

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Heat of Formation of Aluminum Oxide

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Introduction

The heat of formation of aluminum oxide is an important thermodynamic value in various metallurgical and industrial calculations. A survey of the literature shows, however, that a wide variation exists in the values reported by different investigators. A summary of these researches is given in Table I. It will be observed from the table that while the estimated precision of the five more recent measurements is never more than $\pm 0.4\%$, the maximum divergence in these values is nearly 7%, and Roth's three values over a period of eleven years show a range of 22 kilocalories in approximately 400 kilocalories. All of the values listed in Table I were obtained in bomb calorimeters, and an explanation of the wide deviations among them must be sought.

Apparatus.—In this study, use was made of the isothermal bomb calorimeter. The calorimeter itself was the one used by the Coal Research Laboratories of the Carnegie Institute of Technology in their determination of the heat of combustion of graphite.⁸ This instrument was patterned after the one used by Dickinson at the Bureau of Standards.⁹ The volume of the bomb empty was 355 ml. With the crucible in place the effective gas volume was 279 ml. The water jacket surrounding the calorimeter was kept constant to within $\pm 0.001^\circ$ by means of a metal toluene regulator having a low thermal lag.¹⁰ This regulator was used in conjunction with an electronic relay¹⁰ which controlled the bath heating system.

The temperature rise of the calorimeter was measured by means of a calorimetric platinum resistance thermometer and a Leeds and Northrup G-1 "Mueller" bridge. To calibrate the thermometer, two primary fixed points were used, the ice and the steam point. The secondary sodium sulfate point was used to determine the "delta" value. These are defined as: (1) the temperature of equilibrium of ice and air-saturated water at 760 mm. pressure, 0.000°

TABLE I

Worker	Date	Purity of Al, %	% Combustion	Type of crucible	Ignition aids used	Form of metal	Heat of formation of Al ₂ O ₃ , kcal./mole	Precision, %
Berthelot ²	1901	99.6	100% probably	Unknown	Camphor	Foil	380.2	
Wartenberg and Witzel ³	1919	95.0	100	Unknown	Collodion	Powder	396.0	± 0.4
Moose and Parr ⁴	1924	98.37	Above 99	Alundum	None	Powder	375.8	± 0.2
Roth and Muller ⁵	1929	99.83	Above 98	Clay	Cotton thread and	Powder	380.8	± 0.4
Meichener and Roth ⁶	1934	99.83	Above 92	Alundum	vaseline	Powder	393.3	± 0.4
Roth, Wolf and Fritz ⁷	1940	99.83	Above 95	Alundum	Cellophane	Powder	402.9	± 0.3

Aside from systematic errors, several possible sources of the discrepancies are: (a) use of impure aluminum; (b) fluxing of the molten Al₂O₃ with the crucible material; (c) use of ignition aids; (d) difference between calibration and aluminum combustion conditions; (e) incomplete combustion.

In the investigation here described every effort was made to eliminate the sources of error and uncertainly believed to exist in the earlier works. The aluminum used was in the form of high purity foil, instead of powder, to minimize surface pre-oxidization. High grade zircon crucibles, lined with a heavy layer of pure Al₂O₃, were used. No ignition aids, aside from the usual iron wire fuse, were used, and complete combustion was achieved in all except two runs. The calibration of the calorimeter with benzoic acid was performed with the crucible in the bomb similar to the actual aluminum combustion.

(1) Abstracted from a thesis presented by Paul E. Snyder to the Graduate Committee of the Carnegie Institute of Technology, in partial fulfillment of the requirements for the Degree of Doctor of Science, May, 1944.

(2) Berthelot, *Ann. Chim. Phys.*, [7] **22**, 479 (1901).

(3) Wartenberg and Witzel, *Z. Elektrochem.*, **25**, 209 (1919).

(4) Moose and Parr, *THIS JOURNAL*, **46**, 2656 (1924).

(5) Roth and Muller, *Z. Physik. Chem.*, **A144**, 253 (1929).

(6) Meichener and Roth, *Z. Elektrochem.*, **40**, 19 (1934).

(7) Roth, Wolf and Fritz, *ibid.*, **46**, 42 (1940).

