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On the Accuracy of Moving-Bomb Calorimetry

S. SUNNER and L. BJELLERUP

Institute of Chemistry, University, Lund, Sweden

In bomb calorimetry it is usually possible to obtain a very high reproducibility within a series of determinations made with the same apparatus and in accordance with the same method. A comparison between values of heats of combustion as measured by different methods (apparatus) often reveals differences between the values obtained. We have determined heats of combustion of compounds containing halogens or sulfur using two different calorimeters both with moving bombs, one designed for the combustion of halogen compounds and the other for sulfur-containing substances. These two apparatuses have now been compared, using the same substances both for calibration (benzoic acid) and measuring experiments (paraffin oil). In this way we have been able to estimate the influence from such systematic errors, which are of different order of magnitude in the two apparatuses and which appear, when burning substances containing carbon, hydrogen and oxygen. Specific systematic errors arrising from the presence of halogen or sulfur are not possible to discover by a direct comparison and will not be treated in this communication.

There is also a particular reason for a comparison of the two methods. In accordance with Washburn's suggestion[1], the Permanent Committee on Thermochemistry of the International Union of Chemistry recommended the use of standardized experimental conditions[2]. When burning halogen- or sulfur-containing substances, one essential factor has to be changed, *viz.* the amount of liquid introduced into the bomb. The Committee recommends 3 ml of water per litre of bomb volume; for halogen compounds we have been forced to use between 70—110 ml and for sulfur compounds 35 ml per litre of bomb volume. Therefore, in the treatment of the Washburn corrections the heat of solution of carbon dioxide becomes of paramount importance. This correction has to be calculated indirectly. This way of calculation together with the difference in magnitude of the CO_2-correction for the different methods rendered it especially desirable to compare corrected values of the heat of combustion obtained by the two methods on the same sample of a suitable substance.

APPARATUS AND METHOD

The accurate determination of heats of combustion of compounds containing halogen or sulfur requires a change in construction of the usual type of bomb calorimeter. The main reason for this change is that the final state, after the combustion is completed, has to be uniform, *i. e.* thermodynamically defined, otherwise it is not possible to compute the heat of combustion under standard conditions.

Chlorine-containing compounds give about 20—30 % free chlorine and 70—80 % hydrogen chloride as combustion products. By the method of Berthelot a solution of arsenic trioxide is introduced into the bomb and the chlorine will be reduced to HCl, so that the final state will be made up of a diluted hydrochloric acid containing hydrated arsenic trioxide and pentoxide.

However, the reduction could not be quantitative until Smith introduced the quartz-wool method [3]. Here, the surface between the liquid and gaseous phase is greatly increased and the reduction is rapid and complete. In stationary combustion bombs the concentration of the HCl will be different in different parts of the bomb.

Substances containing bromine give about 96 % free bromine and 4 % HBr. Owing to the great quantity of free bromine present, the quartz-wool method is not suitable for the complete reduction of the bromine in this case, and bromo-compounds have hitherto not been burned with modern precision in stationary-bomb systems.

Organo-sulfur substances give sulfuric acid of different concentration in different parts of the bomb. For calorimeters with stationary bombs this causes an appreciable error due to the great heat of dilution of sulfuric acid.

Calorimeters with rotating bomb systems will overcome the difficulty resulting from ill-defined final states. Several such calorimeters have been constructed (Popov and Shirokich [4], Smith and Sunner [5], Sunner [6], Smith and Bjellerup [7], Sunner [8]). Common to all of them is the fact that the bomb liquid will wash the inside of the bomb more or less thoroughly and that they must work with rather much liquid in the bomb.

A uniform final state is reached and the heat evolved, $-\Delta E_B$, when the reaction between the following initial and final states takes place, may be determined with a reproducibility of about 0.01 %:

A. Actual bomb process:

I. *Initial state* (at the initial temperature 20.00 °C):

1. The substance in liquid or solid state under a pressure of 30 atm of oxygen.

2. Bomb liquid, which is water (organo-sulfur substances) or a solution of arsenic trioxide in water (for halogen compounds) under a pressure of 30 atm of oxygen. The gas-phase is saturated with water vapor.

