be calculated from the data of Kunzler and Giauque.[11]

The entropy of liquid water[12] is 16.71 cal. deg.$^{-1}$ mole^{-1} at 298.16°K. and the entropy of sulfuric acid dihydrate[4] is 66.04 cal. deg.$^{-1}$ mole^{-1} at 298.16°K.

For equation 1, $\Delta S_{298.16} = (-1788 + 1720)/298.16 = -0.23$ cal. deg.$^{-1}$ mole^{-1}. From the third law of thermodynamics, $\Delta S_{298.16} = 82.55 - 66.04 - 16.71 = -0.20$ cal. deg.$^{-1}$ mole^{-1}.

For equation 2, $\Delta S_{298.16} = (-2978 + 2857)/298.16 = -0.41$ cal. deg.$^{-1}$ mole^{-1}. From the third law of thermodynamics $\Delta S_{298.16} = 99.07 - 66.04 - 2\,(16.71) = -0.39$ cal. deg.$^{-1}$ mole^{-1}.

The close agreement of the results indicates that the above hydrates of sulfuric acid approach zero entropy and thus have no hydrogen bond or other type of disorder as the absolute zero of temperature is approached.

We thank W. P. Cox for assistance with the measurements on sulfuric acid tetrahydrate and R. H. Sherman and M. N. Papadopoulos for assistance with the measurements on sulfuric acid trihydrate.

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[11] J. E. Kunzler and W. F. Giauque, THIS JOURNAL, **74**, 3472 (1952).

[12] M. N. Papadopoulos and W. F. Giauque, *ibid.*, **77**, 2740 (1955).

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

The Heat of Formation of Molybdenum Dioxide and Molybdenum Trioxide[1]

BY BERNARD A. STASKIEWICZ, JAMES R. TUCKER AND PAUL E. SNYDER

RECEIVED JANUARY 8, 1955

A study has been made of the heats of combustion of molybdenum and molybdenum dioxide. The metal was used in the form of purified wire while the dioxide was a powder obtained by hydrogen reduction of purified trioxide. It was found that oxidation of the combustible was only 70–80% complete. In the case of the metal both dioxide and trioxide were formed. The data obtained in the two sets of experiments were sufficient to calculate three heat values: the standard heat of formation of MoO_3 of -744.6 ± 0.4 int. kjoules; the standard heat of formation of MoO_2 of -589.4 ± 0.5 int. kjoules; and the standard heat of combustion of MoO_2 to MoO_3 of -155.3 ± 0.13 int. kjoules.

In line with the program of this Laboratory to attempt to obtain more reliable values for the heat of formation of metallic oxides, a study has been made of such data for molybdenum dioxide and molybdenum trioxide. A survey of the literature yielded several previous determinations with the usual wide spread in the values reported. These data are listed in Table I.

TABLE I

Investigators	Date	$-\Delta Hf$, kcal./mole
Of MoO_3		
Delépine[2]	1903	167
Mixter[3]	1910	181.5
Moose and Parr[4]	1924	175.6
Neumann, Kröger and Kunz[5]	1934	180.4
This work	1953	178.0
Of MoO_2		
Mixter[3]	1910	142.8
Chaudron[6]	1921	134.0
Tonosaki[7]	1940	131.7
This work	1954	140.9

The values shown for MoO_3 were obtained by means of the oxygen bomb with the exception of that by Mixter who used the Na_2O_2 bomb on both MoO_3 and MoO_2. On the other hand, the data of Chaudron and Tonosaki were obtained by means of equilibrium studies involving Mo, H_2O, MoO_2 and H_2. Ignoring the earliest work of Delépine, it is seen that a spread of about 3% exists in the other three values for MoO_3. While this is not nearly as bad as is usually the case in connection with the literature values for the heat of formation of a given compound, it was felt that another determination was worthwhile. As will be indicated below, it was found necessary to investigate the heat of combustion of MoO_2 as well.

Experimental

Apparatus.—The apparatus employed in this investigation has been in use for a number of years in this Laboratory and has been previously described.[8] The model G-1 bridge that was formerly in use has been replaced by a Leeds and Northrup model G-2 in order to obtain better precision and more convenient operation of the calorimetry. Calibration of the several parts of the system was carried out in the usual way as has been described in the earlier publication.