C.; (2) the temperature of equilibrium between liquid water and its vapor at 760 mm. pressure, 100.000°C.; (3) the temperature of transition of Na₂SO₄·10H₂O at 760 mm. pressure, 32.384°C.

The ice-point was obtained by means of the cold cell described by White.¹¹ The operation of such a cell was found to be entirely satisfactory; the constancy of resistance of the thermometer between several renewals of water in the cell did not exceed 0.00001 ohm. The resistance of the thermometer at this temperature was approximately 25.0 ohms.

In the determination of the steam-point, use was made of a hypsometer described by Mueller and Sligh.¹² Here again the performance of the apparatus was excellent. The fundamental interval of the thermometer as obtained from these two primary points in one series of twelve determinations of the steam-point showed a probable error of 0.00004 ohm out of approximately 10.0 ohms. Two values of the fundamental interval over a nine-month period were:

Date	F. I.
12/9/41	9.94677 ohms
9/2/42	9.94674 ohms

Since the transition temperature¹³ of Na₂SO₄·10H₂O was used to obtain the "delta" value of the thermometer, it was

(8) Harper, *J. Research Natl. Bur. Standards*, **21**, 457 (1938).

(9) Dickinson, *Bull. of Bur. of Standards*, **11**, 189 (1915).

(9a) Snyder and Seltz, *Ind. Eng. Chem., Anal. Ed.*, **17**, 126 (1945).

(10) Rudy and Fugassi, *ibid.*, **12**, 757 (1940).

(11) White, *THIS JOURNAL*, **56**, 20 (1934).

(12) Mueller and Sligh, *J. Opt. Soc. Am., Rev. Sci. Instruments*, **6**, 958 (1922).

(13) *Bull. Bur. of Standards*, **3**, 641 (1907).

necessary to purify the material used. The starting material was the c. p. salt. This was then recrystallized very carefully and the transition point determined. From the thermometer resistance so obtained, the "delta" value was then calculated. After this, the salt was purified again. In all, nine consecutive crystallizations were performed. After each recrystallization a redetermination of the "delta" value was made. The values so obtained kept increasing until the sixth purification, beyond which a constant "delta" was obtained.

The water placed in the calorimeter was weighed on a large torsion balance with a sensitivity of ± 0.05 mg. The mass of the sample to be burned was determined by using an Ainsworth balance to which was attached an optical pointer giving a magnification of twelve times over the mechanical pointer. By making use of double weighings combined with the method of swings, the mass of the sample could be obtained with a precision of ± 0.00001 g. The reference masses used in this weighing was a set of gold-plated class "S" weights. These were calibrated against a one-gram standard that had been certified by the Bureau of Standards.

Since, in precision calorimetry, the oxygen should be entirely free of combustible gases, a high-pressure purification train was used to accomplish this end. The arrangement was such that any hydrogen and hydrocarbons present were oxidized by palladized asbestos. The water and carbon dioxide formed, as well as that originally present, were removed by suitable absorbents. Carbon monoxide was removed by means of hopcalite.

Units.—In order to change from the international joule to calories, use is made of the definition, 1 calorie = 4.1833 international joules.¹⁴ The unit of mass is the "gram mass *in vacuo*" since all weighings were corrected for the mass of the displaced air in order to obtain the mass of the sample "*in vacuo*."

Precision of Results.—In calculating the precision of the results obtained, use was made of the procedure proposed by Rossini and Deming.¹⁵ In line with this recommendation fifteen experiments were performed in order to calibrate the calorimeter. Fifteen runs were likewise made in order to determine the heat of combustion of the aluminum sample.

Calibration of the Calorimeter.—In order to obtain the heat capacity of the calorimeter, it is necessary to use a calibrating substance. For this purpose, benzoic acid has been selected by the Standing Committee for Thermochemistry of the International Union of Chemistry.¹⁶ For this purpose, standard sample No. 39f was obtained from the Bureau of Standards. Its heat of combustion was reported by R. S. Jessup¹⁷ to be Q (under standard bomb conditions) = 26,428.4 \pm 2.6 international joules per gram mass.

