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ALUMINUM**

By
Charles E. Holley, Jr.
Elmer J. Huber, Jr.

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CHEMISTRY

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THE HEAT OF COMBUSTION OF MAGNESIUM AND ALUMINUM*

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By Charles E. Holley, Jr. and Elmer J. Huber, Jr.

ABSTRACT

Precise measurements of the heats of combustion of magnesium and aluminum have been made. The apparatus used, an oxygen bomb calorimeter of rather standard design, is briefly described. For precise work it was necessary to correct for the electrical energy used in firing the charge and to determine the completeness of the combustion. The latter was done by treating the combustion products with acid and measuring the hydrogen evolved.

The results are: for magnesium, heat of combustion in 25 atm. oxygen = 5896.0 ± 3.6 cal/gram; heat of formation of MgO , $\Delta H_{299^\circ K} = -143.73 \pm 0.09$ kilocal/mole; for aluminum, heat of combustion in 25 atm. oxygen = 7405.6 ± 5.2 cal/gram; heat of formation of Al_2O_3 , $\Delta H_{299^\circ K} = -400.41 \pm 0.28$ kcal/mole.

A comparison of these results with those of other investigators is made.

Introduction: In connection with work on the heats of formation of the oxides of some of the rare earth elements and of some of the elements of high atomic number it was decided to set up an oxygen bomb calorimeter. Experiments were run on magnesium and aluminum to test the apparatus and to gain experience in its use. We believe the results obtained on these two metals are sufficiently interesting to be worth reporting.

There are little precise data in the literature on the heat of formation of magnesium oxide. Shomate and Huffman¹, on the basis of heats of solution in 1N

1. C. H. Shomate and E. H. Huffman, J. Am. Chem. Soc. 65, 1625(1943)

hydrochloric acid give $\Delta H_f = -143.84 \pm 0.05$ kcal/mole. Moose and Parr² by dir-

2. J. E. Moose & S. W. Parr, J. Am. Chem. Soc., 46, 2656(1924)

ect combustion find $\Delta H_f = -146.1 \pm 0.3$ kcal/mole. As can be seen, these two results are not in complete agreement. Earlier work was lacking in precision.

In the case of aluminum oxide there are many precise results given in the literature which disagree widely among themselves. The situation is discussed critically by Snyder and Seltz³. The two best values seem to be those of Snyder

3. P. E. Snyder and H. Seltz, J. Am. Chem. Soc. 67, 683(1945)

and Seltz³ who got $\Delta H_f = -399.04 \pm 0.24$ kcal/mole and Roth, Wolf, and Fritz⁴

4. W. A. Roth, U. Wolf, and O. Fritz, Z. Elektrochem 46, 42(1940)

who got $\Delta H_f = -402.9 \pm 0.4$ kcal/mole.

Method: The method was to burn a weighed sample of the metal in question in an atmosphere of oxygen of known pressure and to measure the amount of heat evolved and the completeness of combustion. The amount of heat evolved was determined by having the reaction take place in a calibrated calorimeter and measuring the temperature rise. The completeness of combustion was determined by treating the combustion products with 6N hydrochloric acid and measuring the amount of hydrogen evolved from any unburned metal present.

Apparatus: The combustion bomb was a Parr oxygen bomb in which the electrodes were replaced with shorter platinum electrodes. In the end of each was a

small hole in which the fuse wire was held by a platinum peg. On the outside of the bomb a heater was wound of #26 Advance wire and cemented in place. The calorimeter can was provided with a lid made of silver sheet.

A convection shield made of 0.005 in. silver sheet was provided as recommended by White⁵. By its use the distance between calorimeter and thermostat could

5. W. P. White, The Modern Calorimeter, The Chemical Catalog Co., Inc., New York 1928, p. 169.

be increased to 3 cm. The calorimeter can was completely surrounded, including top and bottom, by the convection shield.

The water thermostat was a covered copper vessel containing approximately 70 liters of water. The temperature was maintained constant to $\pm 0.005^{\circ}\text{C}$ at about 27°C . The water thermostat was enclosed in an air thermostat in which the temperature was maintained at $25^{\circ} \pm 0.5^{\circ}\text{C}$.

