mole and the dissociation energy of hydrogen as 103.2 kcal./mole, both at 0°K. These bond energies, however, are not the proper ones to use for normal thermochemical calculations unless electron correlation, strain and zero point energies are used throughout. Bond energies as calculated without the inclusion of the dispersion forces and zero point energies are[9] 80.5 and 98.2 kcal./mole for C–C and C–H, respectively. In the calculations of bond energies, it will be noted that the zero point energy almost compensates the dispersion energy yielding bond energies which do not differ greatly from those calculated in the usual manner.

It should be emphasized that there are the same number of C–C and C–H bonds in isomeric hydrocarbons. Consequently, the empirical adjustment of these bond energies in no way affects the isomerization energies. For the *iso*- to *n*-butane isomerization the observed ΔH is 1.63 kcal./mole and the calculated value, considering zero point energy differences, is 1.50. In the case of *neo*- to *n*-pentane the observed ΔH is 4.07 and the calculated value is 4.85 kcal./mole. These agreements are quite satisfactory in view of possible experimental errors and theoretical approximations. In judging the accuracy of these comparisons it should be remembered that the total dissociation energy of a pentane is approximately 1500 kcal./mole.

It has long been known that the skew or *gauche* conformation of *n*-butane or a larger paraffin involves a significant repulsive strain between two hydrogen atoms which are brought close together. The net increase in energy over the all *trans* conformation has been found to lie in the range of 0.5–0.8 kcal./mole.[10] When the attraction arising from electron correlation is taken into account, the repulsive strain energy term becomes 2.50 kcal./mole. This value yields practically perfect agreement for the energy difference between *trans–trans* and *trans–gauche* for *n*-pentane and satisfactory agreement for *gauche n*-butane. Unfortunately the zero point energy is not known precisely for the *gauche* conformations and must be estimated to be equal to that of *trans* conformations. This same strain energy appears in isopentane and when it is appropriately considered, the theoretical energy is in excellent agreement with the observed value.

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[9] K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, Inc., New York, N. Y., 1953, p. 170.

[10] K. S. Pitzer, *J. Chem. Phys.*, **8**, 711 (1940); N. Sheppard and G. J. Szasz, *ibid.*, **17**, 86 (1949); S. Mizushima, "Structure of Molecules," Academic Press, Inc., New York, N. Y., 1954, p. 98 f.

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[CONTRIBUTION FROM COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Heats of Formation of Sodium Molybdate, Molybdic Acid and Aqueous Molybdate Ion

BY ROBERT L. GRAHAM AND LOREN G. HEPLER

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The construction of a calorimeter for the measurement of heats of solution has been described. Heats of solution of H_2MoO_4, MoO_3 and Na_2MoO_4 have been determined in various solutions. From these data we have calculated the heats of formation of H_2MoO_4(c), Na_2MoO_4(c) and $MoO_4^{=}$(aq) to be, respectively, −249.9, −350.4 and −238.2 kcal./mole. The free energy of $MoO_4^{=}$(aq) has been calculated to be −201.8 kcal./mole and the standard oxidation potential of the Mo/$MoO_4^{=}$ couple calculated to be 0.92 v.

In connection with the determination of the heat of formation of several slightly soluble molybdates it became desirable to have a reliable value for the heat of formation of sodium molybdate and aqueous molybdate ion. A search of the literature indicated that the reported values for these heats of formation might not be entirely reliable and that the whole problem could profitably be reinvestigated. A series of exploratory calorimetric determinations of the heats of solution of molybdic acid, molybdic oxide and sodium molybdate gave rough values for the various heats of formation that were considerably different from those tabulated by the Bureau of Standards[1] and Bichowsky and Rossini.[2] In order to resolve these discrepancies a series of careful calorimetric determinations was undertaken.

Experimental

The calorimeter consists of a Pyrex vacuum flask, specially built without spacers, and an evacuated stopper which fit together by means of a ground glass joint. Electrical leads and the calorimeter stirrer pass through a small glass tube in the stopper. The stopper is permanently fastened to the underside of the lid of the constant temperature bath so that while the calorimeter is in operation it is completely below the surface of the water in the bath. During a calorimetric run the temperature in the bath is controlled to within 0.003°. The flask is of such size that it holds 950 ml. of solution with a very small space above the surface of the liquid which minimizes the opportunity for evaporation. The sample is contained in a thin-walled glass bulb which is taped and waxed to the bottom of the stirrer. The stirrer shaft is so arranged that we can slide it down and break the sample bulb on the bottom of the flask. There is a propeller immediately above the sample bulb to aid in effecting rapid solution when the sample bulb is broken. The stirrer shaft is driven by a small synchronous motor.

A resistance thermometer consisting of about 45 ohms of no. 40 nylon insulated copper wire and a heater of about 120 ohms of no. 40 enameled manganin wire are contained in a closely wound glass coil made of 6 mm. Pyrex tubing and filled with HyVac oil. The coil also serves as a stirring well. The heater and thermometer wires were wound bifilarly on small metal rods in order to get the wires into a coil suitable for introduction into the glass coil. With the aid of an aspirator the heater wire was introduced into the bottom part of the glass coil and the thermometer into the top. Leads to the heater are of no. 24 copper wire and the leads to the thermometer are no. 24 manganin wire.

Resistance changes of the thermometer are determined

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[1] "Selected Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, 1952.