One of the necessary conditions to be fulfilled in the use of Dickinson's graphical method is that the shape of the heating curve be the same in all experiments. To this end the weights of the several samples were adjusted to a value between 1.63 and 1.64 g. For a reason mentioned later, it was not possible to leave the heat obtained from the iron fuse as an integral part of the heat ca-

capacity of the bomb. Therefore, measurements were made with only the iron fuse in the calorimeter. It was found that the ignition and burning of the fuse (that is, the total firing energy) supplied 15.7 int. joules to the calorimeter. The observed heat capacity of the calorimeter was corrected to the standard bomb conditions as given by Jessup.¹⁷ Table II presents the results of the fifteen calibration experiments.

TABLE II
RESULTS OF CALIBRATION EXPERIMENTS

Expt.	Mass of sample, g.	Energy equivalent cor. to stand. cal., int. joule/°C.	Deviation from mean, int. joule/°C.
C-19	1.61594	14147.7	-19.7
C-20	1.63905	14162.7	-4.7
C-21	1.63322	14193.6	+26.2
C-22	1.63720	14157.0	-10.4
C-23	1.63534	14165.6	-1.8
C-24	1.62983	14181.9	+14.5
C-25	1.63560	14165.9	-1.5
C-26	1.63531	14169.6	+2.2
C-27	1.63362	14163.5	-3.9
C-28	1.63841	14146.2	-21.2
C-29	1.63690	14159.6	-7.8
C-30	1.63880	14187.7	+20.3
C-31	1.63782	14168.0	+0.6
C-32	1.63279	14169.6	+2.2
C-33	1.63768	14172.3	+4.9

Mean = 14167.4 \pm 6.8 int. joules/°C.

From the results given in Table II, the energy equivalent of the calorimeter was assigned the value of 14,167.4 international joules per degree centigrade temperature rise at a mean temperature of 25°C.

Combustion of Aluminum.—The aluminum foil used in this investigation was supplied by the Research Laboratories of the Aluminum Company of America. The metallic impurities consisted of Si, Fe, Cu, Mg, Ca, and Na. The aggregate amount of these amounted to 0.006%. In addition, it was estimated that the carbon amounted to 0.001%. The nitrogen content was not determined. The estimated thickness of the natural oxide film was such as to give an oxide content of 0.01%. Since the heat of combustion of the above combustibles is of the same order of magnitude as that for aluminum, only the oxide should be considered in obtaining the heat of combustion of the pure metal.

Since it was necessary to burn aluminum in a crucible protected by pure Al₂O₃, a number of crucibles were prepared beforehand in order to expedite the work. This meant that the weight of crucible and Al₂O₃ was different in each experiment. Therefore, it was necessary to correct the mean observed energy equivalent of the calorimeter for these weight differences in each combustion experiment. These corrected values are listed in column 3 of Table III.

It was found that aluminum is very hard to ignite, even in 40 atmospheres of oxygen. How-

(14) Mueller and Rossini, *Am. J. Physics*, **12**, 1 (1944).

(15) Rossini and Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

(16) Premier Rapport de la Commission Permanente de Thermochemie, Union Internationale de Chemie, Paris, 1934.

(17) Jessup, *J. Research Natl. Bur. Standards*, **29**, 247 (1942).

TABLE III
RESULTS OF Al COMBUSTION

	Mass of Al burned, g.	Actual val. of energy equivalent for use, int. joules/°C.	Heat of combustion of Al, int. joules/g.	Deviation from mean
Al-6	1.43476	14178.4	30861.4	- 6.7
Al-7	1.38432	14170.9	30853.5	-14.6
Al-8	1.39546	14188.7	30881.8	+13.7
Al-9	1.39222	14189.7	30863.3	- 5.0
Al-10	1.39516 ^a	14188.9	30883.0	+14.9
Al-11	1.39550	14192.3	30855.3	-12.8
Al-12	1.39560	14172.4	30854.3	-13.8
Al-13	1.39284	14186.4	30820.8	-47.3
Al-14	1.39416 ^b	14171.0	30900.4	+32.3
Al-15	1.39669	14166.9	30892.3	+24.2
Al-16	1.39410	14189.3	30886.5	+18.4
Al-17	1.39584	14178.9	30867.7	- 0.4
Al-18	1.39537	14153.9	30494.1	+26.0
Al-19	1.39558	14173.7	30848.5	-19.6
Al-20	1.39572	14160.2	30859.4	- 8.7

Mean = 30868.1 ± 11.1 int. joules

^a 0.00083 g. of Al was left after combustion. ^b 0.00146 g. of Al was left after combustion.

