[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

A RE-DETERMINATION OF THE HEATS OF OXIDATION OF CERTAIN METALS[1]

BY JOE E. MOOSE WITH S. W. PARR

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Introduction

An examination of the various tables of physical constants[2] will show that there is considerable variation in the values given for the heat of oxidation of several metals. Some of the variations noted in the tables do not seem justified, since modern calorimetric methods and apparatus have limits of accuracy which should yield more concordant results. In general, the causes for variations are as follows: (1) the impurities contained in the metals used and (2) the methods employed.

In regard to the first cause it is sufficient to state that some of the metals used in past determinations were not as pure as those which are available at the present time.

Concerning the methods employed, there are two which have been used in determining the heats of oxidation. One is by direct combustion of the metal in oxygen. Values thus obtained are generally considered more accurate, since they are independent of other determinations. However, very few such values are available because the complete combustion of metals has rarely been accomplished. In most cases analytical determinations have been necessary in order to arrive at the amount of metal oxidized. Also, accelerators have been used extensively in order to start the combustion. In such cases the value depends upon the accuracy of analytical determinations and of the values accepted for the heats of oxidation of the accelerators. It is obvious that the greater the number of variable factors upon which a value depends, the greater the probability of error.

A number of the values determined are the result of indirect methods of determination. They have been calculated from the values obtained by measuring the heat of the reaction of a metal and its oxide with water, acids and sodium peroxide. Obviously this method includes the errors of three or more determinations which may be either cumulative or compensating, but there is no assurance that they are the latter. Different

[1] This paper constitutes a portion of a thesis presented by Joe E. Moose to the Graduate School of the University of Illinois, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1924.

[2] Landolt and Börnstein's "Tabellen," Julius Springer, 1912, pp. 858–873. "The Tables of the Société Français de physique," H. Abraham and P. Sacerdote, 1913, p. 335. Abegg's "Handbuch der Anorganischen Chemie," Hirzel, 1921, vol. IV, p. 591.

investigators[3] have measured the heats of certain of the above reactions and the values obtained vary appreciably.

One cause for the variation of the values recorded for the heats of oxidation is the apparatus which was employed in determining some of them. The calorimeters used by Count Rumford, Dulong, Favre and Silberman and Andrews would now be considered inadequate,[4] and it was not until the advent of the bomb calorimeter of Berthelot[5] in 1881 that an apparatus of present-day type was available. With the modern type of adiabatic oxygen bomb calorimeter, heats of oxidation can be measured very accurately.

From the previous discussion of the causes of variation and error in values it should be apparent that such values need to be verified or corrected in accordance with modern calorimetric apparatus, pure materials, and a method which eliminates all the variable factors possible.

Experimental Part

Purity of Metals.—The metals used in this investigation, their purities and sources are listed in Table I.

TABLE I

THE PURITIES AND SOURCES OF THE METALS USED

Metal	Purity	Impurities in percentages					Source
Aluminum	98.37	C	1.60	Fe	0.03		Aluminum Co. of America
Beryllium	98	BeO	1.5	C	.5		B. S. Hopkins, Univ. of Illinois
Cadmium	99.98	Zn	0.01	Fe	.01		Anaconda Copper Mining Co.
		Cu	.0038	Pb	trace		
Lanthanum	99.95	Fe	.03	La_2O_3	.02		H.C. Kremers, Univ. of Illinois
Magnesium	99.99	...	...	...	..		Aluminum Co. of America
Molybdenum	99.94	MoO_3	.04	Fe	.02		C. W. Balke, Fansteel Products Co.
Tantalum	99.96	Fe	.03	C	.01		C. W. Balke, Fansteel Products Co.
Tin	99.95	Pb	.014	Fe	.017		Merck and Co.
		ZnO	.02				
Tungsten	99.98	Ca	Mo	Fe	trace		C. W. Balke, Fansteel Products Co.
Zinc	99.92	Cd	.025	Fe	.001		Anaconda Copper Mining Co.
		Pt	.055				
Cerium	99.97	Fe	.01	oxide	.02		H. C. Kremers, Univ. of Illinois

[3] Thomsen, "Thermochemistry," Longmans, Green and Co., 1908, p. 260. Richards, THIS JOURNAL, **32**, 1176 (1910). Somermeier, *Phys. Rev.*, [2] 1, 141 (1913). Biltz and Hohorst, *Z. anorg. allgem. Chem.*, 121, 1 (1922).

