fairly high concentration of 122 moles of ammonia per mole of salt formed while our measurements were made at a concentration of some 500 moles of solvent per mole of salt. However, the discrepancy cannot be due entirely to a heat of dilution effect. These investigators made only one determination using ammonium bromide and potassium amide.

Selenium

Selenium combines with sodium in anhydrous liquid ammonia to form insoluble Na_2Se and soluble Na_2Se depending on the number of equivalents used.

The heats of reaction measured in this investigation, shown in Table IV, are represented by the equations

$$(1)\quad 2\text{Na·am.} + \text{Se} \longrightarrow \text{Na}_2\text{Se} \qquad \Delta H = 84.7 \text{ kcal.}$$

$$(2)\quad 2\text{Na·am.} + 2\text{Se} \longrightarrow \text{Na}_2\text{Se}_2 \text{ am.} \qquad \Delta H = 100.0 \text{ kcal.}$$

$$(3)\quad 2\text{Na} + \text{NH}_3 \longrightarrow 2\text{Na·am.}^{4} \qquad \Delta H = -2.7 \text{ kcal.}$$

TABLE V

MOLAR HEATS OF REACTION OF SODIUM WITH SELENIUM IN ANHYDROUS LIQUID AMMONIA

Gram atom Na	Gram atoms Se	ΔH reaction, kcal.
	Na_2Se	
1.24×10^{-3}	6.25×10^{-3}	84.3
9.3×10^{-3}	2.5×10^{-3}	85.9
1.4×10^{-3}	2.4×10^{-3}	83.9
	Mean	84.7
	Na_2Se_2	
1.16×10^{-3}	1.16×10^{-3}	100.00

Subtracting equation (3) from equation (1), the heat of formation of solid Na_2Se from its elements at −33.5° is found to be 82.0 kcal. Kraus[3] measured the heat of formation of solid Na_2Te from its elements in essentially the same manner and found it to be 84.3 kcal.

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[UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

The Heats of Combustion of Magnesium and Aluminum[1-3]

BY CHARLES E. HOLLEY, JR., AND ELMER J. HUBER, JR.

Precise measurements of the heats of combustion of magnesium and aluminum have been made. The results are: for magnesium, heat of combustion in 25 atm. oxygen = 5895.6 ± 4.8 cal./gram; heat of formation of MgO, $\Delta H_{25°} = -143.70 \pm 0.12$ kcal./mole; for aluminum, heat of combustion in 25 atm. oxygen = 7403.4 ± 5.7 cal./gram; heat of formation of Al_2O_3, $\Delta H_{25°} = -400.29 \pm 0.31$ 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.

Method.—The method involved the determination of the heat evolved from the burning of a weighed sample of the metal in question in an atmosphere of oxygen of known pressure. The energy equivalent of the calorimeter was determined from the heat of combustion of standard benzoic acid and the heat of combustion was evaluated from this value and measurement of the temperature rise per unit mass of metal. Dickinson's method[4] was used in correcting the temperature rise for heat interchange with the surroundings. The completeness of combustion was determined by treating the combustion products with 6 *N* 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. The volume of the bomb was about 360 ml. On the outside of the bomb a heater was wound of No. 26 Advance wire and cemented in place with clear Glyptal varnish. The calorimeter can was provided with a lid made of silver sheet.

A convection shield made of 0.005 inch silver sheet was provided as recommended by White.[5] By its use the distance between calorimeter and thermostat could 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 in which the temperature was maintained constant to ±0.005° at about 27°. It was enclosed in an air thermostat in which the temperature was maintained at 25 ± 0.5°.

The temperature of the calorimeter was measured to 0.001° with a precision platinum resistance thermometer and a L and 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 cyles 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 calculated from measurements of 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% O_2, was treated to remove any traces of combustible gases by passing over heated palladized asbestos followed by a drying train. Atmospheric nitrogen was removed by flushing with the purified O_2. All runs were made at 25 atm. O_2 pressure.

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(1) This work was done under the auspices of the A. E. C.