Material.—The molybdenum used in this investigation consisted of 20 mil wire. It was wound into coils and purified electrically in a vacuum in the same way that tungsten[9] was treated some years ago. As before, the purification yielded a material of very high purity. Analysis by methods suitable for the element in question showed the following amounts of impurities: 0.004% carbon; 0.0057% oxygen; 0.004% nitrogen; 0.006% silicon; and less than 0.001% each of Fe, Cu, and Mg. Purity of the wire by difference was 99.98%.

The MoO_2 was prepared in the usual way by the reduction of highly purified MoO_3 with purified hydrogen gas. Spectrographic analysis showed only trace (0.001%) amounts of Fe, Cu, Mg and Ca with 0.01% W. The question of these minor impurities is not the important one, however. The method of preparation carries along with it an uncertainty concerning the amount of MoO_3 left unchanged and the amount of Mo that might be produced. Unfortunately, there is no elegant way by which MoO_2 may be determined in such a mixture. Recourse was had to two methods for

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[1] From a thesis submitted by Bernard H. Staskiewicz to the Carnegie Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] M. Delépine, *Bull. soc. chim.*, **29**, 1166 (1903).

[3] W. G. Mixter, *Am. J. Sci.*, **29**, 488 (1910).

[4] J. E. Moose and S. W. Parr, THIS JOURNAL, **46**, 2656 (1924).

[5] B. Neumann, C. Kröger and H. Kunz, *Z. anorg. allgem. Chem.*, **218**, 379 (1934).

[6] G. Chaudron, *Ann. chim.*, **16**, 221 (1921).

[7] K. Tonosaki, *Bull. Inst. Phys. Chem. Res.* (*Tokyo*), **19**, 126 (1940).

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

[9] G. Huff, E. Squitieri and P. E. Snyder, *ibid.*, **70**, 3380 (1948).

the determination of the MoO_2. On the one hand, the material was reduced at 700° with H_2 to Mo. On the other hand, it was carefully oxidized at 450° to MoO_3. At this temperature vaporization of MoO_3 is not a serious source of error. As first produced, the material contained 8% MoO_3. Digestion with NH_4OH removed this, yielding a purified powder which was 100% MoO_2 within the error of the weighing. This result was obtained both on oxidation and reduction.

Calibration of the Calorimeter.—Here again calibration of the calorimeter was carried out in the usual manner. More specifically, calibration for this work was done under exactly the same conditions as was the case with tungsten in reference 9. Its energy equivalent checked very closely with that obtained before. In this type work the standard energy equivalent must be corrected to conditions actually existing in each individual combustion run. The use of protection crucibles gives rise to slightly different conditions in each run, and this in turn gives rise to individually different energy equivalents for each run.

As usual, twelve determinations were made, enabling the use of the equation for the precision error as recommended by Rossini and Deming.[10] This is given by precision error $= 2\sqrt{\Sigma\Delta^2/n(n - 1)}$.

Combustion of MoO_2 and Mo.—Here again the work paralleled that of tungsten. The molybdenum coils were stacked in a shallow silica crucible as before. It was found that the oxides formed by combustion did not slag with the silica since the combustion temperature, even with 40 atm. of O_2 was not very high.

In every case combustion of the metal was complete. Unfortunately, however, oxidation was not complete; that is, only about 80% of the metal went to MoO_3 while the remainder stopped at MoO_2. This was totally unexpected since previous workers inferred that oxidation was complete. Various attempts were made to obtain complete oxidation but none of them were successful. While insufficient data are available at present to make equilibrium calculations involving MoO_2, O_2 and MoO_3, it is felt that oxidation to MoO_3 cannot be complete at the temperatures involved. To obtain useful results from the combustion data, it was necessary to obtain values of the heat of combustion of MoO_2.

Molybdenum dioxide was burned in the bomb under the same conditions as obtained in the case of molybdenum metal. The powder was placed in a shallow silica dish and ignited in the usual way with an iron fuse wire. While ignition and combustion always took place, here again oxidation was not complete. Only about 70% of the dioxide went to the trioxide; the remainder stayed unchanged. Again, attempts were made to increase the percentage conversion, but they were unsuccessful.

In view of the incomplete conversion in each case above, it was necessary to determine the amount of dioxide present in the bomb at the end of each run. This was done by oxidation of the bomb contents in a tube furnace at 450° using purified oxygen.

It should be mentioned that concern was felt when molybdenum metal did not go 100% to MoO_3. It was necessary to prove that the black residue mixed with the MoO_3 was actually MoO_2 and not some other oxidation state. This was done by digesting the bomb contents, from preliminary experiments, with NH_4OH to remove the trioxide. Here again the unavailability of an assay method was unfortunate. The black residue from the digestion was divided into two parts. One part was oxidized to MoO_3 while the other half was reduced to metal. The mass balance in each case indicated that the residue was MoO_2.