[4] Count Rumford, *Nicholson's J.*, **32**, 105 (1813). Dulong, *Pogg. Ann.*, [2] **45**, 461 (1838). Glïken, "Kalorimetrische Methodik," Gebrüder Bornträger, 1911, pp. 27–49.

[5] (a) Berthelot, *Ann. chim. phys.*, [5] **23**, 160 (1881). (b) Mahler, *Ber.*, **30**, 202 (1897). (c) Atwater, THIS JOURNAL, **25**, 7 (1903). (d) Richards, *Z. physik. Chem.*, **52**, 551 (1905). (e) Parr, *J. Ind. Eng. Chem.*, **4**, 746 (1912).

An examination of this table shows that an error of 40 calories may result in determining the heat of oxidation of 1 g. of beryllium due to the 0.5% of carbon present. Although this condition is not desirable, it is not serious when one considers that the beryllium used by earlier investigators[6] was only 70 to 80% pure.

The next largest error due to the impurities present in the metals would occur in the value for aluminum.[7] This, however, would amount to fifteen calories. The errors due to the impurities in the other metals are much smaller and hence are well within the limits of error of the determinations.

Apparatus and Method.—The calorimeter used throughout this investigation was the latest type of Parr adiabatic oxygen bomb.[5e] The water equivalent of the calorimeter was determined by burning 2 g. of test sugar supplied by the United States Bureau of Standards within the assembled bomb (Fig. 1) and measuring the thermal effect. Three determinations gave values of 2434, 2433 and 2438 calories, corresponding to an average of 2435 calories.

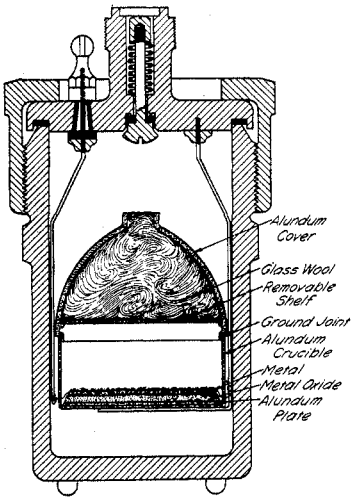


Fig. 1.—Cross section of assembled bomb and crucible.

A Beckmann thermometer standardized by the Bureau of Standards and bearing test No. 27378 was used for determining the temperature rise.

Many of the difficulties encountered in making direct oxidations and complicated analytical determinations were eliminated in this investigation by the use of a specially designed combustion crucible (Fig. 1). The crucible is made of alundum and consists of a bottom, cover and cover shelf. The bottom is of 6 cm. outside diameter, 2.5 cm. deep and 2 mm. thick. About 4 mm. from the bottom are two holes, diametrically opposite, which are just large enough to admit a fuse wire 0.127 mm. (0.005 inch) in diameter. The cover is 2 mm. thick, 5 cm. high and the bottom edge fits snugly into and over the edge of the top of the bottom crucible. The bottom and cover are ground so as to fit practically air-tight, so that no volatile oxides can escape from the interior. The cover shelf is supported at the top by slots and lugs so that it may be removed. It is full of small holes to admit the oxygen needed for the oxidation to enter the combustion chamber and at the same time afford a large cooling surface for condensing all volatile oxides formed. In the bottom of the crucible is placed a circular disk of alundum 2 mm. thick. This disk is covered with a layer of fused (if fusible) or packed oxide of the metal to be oxidized, 2 to 5 mm. thick. These disks are removable and may be replaced.