3. Oxygen, compressed to 30 atm. The bomb liquid is saturated with oxygen.

II. *Final state* (at the final temperature, 21.00 or 21.35° C):

1. The gas-phase contains the excess of oxygen, part of the carbon dioxide and water vapor.

2. The liquid phase is composed of a diluted sulfuric or halogen acid with dissolved carbon dioxide and oxygen in equilibrium with the gases at their respective partial pressures in the gas phase. In experiments with halogen-containing substances the bomb liquid will also contain a mixture of arsenious and arsenic acids. However, the thermochemically most valuable reaction takes place between the following states (the heat of combustion with the substances in their standard states, $-\Delta Hc^{\circ}_{293.16}$).

B. Idealized process (occuring at a constant temperature of 20.00 °C and at a constant pressure of 1 atm of both reactants and reaction products):

$$C_aH_bO_cX_d \text{ (sol or liq)} + (a + b/4 - c/2)\ O_2 \text{ (gas)} \rightarrow$$
$$\rightarrow aCO_2 \text{ (gas)} + b/2\ H_2O \text{ (liq)} + d/2\ X_2 \text{ (liq or gas)};$$
$$C_aH_bO_cS_d \text{ (sol or liq)} + (a + b/4 - c/2)\ O_2 \text{ (gas)} \rightarrow$$
$$\rightarrow aCO_2 \text{ (gas)} + b/2\ H_2O \text{ (liq)} + dS \text{ (rhomb.)}$$

In order to transform process A into process B the following corrections must be made:

1. The Washburn corrections. Washburn calculated the different corrections which have to be applied for the transformation of the actual bomb process into the idealized process for substances containing carbon, hydrogen and oxygen [2].

For compounds containing halogen or sulfur in addition, it is possible to recalculate the Washburn corrections to a final state consisting of pure carbon dioxide at 1 atm pressure and a diluted acid (halogen or sulfuric acid) of the actual concentration under 1 atm pressure.

2. Corrections for the heat of formation of the diluted acid from free halogen or sulfur, water and oxygen according to the equations:

$$(n+1)\ H_2O\ (liq) + X_2\ (gas\ or\ liq) \rightarrow 2HX,\ nH_2O\ (liq) + 1/2\ O_2\ (gas)$$
$$(n+1)\ H_2O\ (liq) + S\ (rhomb) + 3/2\ O_2\ (gas) \rightarrow H_2SO_4,\ nH_2O\ (liq)$$

These corrections are calculated either from combustion experiments (sulfur, Sunner[8]) or from data in the literature (halogens). A detailed calculation of the corrections applied for sulfur compounds is given elsewhere (Sunner[8]).

When burning substances containing halogen or sulfur, about 10 to 30 times as much bomb liquid has been used, as recommended by the Permanent Committee on Thermochemistry. (The amount of substance and the oxygen pressure may be chosen according to the recommendations.) The recalculation of the Washburn corrections to the actual conditions valid for compounds containing halogen or sulfur, shows that the heat of solution of carbon dioxide is by far the most important correction term. With 10 ml of bomb liquid in a bomb of 280 ml volume, this correction lies between 7 and 5 cal and with 30 ml of bomb liquid the correction lies between 19 and 14 cal depending on the amount of carbon dioxide formed during the combustion.

Therefore, it was found conveniant to treat this correction separately. The solubility of carbon dioxide in liquids of proper compositions was determined in a range of conditions actually found in the combustion experiments and at different temperatures. The molar heat of solution of carbon dioxide was calculated from the solubility data at different temperatures. The weight of substance burned gave the number of moles of carbon dioxide formed, and from this value the pressure was deduced. The amount of carbon dioxide dissolved was calculated and thus the heat of solution was found.

The accuracy of the calculation of the heat of solution is difficult to estimate. However, the fact that, when burning bromo-compounds we use 30 ml of bomb liquid and, when burning sulfur compounds, we use only 10 ml of liquid in the bomb made it possible to check the usefulness of the correction method.

The magnitude of the correction depends on the amount of carbon in the substances burned and the amount of liquid in the bomb. The carbon content ranges between 50 milliatoms of carbon (aromatic compounds) down to about 30 milliatoms (pure alifatic substances). The heat equivalents of our calorimeters have been determined by burning benzoic acid which has a high carbon content. The correction for dissolved carbon dioxide has thus a high value. We have then burned the same paraffin oil corresponding to about 30 milliatoms of carbon. Here the correction is about 75 % of the correction in the case of benzoic acid. If the calculations of the corrections for the heat of

Table 1.