The temperature of the calorimeter was measured to 0.001°C with a precision platinum resistance thermometer and a L & N Type G-2 Mueller Bridge. The resistance thermometer was calibrated by comparing it at several temperatures with a standard resistance thermometer which had been calibrated by the National Bureau of Standards.

The heater wound on the bomb was used for the electrical calibration. The voltage was measured directly by means of a volt box and a Rubicon Type B potentiometer. The potential leads were placed outside the convection shield but as close to it as possible. The current was determined by measuring the potential drop in a precision 0.1 ohm resistor. The time of heating was measured by counting the cycles of a precision 60 cycle tuning fork with a scaling circuit run off the output of the fork. A special switch turned heater and counter on and off simultaneously.

The electrical energy used in igniting the fuse wire was determined by measuring the resistance of the firing circuit, the resistance of the fuse wire, the voltage of the batteries, and the time during which the current was on.

The oxygen, furnished by Linde Air Products Corp. as at least 99% O₂ was treated to remove any traces of combustible gases by passing over heated palladized asbestos followed by a drying train. The atmospheric nitrogen in the bomb was removed by flushing with the purified O₂. All runs were made at 25 atm. O₂ pressure.

Units and Precision: The results of this work are expressed in absolute joules. For purposes of comparison with the older literature the results are also expressed as calories using the definition 1 calorie = 4.1840 absolute joules.

The unit of mass is the gram mass in vacuo. The materials to be burned were weighed to the nearest 0.0001 gram. The water for the calorimeter was weighed to the nearest 0.01 gram.

In accordance with the recommendations of Rossini and Deming⁶ the uncertain-

6. F. D. Rossini and W. E. Deming, J. Wash. Acad. Sci. 29, 416(1939)

ty interval attached to the final average value is taken as twice the standard deviation.

Calibration of the Calorimeter: The calorimeter was calibrated electrically and with benzoic acid. The two methods gave substantial agreement. By the electrical method the water equivalent of the calorimeter filled with oxygen to 25 atm. and based on 15 runs, was 10,092.4 $\pm$ 5.0 absolute joules/degree C where the uncertainty given includes the uncertainties in the measuring instruments as well as the uncertainty due to random errors.

For the benzoic acid calibration a small platinum cup was gold-soldered to one of the electrodes to hold the benzoic acid pellet. This platinum had a calculated water equivalent of 1.3 joules/degree C. In addition, 1 ml water was added to the bomb, which contributed 4.2 joules/degree C to the water equivalent. And, the water equivalent of the combustion products minus the oxygen used up was calculated to be 0.9 joules/degree C based on the use of 0.46 gram benzoic acid. Thus 6.4 joules/degree C should be subtracted from the water equivalent determined with benzoic acid to obtain the water equivalent of the calorimeter itself.

The benzoic acid used was NBS sample 39f which had a certified calorific value of $26,428.4 \pm 2.6$ international joules/gram mass when burned under the specified conditions. Using the factor given on the certificate and converting to absolute units, the calorific value of this benzoic acid was calculated to be $26,427.6 \pm 2.6$ absolute joules per gram mass when converted to the conditions in our bomb, specifically 25 atm. oxygen, approximately 0.46 gram sample of benzoic acid, 1 ml water, initial temperature 24.6°C , final temperature approximately 25.8°C .

Combustion of the benzoic acid was complete as determined by the absence of carbon particles in the platinum cup.

The results of the 12 runs made with benzoic acid are summarized in Table I.