When a metal is oxidized inside the crucible described above, there is no possibility of side reactions between the hot oxide and foreign materials. Also, there is no metal

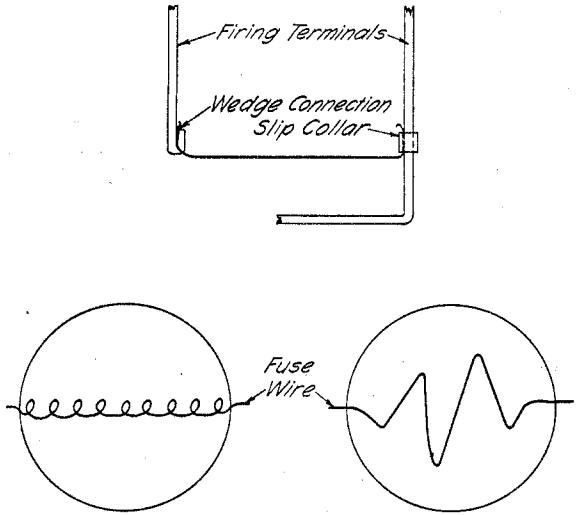
[6] Copaux and Philips, *Compt. rend.*, 171, 630 (1920). Mielenenz and von Wartenburg, *Z. anorg. allgem. Chem.*, 116, 267 (1921).

[7] Since the completion of the determination of the values for aluminum, a metal is available through the Aluminum Company of America, which is 99.96% pure.

surface to alloy with the molten metal. Such a crucible retains all the oxide formed and it can be weighed directly without handling, from which the percentage oxidation can be determined.

When the state of division of a metal is not sufficiently fine the oxide, as it is formed, fuses on the surfaces and prevents the oxidation of the interior of the particles. This difficulty was overcome in a large measure by dividing the materials into states of division ranging from the powdered metal to turnings which would pass through a 15-mesh sieve. Preliminary trials were made with each of the states of division and the thickness of the metal layer, on the oxide plate, varied until the state of division and the thickness of metal layer were determined which would give the greatest percentage of complete oxidations.

The surface tension of the molten metal often causes globules to form, thus increasing the size of the particle and leaving the interior of the particle unoxidized. This



Preferred arrangement of fuse wire for: zinc, tin, molybdenum, beryllium, cadmium, cerium, lanthanum, magnesium.

Preferred arrangement of fuse wire for: tungsten, aluminum, tantalum.

Fig. 2.—Arrangement of fuse wire.

difficulty was prevented by making the layer of metal thinner and by the proper arrangement of fuse wire. In such cases it is necessary that the layer be not only thin, but uniform as well. A very small space on the layer floor not covered with metal will cause globules of metal to form.

The proper arrangement of fuse wire was determined experimentally for each metal. Three types were tried, the straight, spiral and zigzag wires. The latter two types are the most satisfactory and are shown in Fig. 2. The spiral type proved most satisfactory for those metals which could be burned in the thicker layers and those having oxides somewhat volatile at the temperature of the combustion. The zigzag type was most applicable with those metals that oxidized best in very thin layers and which had the greatest tendency to form globules during the combustion period. The zigzag effect causes the oxidation to start at several points on the surface at once and to burn in all

directions. Only 1 cm. of the ends of the fuse wire protruded through the holes in the sides of the combustion crucible and the bomb terminals were against the sides of the crucible.

The variable correction factors are eliminated in this investigation since no accelerators are used. The only corrections made necessary are those for the heat of oxidation of the iron fuse wire and for the weight of the ferric oxide formed. These corrections were made by determining the amount of fuse wire oxidized and subtracting its thermal effect from the total thermal effect of the determination and by subtracting the equivalent weight of ferric oxide from the weight of the metal oxide formed. These corrections are eliminated from the determinations made on tungsten, tantalum, molybdenum, magnesium and aluminum. The fuse wire used with these metals was made of the metals under investigation.