Investigator	L. B. (L. Bjellerup)	S. S. (S. Sunner)
Apparatus	A modification of the apparatus described by Smith and Bjellerup[7] *)	Described by Sunner[8]
Temperature of the environment	Constant 21.3 ± 0.001 °C	Constant 21.6 ± 0.001 °C
Bomb	Two-parted, Pt-lined 275 ml volume	Two-parted, Pt-lined 282 ml volume
Bomb liquid	30 ml 0.062-molar As_2O_3	10 ml pure water
Temperature reading system	See Sunner[8]	ditto
Temperature increase	20.00—21.00 °C	20.00—21.35 °C
Length of main period	21 min.	10 min.
Heat equivalent	4 700 cal/°C	3 900 cal/°C
Correction for the formation of HNO_3	1—2 cal	7—9 cal
Heat exchange correction in % of the total heat evolved	1.1	0.8
The isothermal combustion given at	20.00 °C	20.00 °C
Heat of solution of carbon dioxide per mole of CO_2 in N normal acid (HBr or H_2SO_4)	4 600 cal 0 to 0.15 N HBr 0.25 to 0.10 N As_2O_3 0 to 0.15 N As_2O_5	4 550 cal 0 to 1.2 N H_2SO_4
Solubility of carbon dioxide in mole per ml of bomb liquid and per atm pressure	3.72×10^{-5} 0 to 0.15 N HBr 0.25 to 0.10 N As_2O_3 0 to 0.15 N As_2O_5 at 21.0_0 °C	$(3.75-0.35n+0.07n^2) \times 10^{-5}$ $0 \leq n \leq 1.2$ at 21.3_5 °C

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* A detailed description will be published later.

solution of carbon dioxide were significantly erroneous, the heats of combustion of the paraffin oil obtained with the two methods should be different.

The desired accuracy of the heats of combustion, 1 part in 10 000, will be diminished if the systematic errors in the heat of solution of carbon dioxide exceed about 10 %. A random error of 1 % gives rise to a discrepancy in the heat of combustion of paraffin oil of about 3 parts in 10 000.

It has, of course, not been possible to check the two methods against each other by burning compounds containing bromine or sulfur. However, the solubility of carbon dioxide in diluted sulfuric acid or diluted hydrobromic acid in arsenious-arsenic acids is about the same as in pure water and arsenious acid respectively. It therefore seems probable, that errors introduced with bromine or sulfur are negligible regarding the over-all accuracy of the correction in question.

The two methods are compared in Table 1.

In the halogen-apparatus the inner lid is made of ebony: this explains why the main period is so long as 21 minutes. The quantity of nitric acid formed is several times greater in the sulfur-apparatus. The presence of a certain amount of nitrogen is necessary when burning sulfur-containing substances otherwise the oxidation to sulfuric acid will not be complete. The gas phase therefore contains 2.6 % nitrogen in this case, which explains the rather high HNO_3-correction.

Both calorimeters were placed in the same room with constant temperature, 21.3 °C. They were operated independently, one by Bjellerup (for halogen) and the second by Sunner (for sulfur).

EXPERIMENTAL

Table 2 gives data on the combustion of benzoic acid and paraffin oil. The determinations in Table 3 and 4 (L. B.) were done between August 1949 and September 1950 and the determinations in Table 5 and 6 were completed in February 1949 (from Sunner[8]; for paraffin oil the values had to be recalculated owing to the use of an erroneous value of the density of the oil).

The amounts of benzoic acid differ, due to different net bomb volumes, but are in accordance with the recommendation given by the Permanent Committee on Thermochemistry. The results in Tables 4 and 6 are in very good agreement, better than 1 part in 10 000. The standard deviation of the mean is calculated to 0.7 cal (L. B.) and to 0.4 cal (S. S.) and the difference between the paraffin oil values is thus negligible.

Table 2.

Investigator	L. B.	S. S.
Benzoic acid	N. B. S. lot 39 f	The same sample
Amount of benzoic acid	734 mg	822 mg
Amount of carbon in the benzoic acid	42 milliatoms	47 milliatoms
Correction for the heat of solution of carbon dioxide	19.2 cal	6.9 cal
Washburn corrections * (Wc)	2.5 cal	3.3 cal
Paraffin oil	b. p. ≥ 150 °C at 0.3 mm Hg	The same sample
Amount of paraffin oil	425 mg	474 mg
Amount of carbon in the paraffin oil	30 milliatoms	33 milliatoms
Correction for the heat of solution of carbon dioxide	14.0 cal	5.1 cal
Washburn corrections * (Wc)	0.5 cal	0.8 cal

* Exclusive the correction for dissolved carbon dioxide.