(2) Presented before the Division of Physical and Inorganic Chemistry at the 119th Meeting of the American Chemical Society, Cleveland, Ohio, April 12, 1951.

(3) For material supplementary to this article order Document 3330 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

(4) H. C. Dickinson, *Bull. Bur. Standards*, **11**, 189 (1914).

(5) W. P. White, "The Modern Calorimeter," The Chemical Catalog Co., Inc., (Reinhold Publ. Corp.), New York, N. Y., 1928, p. 169.

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 g. The water for the calorimeter was weighed to the nearest 0.01 g.

In accordance with the recommendations of Rossini and Deming[6] the uncertainty 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 energy equivalent of the calorimeter filled with oxygen to 25 atm., based on 15 runs, was 10,092.4 ± 5.3 absolute joules/°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 energy equivalent of 1.3 joules/°C. In addition, 1 ml. of water was added to the bomb, which contributed 4.2 joules/°C. to the energy equivalent, and the energy equivalent of the combustion products minus the oxygen used up was calculated to be 0.9 joule/°C. based on the use of 0.46 g. benzoic acid. Thus 6.4 joules/°C. should be subtracted from the energy equivalent determined with benzoic acid to obtain the energy equivalent of the calorimeter itself.

The benzoic acid used was NBS sample 39f which had a certified calorific value of 26,428.4 ± 2.6 international joules/gram 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 ± 2.6 absolute joules per gram mass when converted to the conditions in our bomb, specifically 25 atm. oxygen, approximately 0.46 g. sample of benzoic acid, 1 ml. of water, initial temperature 24.6°, final temperature approximately 25.8°.

The benzoic acid was ignited by a short length of No. 34 B and S gage nickel–chromium alloy wire supplied by the Parr Instrument Co. for use as a fuse wire. It was reported by them to have a heat of combustion of 1600 calories/gram and this value was used. Combustion of the benzoic acid was complete as determined by the absence of carbon particles in the platinum cup.

The results of the calibration made with benzoic acid are summarized as follows: number of experiments, 12; mass of benzoic acid, 0.41 to 0.53 g.; firing energy, 7 to 49 joules; combustion of fuse wire, 40 to 100 joules; temperature rise, 1.08 to 1.40°; energy equivalent, 10,087.7 to 10,112.0, with an average value of 10,101.8 joules/°C.; average deviation from the mean ± 6.4 joules/°C.; standard deviation of the mean ±2.0 joules/°C.

When the 6.4 joules/°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 energy equivalent of the calorimeter was 10,095.4 ± 4.2 absolute joules/°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 over-all purity was at least 99.98%. Of the nonmetallic 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, 0.010 in. ribbon, and 0.010 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 energy equivalent of the calorimeter as used was computed by taking account of the disc, the platinum, and the difference in energy equivalents between the magnesium oxide formed and the oxygen used up. The initial temperature was 24.6° and the average final temperature was 25.9°. Fifteen runs were made and they are summarized as follows: mass of magnesium 0.42 to 0.61 g.; per cent. burned 99.78 to 99.99; firing energy, 10.9 to 32.4 joules; temperature rise 1.04 to 1.48°; energy from magnesium 24,610 to 24,731 joules/gram with an average value of 24,667 joules/gram; average deviation from the mean ±24 joules/gram; standard deviation of the mean ±8 joules/gram. The final average value for the heat of combustion of magnesium, taking into account the uncertainty in the energy equivalent, is 24,667 ± 20 absolute joules/gram or 5895.6 ± 4.8 cal./gram.