The bomb was evacuated before admitting the oxygen in order to avoid the formation of nitrides. The increase in weight due to the oxide formed was made the basis for calculating the amount of metal which had entered into the reaction.

Results

More than 600 determinations have been made and out of this number, with the exception of those for beryllium, from six to ten determinations in each case have resulted in oxidations of 99% or above. All determinations which resulted in less than 99% oxidation were discarded. The best six to ten determinations for each metal, when calculated on the basis of 100% oxidation, did not vary more than 11 to 42 calories per gram of metal oxidized. The maximum amount of metal oxidized in any determination was 2 g. These values have been averaged and the average value is considered as an accurate value for the heat of oxidation of the metal. These average values are included in Table II. The calculations per mole are based on the atomic weights for 1923.

TABLE II

AVERAGES OF VALUES ACCEPTED AS CORRECT

	Number of determinations	Average deviation	Average values Cal. per g.	Average values Cal. per mole
Aluminum	6	13	6970	375.8
Beryllium[8]	3	31	14879	134.2
Cadmium	6	7	580	65.2
Cerium	9	3	1661	232.9
Lanthanum	4	20	1641	455.8
Magnesium	8	12	5996	146.1
Molybdenum	9	7	1829	175.6
Tantalum	7	4	1373	498.3
Tin	8	5	1164	138.2
Tungsten	10	4	1059	194.9
Zinc	10	7	1298	84.9

Summary

1. The heat of oxidation has been determined for aluminum, beryllium, cerium, cadmium, lanthanum, magnesium, molybdenum, tantalum, tin, tungsten and zinc.

[8] The oxidation obtained with beryllium ranged from 30.3 to 57.6%. The number of determinations was limited, due to the limited supply of beryllium.

2. It is believed that the new values here reported are more accurate than those heretofore available in the literature for the following reasons: (*a*) the purities of the various metals worked with have been greater than those formerly used; (*b*) a calorimeter capable of a higher degree of accuracy, of modern type and adiabatic in operation was used; (*c*) a new method of procedure was employed for determining the completeness of oxidation of samples; the operation of the accessory apparatus devized made it possible to weigh with accuracy the metallic oxide formed and thus furnish a direct check upon the completeness of oxidation in each case; (*d*) while metals of a very high degree of purity have been obtained for samples, special interest is connected with some of the samples because heretofore they have been available only in impure form; the list includes cerium, cadmium, lanthanum and tantalum; also, the values of these elements have been reported heretofore in each case by only one investigator.

3. Beryllium has been only partially oxidized. It is believed, however, that owing to the method of checking by weighing the oxide formed, acceptable results have been secured.

4. All values here determined have been obtained by the direct method.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

A NEW ORGANIC REAGENT FOR THE DETECTION OF NITRATES AND PERCHLORATES

BY C. S. MARVEL AND V. DU VIGNEAUD

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In some recent work[1] it was noticed that the nitrate of α-phenyl-β-diethylaminoethyl-*p*-nitrobenzoate was fairly insoluble. On account of the interest in finding a suitable reagent for precipitating nitrates it was thought to be desirable to determine the solubilities of the nitrate and of other common salts with considerable accuracy.

The only organic reagent now in common use for the determination of nitrates is nitron.[2] It gives a highly insoluble salt with nitric acid (0.0099 g. of nitron nitrate per 100 cc.) and also with perchloric acid (0.0082 g. of nitron perchlorate in 100 cc.). The two objections to the general use of nitron are, first, many anions interfere on account of giving slightly soluble salts and second, its solutions are not particularly stable.

Rupe and Becherer[3] have recently advocated di-(α-naphthylmethyl)-amine as a reagent for nitrates, as the salt with nitric acid is exceedingly

[1] Marvel and du Vigneaud, THIS JOURNAL, **46**, 2095 (1924).

[2] Cope and Barab [THIS JOURNAL, **39**, 504 (1917)] give a good bibliography on nitron.

[3] Rupe and Becherer, *Helvetica Chim. Acta*, **6**, 674, 885 (1923).