The results of the MoO_2 combustions are shown in Table II. The masses shown in the first column are the actual quantities, corrected to vacuum, of MoO_2 that burned to the trioxide.

The results of the molybdenum metal combustion are given in Table III. In this table the first column gives the mass of Mo, corrected to vacuum, that oxidized to MoO_3 while the second column gives the mass that oxidized to MoO_2. By making use of the average value for the MoO_2 combustion in table II and the data in columns 3 and 4, it is possible to set up two algebraic equations from which the data in column 5 are obtained. This column gives ΔE of formation of a mole of MoO_3.

TABLE II

RESULTS OF MoO_2 COMBUSTION

Atomic Weight of Mo = 95.95.

Mass of sample going to MoO_3, g.	Cor. temp. rise (ohms)	Cor. energy equiv., int. joules/ohm	$-\Delta E$, int. joules/mole
15.7686	0.13582	139,485	153,725
15.8744	.13715	139,486	154,194
19.6454	.16937	139,522	153,907
16.1290	.13910	139,490	153,922
15.9935	.13790	139,490	153,888
16.6603	.14372	139,499	153,973

Av. 153,935 ± 124 int. joules/mole

TABLE III

RESULTS OF Mo COMBUSTION

Mass of Mo going to MoO_3, g.	Mass of Mo going to MoO_2, g.	Cor. temp. rise (ohms)	Cor. energy equiv., int. joules/ohm	$-\Delta E$ for MoO_3, int. joules/mole
5.06497	0.56071	0.30516	139,444	741,115
4.60574	1.31032	.31225	139.411	740,105
4.92123	0.94211	.31397	139,405	740,988
4.71781	1.16579	.31212	139,417	740.146
4.86625	1.04466	.31504	139,434	740,259
4.90727	0.94561	.31322	139,429	740,812
4.69761	1.13128	.30954	139,417	740,255
4.90311	0.93906	.31306	139,423	741,606
4.69440	1.15460	.31036	139,418	740,212
4.75602	1.12380	.31225	139,417	739,816

Av. 740,531 ± 358 int. joules/mole

Calculations.—From the data shown in Table II, the following reaction may be written

$$MoO_2(c) + {}^1/_2O_2(g.\ 40\ atm.\ 300.36°K.) = MoO_3(c)$$
$$\Delta E = -153.935\ int.\ kjoules$$

The data in Table III is for the process

$$Mo(c) + 3/2O_2(g.\ 40\ atm.\ 300.36°K.) = MoO_3(c)$$
$$\Delta E = -740.531\ int.\ kjoules$$

By means of the data of Rossini and Frandsen[11] these ΔE values may be corrected to unit fugacity. To change to ΔH, use is made of the relation ΔH =

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

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

$\Delta E + RT\,\Delta n$. In addition by using published heat capacity data[12] and Kopp's rule for MoO_2, a change is made to the customary standard temperature. There then result the equations

$$Mo(c) + 3/2O_2(g.\ 298.16°K.,\ \text{unit fugacity}) = MoO_3(c)$$
$$\Delta H = -744.65 \pm 0.40\ \text{int. kjoules}$$

$$MoO_2(c) + 1/2O_2(g.\ 298.16°K.,\ \text{unit fugacity} = MoO_3(c)$$
$$\Delta H = -155.30 \pm 0.127\ \text{int. kjoules}$$

By combining these reactions properly, there is obtained

$$Mo(c) + O_2(g.\ 298.16°K.,\ \text{unit fugacity}) = MoO_2(c)$$
$$\Delta H = -589.36 \pm 0.53\ \text{int. kjoules}$$

The uncertainties are obtained from the square root of the sum of the squares of the precision error assigned to the combustion value, the calibration value, and the benzoic acid heat value. That for the last reaction, above, is obtained by summing the extremes of the first two reactions.

PITTSBURGH, PA.