Table I

Benzoic Acid Calibration of Calorimeter

Benzoic Acid grms mass	Firing Energy joules	Fuse Wire energy joules	Temp. Rise °C	Water Equiv. joules/°C	Dev. fr Mean joules/°C
0.4089	27.2	100.4	1.082	10,105.2	3.0
0.4293	6.7	52.7	1.128	10,110.6	8.3
0.4292	9.6	64.4	1.130	10,103.3	1.0
0.4602	49.4	54.8	1.213	10,112.3	10.0
0.4730	10.9	61.1	1.244	10,106.4	4.1
0.4611	9.6	53.6	1.213	10,098.1	4.2
0.4522	39.7	76.1	1.194	10,105.9	3.6
0.4681	27.2	97.9	1.238	10,093.6	8.7
0.4807	25.5	91.6	1.270	10,095.1	7.2
0.5312	8.9	97.9	1.399	10,110.9	8.6
0.4593	7.9	40.2	1.208	10,088.0	14.3
0.4712	12.1	97.1	1.244	10,098.0	4.3
Ave. =				10,102.3	6.4

When the 6.4 joules/deg. C mentioned above were subtracted from this average value and the uncertainty due to the certified value of the benzoic acid was taken into consideration the final value for the water equivalent of the calorimeter was $10,095.9 \pm 3.8$ absolute joules/degree C. This is in satisfactory agreement with the electrical value. Since the conditions prevailing in the benzoic acid experiment were more nearly like those in the combustion of aluminum and magnesium, the benzoic acid value is used in the subsequent calculations.

The Combustion of Magnesium: Doubly distilled magnesium from the Dow Chemical Company was used. The chief metallic impurity was silicon, present to less than 0.01% and the overall purity was at least 99.98%. Of the non-metallic impurities analysis was made for nitrogen and 0.004% was found. The oxide layer present was removed with dilute hydrochloric acid. A piece of Mg thus cleaned was kept in dry oxygen at 25 atm. for a few hours without gaining as much as 0.1 mg in weight.

The magnesium was used in the form of chunks, .010 in. ribbon, ^{and} .010 in. wire. The wire was ignited electrically, it ignited the ribbon which in turn ignited the chunk. The combustion took place on a disc of sintered magnesium oxide supported

on a platinum cup which weighed 37.6 grams. Preliminary experiments showed that combustions taking place on powdered magnesium oxide gave low results. Since the disc cracked during each combustion a new one was used each time. The total water equivalent of the calorimeter as used was computed by taking account of the disc, the platinum, and the difference in water equivalents between the magnesium oxide formed and the oxygen used up. The initial temperature was 24.6°C and the average final temperature was 25.9°C. Fifteen runs were made and they are summarized in Table II. The final average value for the heat of combustion of magnesium, taking into account the uncertainty in the water equivalent, is $24,669 \pm 15$ absolute joules/gram or 5896.0 ± 3.6 cal/gram.

Table II

Heat of Combustion of Magnesium

Mg gms mass	% Burned	Firing Energy joules	Temp. Rise °C	Energy from Mg joules/gram	Dev. from mean joules/gram
.5632	99.92	16.3	1.373	24,674	5
.5500	99.78	15.5	1.338	24,658	11
.5319	99.98	10.9	1.298	24,667	2
.5287	99.95	11.3	1.289	24,662	7
.5866	99.98	18.0	1.429	24,620	49
.5372	99.95	12.5	1.311	24,683	14
.5900	99.90	13.4	1.442	24,726	57
.4243	99.99	23.4	1.037	24,677	8
.4585	99.86	32.4	1.117	24,611	58
.6065	99.99	17.1	1.481	24,684	15
.5784	99.98	15.9	1.413	24,690	21
.5056	99.88	19.6	1.232	24,647	22
.4583	99.98	17.5	1.119	24,672	3
.4522	99.86	13.4	1.105	24,727	58
.5441	99.94	15.1	1.326	24,643	26
Ave. =				24,669	24

The Heat of Formation of MgO: The heat of combustion reported above gives a value of $\Delta E = -599.95$ kilojoules/mole for the reaction in the bomb. To get the heat of formation ΔH_f we have to correct for the deviation of oxygen from the perfect gas law and convert from ΔE to ΔH . According to Rossini and

Frandsen⁷ the value of $\left(\frac{\Delta A E}{\Delta P}\right)_{301^{\circ}\text{K}}$ for oxygen is -6.51 joules/atm./mole. Using