Table 3. Benzoic acid. (L. B.)

$S_F = 0.4$ cal/I. U.*

Determination Nr.	Mass of sample mg	ΔT (corr) I. U.	Corr. ** cal	*Wc* cal	CO_2 cal	S_B^0 cal/I. U.
135	734.58	0.99413	20.5	2.5	19.2	4707.7
137	733.19	0.99202	19.9	2.5	19.2	4708.3
136	734.04	0.99289	19.0	2.5	19.2	4708.7
140	734.50	0.99384	20.8	2.5	19.2	4708.9
139	735.08	0.99438	20.5	2.5	19.2	4709.7
138	733.40	0.99144	17.6	2.5	19.2	4710.0

Mean: 4 708.9 cal/I. U.

Table 4. Paraffin oil. (L. B.)

Determination Nr.	Mass of sample mg	$S_B + S_F$ cal/I. U.	ΔT (corr) I. U.	Corr. ** cal	*Wc* cal	CO_2 cal	$-\Delta Ec^0_{293.16}$ cal/g
132	424.65	4709.7	0.99644	18.5	0.5	13.9	10 973.7
219	424.74	4709.6	0.99711	20.6	0.5	13.9	10 973.8
217	424.28	4707.5	0.99652	20.4	0.5	13.9	10 974.6
133	425.16	4709.7	0.99824	20.2	0.5	14.0	10 976.3
134	424.91	4709.7	0.99709	17.3	0.5	13.9	10 977.1

Mean: 10 975.1 cal/g

* I. U. = interval unit = temp.diff. between the 1.97 and 2.97 scale divisions on the Beckmann thermometer.

** Heat of combustion of cotton thread and heat of formation of HNO_3.

Table 5. Benzoic acid. (S. S.)

$S_F = 0.6$ cal/I. U. *

Determination Nr.	Mass of sample mg	ΔT (corr.) I. U.	Corr. ** cal	*Wc* cal	CO_2 cal	S_B^0 cal/I.U.
10	821.16	0.99493	19.7	3.3	6.9	5 246.2
7	822.53	0.99526	18.6	3.3	6.9	5 246.8
9	822.63	0.99530	18.3	3.3	6.9	5 246.9
5	823.28	0.99632	19.6	3.3	6.9	5 247.0
8	822.58	0.99543	19.5	3.3	6.9	5 247.1

Mean: 5 246.8 cal/I. U.

Table 6. Paraffin oil. (S. S.)

$S_B + S_F = 5\,247.6$ cal/I. U. *

Determination Nr.	Mass of sample	ΔT (corr.) I. U.	Corr. ** cal	*Wc* cal	CO_2 cal	$-\Delta Ec^0_{293.16}$ cal/g
5	473.56	0.99536	19.8	0.8	5.1	10 975.3
3	473.50	0.99553	21.3	0.8	5.1	10 975.4
4	473.63	0.99573	20.9	0.8	5.1	10 975.6
2	474.48	0.99750	20.6	0.8	5.1	10 976.2
6	473.86	0.99560	17.0	0.8	5.1	10 977.0

Mean: 10 975.9 cal per g mass ***.

* I. U. = interval unit = temp.diff. between the 0.75 and 2.10 scale divisions.

** Heat of combustion of cotton thread, heat of formation of HNO_3 and HNO_2.

*** A redetermination of the heat of combustion of the same paraffin oil with this calorimeter gave a mean of 10 975.6 cal per g mass (Mr B. Lundin).

SUMMARY

When using moving-bomb calorimeters for the determination of heats of combustion for substances containing halogen or sulfur, in addition to carbon, hydrogen and oxygen, two kinds of systematic errors will appear: one of a specific character depending on the presence of halogen or sulfur, and another of a general character which will cause erroneous results for all substances burned. The practical importance of the last type of errors in methods currently used in this laboratory has been investigated by comparing results from two different, independently operated moving-bomb calorimeters. The heat-equivalents were determined with N.B.S. benzoic acid, and paraffin oil was used for comparison. The mean values of the heat of combustion of the paraffin oil were found to be 10 975.1 and 10 975.9 cal per g mass. The difference is less than the sum of the standard deviations of each series, 1.1 cal. It seems therefore justified to assume that general systematic errors do not influence the accuracy of our methods.

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