious error in coal calorimetry when the instrument is used empirically.

There is an unfortunate tendency, frequently commented upon, for chemists to give their analytical results to more significant figures than is justified by the experimental methods employed. This is especially the case with determinations of calorific value. The calorific value of ordinary fuels, expressed in B.T.U. per pound, is of the order 10,000 to 20,000. Hence has arisen the custom of reporting to the last figure, such as 12,831 B.T.U. per pound. The last figure is purely arithmetical, and even under the best conditions of working has no meaning. Results agreeing closer than 30 B.T.U. must be regarded as accidental; indeed, having regard to the possibilities of constant errors indicated above, the agreement of duplicates, taken probably on the same thermometer and upon the same portion of the scale, is apt to give completely false ideas of the accuracy of the measurement. With uncalibrated thermometers reading to 0.005, errors of 200 B.T.U. per pound are quite possible. In such cases the accuracy of the measurement will be fully expressed by three significant figures only.