7. F. D. Rossini and M. Frandsen, J. Res. Natl. Bur. Standards **2**, 733(1932)

this value and taking $\Delta H = \Delta E + \Delta(PV)$ we have for the heat of formation of MgO , $\Delta H_{299^{\circ}\text{K}} = -601.31$ absolute kilojoules/mole. The uncertainty to be attached to this value, including the uncertainty in the water equivalent, is ± 0.37 absolute kilojoules/mole. In defined calories this is $\Delta H_{299^{\circ}\text{K}} = -143.73 \pm 0.09$ kcal/mole.

This value is in agreement with the -143.84 ± 0.05 kcal/mole obtained by Shomate and Huffman¹ from heats of solution in 1N hydrochloric acid. It differs appreciably from the -146.1 ± 0.3 kcal/mole obtained by Moose and Parr² which is the only precise value we have found in the literature obtained by direct combustion.

The Heat of Combustion of Aluminum: The aluminum used was furnished by the Aluminum Company of America and was nominally 99.9968% aluminum. A portion of the 0.005 in. sheet used was analyzed for nitrogen, carbon, and oxygen and the findings were 0.002% N, 0.03% C and 0.01% O.

Aluminum is difficult to ignite and it does not always burn completely, sometimes throwing off portions of material which cease to burn on hitting a cold surface. The main part of the sample consisted of 0.005 in. sheet. The use of a few milligrams of 0.001 in. sheet facilitated ignition of the main mass. A magnesium fuse wire 0.010 in. in diameter was used to ignite the 0.001 in. sheet. The combustion took place on an alumina disc surrounded by an alumina cylinder with a cover also of alumina. To permit free access of oxygen, holes were made in this cylinder and guarded by a larger concentric alumina cylinder. The assembly was supported on a platinum platform weighing 108.1 gm. In this

manner any material thrown out in the combustion was captured. As in the case of magnesium, new alumina parts had to be used for each run, and in each case the water equivalent was corrected correspondingly. The initial temperature was 24.6°C and the average final temperature was 26.0°C. Sixteen runs were made and they are summarized in Table III. The final average value for the heat of combustion of aluminum, taking into account the uncertainty in the water equivalent, is $30,985 \pm 22$ absolute joules/gram or 7405.6 ± 5.2 cal/gram.

Table III

Heat of Combustion of Aluminum

Al gm mass	% Burned	Energy from Firing plus Mg wire joules	Temp. Rise °C	Energy from Al joules/gram	Dev. fr mean joules/gram
.4012	99.97	185.8	1.249	31,094	109
.4309	99.88	156.9	1.331	30,980	5
.4344	99.84	167.6	1.344	31,023	38
.4419	99.36	139.2	1.355	30,959	26
.4328	99.95	185.1	1.340	30,965	20
.4519	99.91	171.4	1.395	30,937	48
.4718	99.98	164.7	1.460	31,018	33
.4543	99.96	182.6	1.404	30,933	52
.4686	99.94	172.2	1.450	31,010	25
.4718	99.75	179.6	1.456	30,975	10
.4731	99.94	173.9	1.462	30,968	17
.4698	99.95	178.8	1.457	31,064	79
.4651	99.96	196.6	1.441	30,988	3
.4891	99.92	175.5	1.509	30,932	53
.4886	99.98	182.9	1.509	30,929	56
.3316	99.96	183.3	1.032	30,985	0
Ave. =				30,985	36

The Heat of Formation of Al_2O_3 : The heat of combustion reported above gives a value of $\Delta E = -1671.3$ kilojoules/mole for the reaction in the bomb. Converting to ΔH of formation in the same manner as described above we find $\Delta H_{299^\circ K} = -1675.3 \pm 1.2$ absolute kilojoules/mole. In calories, this is -400.41 ± 0.28 kcal/mole.

This value differs by about 0.3% from the value obtained by Snyder and Seltz³ and by 0.6% from the value obtained by Roth, Wolf, and Fritz⁴.

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