The Heat of Formation of MgO.—The heat of combustion reported above gives a value of $\Delta E_{24.6°} = -599.90$ kjoules/mole for the reaction in the bomb. The correction of this value to 25° is less than the uncertainty in the result. To get the heat of formation, ΔH_f, it is necessary to correct for the deviation of oxygen from the perfect gas law and convert from ΔE to ΔH. According to Rossini and Frandsen[7] the value of $(\partial \Delta E/\partial P)_{301°\text{K.}}$ for oxygen is -6.51 joules/atm./mole. Using this value and taking $\Delta H = \Delta E + \Delta(PV)$ we have for the heat of formation of MgO, $\Delta H_{25°} = -601.23$ absolute kjoules/mole. The uncertainty to be attached to this value, including the uncertainty in the energy equivalent, is ±0.49 absolute kjoules/mole. In defined calories this is $\Delta H_{25°} = -143.70 \pm 0.12$ kcal./mole.

This value is in agreement with the −143.84 ± 0.05 kcal./mole obtained by Shomate and Huffman[8] from heats of solution in 1 *N* hydrochloric acid. It differs appreciably from the −146.1 ± 0.3 kcal./mole obtained by Moose and Parr[9] 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 g. Thus 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 energy equivalent was corrected correspondingly. The initial temperature was 24.6° and the average final temperature was 26.0°. Fifteen runs were made and they are summarized as follows: mass of aluminum, 0.33 to 0.49 g.; per cent. burned 99.36 to 99.98; firing energy, 11 to 25 joules; energy from magnesium fuse wire 128 to 173 joules; temperature rise 1.03 to 1.46°; energy from aluminum 30,931 to 31,074 joules/gram with an average value of 30,976 joules/gram; average deviation from mean ±28 joules/gram; standard deviation of mean ±10 joules/gram. The final average value for the heat of combustion of aluminum, taking into account the uncertainty in the energy equivalent, is 30,976 ± 24 absolute joules/gram or 7403.4 ± 5.7 cal./gram.

The Heat of Formation of Al_2O_3.—The heat of combustion reported above gives a value of $\Delta E_{24.6°} = -1670.8$ kjoules/mole for the reaction in the bomb. Converting to ΔH of formation in the same manner as described above we find $\Delta H_{25°} = -1674.8 \pm 1.3$ absolute kjoules/mole. In calories, this is -400.29 ± 0.31 kcal./mole.

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

(7) F. D. Rossini and M. Frandsen, *J. Research Natl. Bur. Standards*, **9**, 733 (1932).

(8) C. H. Shomate and E. H. Huffman, THIS JOURNAL, **65**, 1625 (1943).

(9) J. E. Moose and S. W. Parr, *ibid.*, **46**, 2656 (1924).

This value differs by about 0.3% from the value of −399.04 ± 0.24 kcal./mole obtained by Snyder and Seltz[10] and by 0.6% from the value of −402.9 ± 0.4 kcal./mole obtained by Roth, Wolf and Fritz.[11]

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[10] P. E. Snyder and H. Seltz, THIS JOURNAL, **67**, 683 (1945).

[11] W. A. Roth, U. Wolf and O. Fritz, *Z. Elektrochem.*, **46**, 42 (1940).

CONTRIBUTION FROM THE RESEARCH SECTION, DIVISION OF CHEMICAL ENGINEERING, TENNESSEE VALLEY AUTHORITY]

Low-Temperature Heat Capacity and Entropy of Hydroxyapatite[1]

BY EDWARD P. EGAN, JR., ZACHARY T. WAKEFIELD AND KELLY L. ELMORE

Heat capacities of hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, are reported for temperatures from 13.18 to 298.16°K. Derived values for the entropy, 186.6 cal. per mole per degree, and the heat content, 30,710 cal. per mole, at 298.16°K. are combined with previously reported high-temperature heat contents to yield the thermodynamic properties of hydroxyapatite at temperatures from 298.16 to 1500°K.

The development of a clear understanding of the chemistry involved in the production and use of phosphatic fertilizers has been retarded by a meagerness of thermodynamic data on the calcium phosphates and certain related compounds. The Tennessee Valley Authority is determining the thermodynamic properties of some of these compounds.

The heat contents and heat capacities of hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, at temperatures above 25° have been reported.[2] The present paper extends the study of heat capacities to low temperatures. The derived heat content and entropy at 25° are combined with previously reported values[2] to obtain the thermodynamic properties of hydroxyapatite.