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(12) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

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

Chemical Effects of the $C^{12}(\gamma,n)C^{11}$ Reaction in Anhydrous Sodium Carbonate[1]

BY L. J. SHARMAN[2] AND K. J. MCCALLUM

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When sodium carbonate crystals, which have been exposed to γ-radiation from a betatron operating at a peak energy of 23 Mev., are dissolved in water, C^{11} is found to be present in carbonate, carbon monoxide, formic acid, oxalic acid, glyoxylic acid and glycolic acid. The distribution of C^{11} activity between these compounds has been measured, and found to be independent of twofold variations in the total γ-ray dose or in the dose rate. The distribution is also independent of the *p*H of the solution in which the crystals are dissolved. The distribution of the C^{11} activity between the two positions of the glyoxylic and glycolic acid molecule has been determined. If the crystals are heated at a series of increasing temperatures before dissolving, the percentage of the C^{11} present as glyoxylic acid, glycolic acid and oxalic acid decreases, each at a different temperature, and the corresponding activity appears instead as carbonate. A mechanism is suggested to account for the experimental results.

Introduction

Only a few studies of the chemical effects following the (γ,n) nuclear reaction have been reported. In particular, Rowland and Libby[3] have studied the distribution of C^{11} between carbon monoxide and carbon dioxide following the irradiation of solid and liquid carbon dioxide, solid sodium bicarbonate and solutions of sodium bicarbonate and sodium carbonate in water, using γ-rays from a betatron operating at a maximum energy of 48 Mev. It was found that the irradiation of samples in the solid phase yielded about 50% of the radioactive atoms in each oxide, while the irradiation of samples in the liquid phase yielded 95–100% of the radioactivity in the form of carbon monoxide.

This work reports the results of an investigation of the $C^{12}(\gamma, n)C^{11}$ reaction in anhydrous sodium carbonate. The recoil energy of the resulting C^{11} nucleus arises from the momentum of the incident γ-ray as well as from the recoil due to the emitted neutron. For a 24 Mev. γ-ray, these energies are approximately 1500 e.v. and a maximum of 0.5 Mev., respectively, the latter figure assuming that all the energy of the γ-ray in excess of the threshold energy for the (γ,n) reaction appears as kinetic energy of the product particles. The recoiling carbon atom will almost certainly be ionized initially, but as it is slowed down through collisions, partial or complete neutralization will soon occur. As the recoiling atom loses energy it may also react with atoms or molecules to form unstable combinations which may later undergo further reactions. When thermal energies are attained, the carbon atom may be combined in the form of a stable molecule or a radical which can react with the solvent when the crystals are dissolved. Some information concerning these processes can be obtained by investigating the chemical forms in which the C^{11} appears in the solution of the irradiated crystals.

Experimental

Two samples of sodium carbonate were prepared by heating reagent grade sodium carbonate and reagent grade sodium bicarbonate to constant weight at 300°. These samples were stored in a desiccator over P_2O_5 until used.

For irradiation, samples of sodium carbonate were placed in sealed lucite capsules and exposed to radiation from the University of Saskatchewan betatron operating at a maximum energy of 24 Mev. The intensity at the position of irradiation varied from approximately 1000 to 2000 roentgens per minute in different experiments. The irradiation time was either 10 or 20 minutes.

Decay measurements on irradiated samples indicated the formation of O^{15} ($t_{1/2}$ = 126 seconds), C^{11} ($t_{1/2}$ = 20.6 minutes) and a small amount of Na^{24} ($t_{1/2}$ = 14.8 hours), the latter presumably due to stray neutrons. The total C^{11} activity produced in each irradiation was determined by counting a weighed amount of the sample with a mica-window end-on counter. Measurements were made at least 30 minutes after irradiation to permit decay of the short lived O^{15} activity. Corrections were made for the small amount of Na^{24} activity. An empirical calibration curve was used to correct for different weights of material counted.

To investigate the gaseous compounds which might contain C^{11} activity, 0.5 g. of irradiated sodium carbonate was dissolved in 10 ml. of water in a flask connected to a gas analysis train. A stream of air containing known amounts of carbon monoxide and methane as carrier gases was bubbled slowly through the solution as it was acidified. The gases passed through a sodium hydroxide solution to absorb the liberated carbon dioxide, then over hot copper oxide at 500° to oxidize carbon monoxide to carbon dioxide which was in turn absorbed in sodium hydroxide solution. The remaining gases were then passed over copper oxide at 800°, where methane was oxidized to carbon dioxide. This also was absorbed in sodium hydroxide solution. The carbonate

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(1) Abstracted from a thesis presented by L. J. Sharman in partial fulfillment of the requirements for the degree of Ph.D. in Chemistry from the University of Saskatchewan.

(2) Holder of a C.I.L. Fellowship, 1952-1953.

(3) F. S. Rowland and W. F. Libby, *J. Chem. Phys.*, **21**, 1493 (1953).