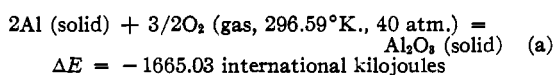
ever, by using two strands of iron fuse wire instead of one, ignition troubles disappeared. The firing energy correction was assumed in this case to be 31.4 int. joules.

Here again the aim was to have the same temperature rise as in the calibration experiments with the additional goal that the mean temperature be about the same as in the calibration runs. Therefore, the weight of the foil was adjusted to between 1.38 and 1.39 g.

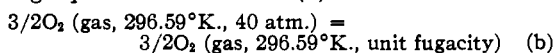
With two exceptions (see note under Table III) the aluminum foil burned completely. Neither visual nor chemical examination of the contents of the crucibles after combustion showed the presence of unburned aluminum. In the two exceptions a small particle of unburned foil was recovered which was readily weighed.

The results of the fifteen combustion experiments are given in Table III. This shows the mean heat of combustion of the aluminum foil to be 30,868.1 int. joules per gram at 23.43°C. under the conditions prevailing in the bomb.

Calculation.—Using 26.97 as the atomic weight of aluminum, there is obtained, from the heat of combustion per gram, the value of the energy change for the formation of the oxide. Thus, for the reaction



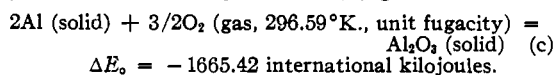
In order to obtain ΔE at unit fugacity, the following equation is added to (a)



From work done at the Bureau of Standards¹⁸ it

(18) Rossini and Frandsen, *J. Res. Natl. Bur. Standards*, **9**, 733 (1932).

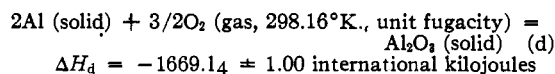
has been found that $(\partial E/\partial P)_{301^\circ\text{K.}}$ for oxygen is -6.51 joules per atmosphere per mole. Since the correction to change this value to 296.59°K. is negligible, then for equation (b) $\Delta E_b = 390.6$ joules. Combining (a) and (b) gives



To change to ΔH for this reaction, use is made of

$$\Delta H = \Delta E + RT\Delta n$$

Then, for reaction (c), $\Delta H_c = -1669.12$ international kilojoules. To correct (c) to the standard temperature, use is made of the reaction: $(\partial \Delta H/\partial T)_P = \Delta C_P$, giving the reaction under standard conditions



or, using the conversion factor to defined kilocalories

$$\Delta H_d = -399.00 \approx 0.24 \text{ kilocalories}$$

This value applies to the actual foil. In order to obtain the value for pure aluminum, correction must be made for the 0.01% surface oxide. Then the heat of formation of Al_2O_3 from pure aluminum under standard conditions will be $\Delta H_{298.16} = -399.04 \approx 0.24$ kilocalories.

The oxide formed by combustion was examined by X-ray powder photographs and found to be in the form of corundum.

Discussion

Using the recommendation of Rossini and Deming as mentioned previously, there are obtained the following values of precision:

"e" (the error assigned to the benzoic acid)	= ±0.010% (from Bureau of Standards)
"c" (calibration error)	= 0.048%
"b" (reaction error)	= ±0.036%

By definition, the precision error "p. e." will be

$$\text{"p. e."} = \pm \sqrt{e^2 + c^2 + b^2}$$

Then, in this work

$$\text{"p. e."} = \pm 0.06\%$$

This, of course, states the purely mathematical value of the random errors.

Summary

1. The heat of formation of aluminum oxide under standard conditions has been found to be $-399.04 \approx 0.24$ kilocalories.

2. The solid Al_2O_3 obtained was the α , or corundum, form.

3. The methods and practices in use at the National Bureau of Standards were used throughout this work.