The heat capacities were measured at temperatures down to 11°K. through use of a Collins[3] helium cryostat manufactured by Arthur D. Little, Incorporated. Since this paper is expected to be the first of a series on low-temperature heat capacities, significant details of the apparatus are presented.

Quality of Hydroxyapatite.—Hydroxyapatite was precipitated by a method that has been described[2] and was thermally aged for 72 hours at 950° in a nitrogen–steam atmosphere. A chemical analysis of the product showed that the CaO and P_2O_5 contents were within a few hundredths of a per cent. of the stoichiometric values, 55.80 and 42.39%, respectively, and that 0.03% Cl was present. The only significant contaminant found in a spectrographic analysis was 0.05% SiO_2. An optical analysis indicated the presence of < 0.3% β-$Ca_3(PO_4)_2$. The refractive index was 1.639 as compared to 1.636 reported by Bale[4] for ignited hydroxyapatite.

Apparatus.—The calorimeter and adiabatic vacuum shield were patterned after those of Scott.[5] The copper calorimeter was about 5 cm. in diameter by 5 cm. deep; it held about 62 g. of hydroxyapatite or 0.06 mole on the basis of a gram-formula weight of 1004.70. Vertical heat-distributing vanes were soldered between the outside wall and the thermometer well. The capsule-type resistance thermometer was soldered in a small copper spool, between the end flanges of which a thin-walled Monel jacket was silver-soldered. A 50-ohm constantan heater was wound on the Monel tube, and the heater-thermometer assembly was immersed in Woods metal in the well. Three chromel–constantan differential thermocouples were located between the top, side and bottom, respectively, of the calorimeter and corresponding positions on the adiabatic shield. The bottom differential couple had three junctions. The potential leads to the heater were divided between the calorimeter bottom and the shield bottom to minimize loss of measured energy, as recommended by Scott.[5]

Temperatures were measured with a Leeds & Northrup capsule-type platinum resistance thermometer that had been calibrated down to 11°K. by the National Bureau of Standards. The thermometer resistance was measured in international ohms by means of a Mueller bridge that had been calibrated by NBS and was recalibrated during use against an NBS-certified standard resistance.

Energy measurements were made by means of a Wenner standardizing potentiometer.[5] The energy was measured in international joules and was converted to defined calories by the relation: 1 cal. = 4.1833 international joules. The potential of the standard cell was checked periodically against three NBS-certified unsaturated cells that were reserved for reference. Time was measured in integral seconds with a Standard Electric Time Company master clock and a "second accumulator" that turned the heating current on and off automatically at the beginning and end of a preselected heating period. The accuracy of timing was ±0.01 second.

The calorimeter was filled in a dry-box under dry nitrogen through a 1-cm. opening in the cap. A $^1/_8$-inch copper tube was attached to the opening by means of solder and an annular copper adapter. The calorimeter was evacuated, and $^1/_3$ atm. of helium was admitted. The copper tube was then pinched closed, cut and soldered close to the calorimeter cap. The calorimeter was hung in the adiabatic shield from the projecting copper tube end with nylon thread.

Heat capacity measurements down to 52°K., attained with pumped solid nitrogen, were made in the conventional manner. For measurements below 52°K., the calorimeter was transferred to a second shield system that was located in the cold zone of the helium cryostat. The calorimeter was cooled to about 10°K., and the cryostat operating pressure of 200 p.s.i. then was reduced to about 100 p.s.i. to balance the refrigeration load as evidenced by lack of motion of the helium gas holder. The calorimeter could have been cooled to 4.2°K., but means of measuring temperatures below 11°K. had not been incorporated into the calorimeter. The present application of the Collins helium cryostat permits the attainment of a temperature of 10°K. without the hazards associated with liquid hydrogen.

Observations.—The observed heat capacities, $\Delta Q/\Delta T$, for the calorimeter plus hydroxyapatite

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[1] For table of observed heat capacities and the corresponding temperature intervals order Document 3309 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

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