[2] F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of Chemical Substances," Reinhold Publ. Corp., New York, N. Y., 1936.

with a Leeds and Northrup G-2 Mueller Temperature Bridge and a H.S. 2284D galvanometer. Power for the heater is supplied by storage batteries that are discharged for about 20 minutes through a dummy heater in order to have a constant voltage for the heating period. Power input is determined by measuring the potential drop across a standard resistance in series with the heater. Potential measurements are made with a Rubicon Type B high precision potentiometer and high sensitivity galvanometer. The time of heating is determined with a calibrated stopwatch. For each calorimetric run the heat capacity is determined both before and after the sample is dissolved.

The accuracy of our measurements was checked by determining the heat of solution of KCl in water and the heat of reaction of NaCl(c) with a dilute solution of $AgNO_3$ to form AgCl(c). Our experimental heats were found to be in excellent agreement with those calculated from the heats of formation tabulated by the Bureau of Standards.[1]

All heats of solution were carried out at 25.0 ± 0.4°.

Materials.—Molybdic acid (H_2MoO_4) was prepared by adding concentrated nitric acid dropwise with vigorous stirring to a solution made by dissolving 40 g. of ammonium molybdate in 400 ml. of water. Best results were obtained by adding a 50% excess of nitric acid over the stoichiometric amount. The resulting precipitate was filtered off, washed and dried at room temperature over P_2O_5. Two separate samples were prepared in this fashion and were found on analysis to be 88.7 and 89.1% MoO_3. The calculated value is 88.88%. It should be mentioned that when the molybdic acid was digested near boiling temperature it was converted to the oxide and the acid was not re-obtained on cooling in contact with the solution.

Fisher's certified reagent grade molybdic oxide (MoO_3) was analyzed for molybdenum and found to contain 67.5% Mo as compared to the calculated value of 66.66%. The analysis and the observed blue-gray color indicated the presence of lower oxides so the commercial molybdic oxide was heated in a muffle furnace at 700° for about an hour. The result was a very light yellow crystalline material that was found on analysis to be 66.7% Mo and was stable if protected from light and dust.

Fisher's certified reagent grade sodium molybdate (Na_2MoO_4) was dried for 24 hours at 110° and found by analysis to be 46.7% Mo as compared with the calculated value of 46.6%.

All of the molybdenum analyses were carried out by the permanganate method.[3]

Results

Heats of solution of molybdic acid and molybdic oxide in 950 ml. of 0.531 M NaOH were measured in order to determine the heat of formation of H_2MoO_4. The calorimetric reactions may be written as in (1) and (2) below. The heat of formation of H_2MoO_4(c) from MoO_3(c) and H_2O(l) is obtained as indicated by (3).

$$H_2MoO_4(c) + 2NaOH(0.531\ M) = \text{soln. I} + 2H_2O \quad \Delta H_1 \quad (1)$$

$$MoO_3(c) + 2NaOH(0.531\ M) = \text{soln. I} + H_2O \quad \Delta H_2 \quad (2)$$

$$MoO_3(c) + H_2O(l) = H_2MoO_4(c) \quad \Delta H_3 = \Delta H_2 - \Delta H_1 \quad (3)$$

The average of four determinations of ΔH_1, using in each experiment about 0.01 mole of H_2MoO_4 and 0.531 M NaOH, was found to be −15.23 kcal./mole with an average deviation of 0.2 kcal./mole. The heat of solution of an equal number of moles of MoO_3 in 0.531 M NaOH was found to be −18.85 kcal./mole with the same average deviation. We therefore calculate $\Delta H_3 = -3.62$ kcal./mole. From this heat and the heat of formation of MoO_3(c) and H_2O(l) we calculate the heat of formation of H_2MoO_4(c) to be −249.9 kcal./mole. For this calculation we have used the heat of formation of MoO_3(c) reported by Snyder and his co-workers[4] (−178.0 kcal./mole) rather than any of the older values. The standard heat of formation of H_2O(l)[1] was used in this calculation and other calculations reported in this paper because $\bar{L}_1$ for H_2O in 0.5 M NaOH is smaller than our calorimetric uncertainty.[5]

Hüttig and Kurre[6] have investigated the dissociation pressure and have calculated the heat of dissociation of H_2MoO_4(c) into MoO_3(c) and H_2O(g). Their heat for this reaction combined with Snyder's heat of formation of MoO_3 leads to a heat of formation of −254.6 kcal./mole for H_2MoO_4(c). We believe that our calorimetric value is to be preferred.

It is interesting to compare our heat of solution of H_2MoO_4 in NaOH with the heats found by Pissarjewsky[7] and Pechard.[8] Both of these workers reported heats considerably higher than ours. We have recalculated Pissarjewsky's results on the assumption that he dissolved MoO_3 rather than H_2MoO_4. This calculation leads to −18.8 kcal./mole for the heat of solution of MoO_3 which is in agreement with the value we have reported. In view of the agreement with our heat of solution of MoO_3 and our experience with the preparation of H_2MoO_4 it appears very likely that he and Pechard worked with MoO_3 rather than H_2MoO_4. Neither reported analyses of the compound in question.

The tabulated heat of formation of $MoO_4^{=}$(aq)[1] is based on the older values for the heat of solution of H_2MoO_4,[7,8] so we have calculated a new heat of formation from our data. The heat of formation we obtain is −238.2 kcal./mole. In this calculation no attempt was made to correct for heats of dilution. Because this heat of formation is in considerable disagreement with that given by the Bureau of Standards,[1] we deemed it advisable to determine it in another manner, namely, from the heat of formation and the heat of solution of sodium molybdate.

Heats of solution of MoO_3 and of Na_2MoO_4 in 950 ml. of 0.531 M NaOH were determined. The calorimetric reactions can be written as in (2) and (4). We obtain the heat of formation of Na_2MoO_4(c) from reaction 5. These heat of solution experiments were carried out in pairs; each pair giving an independent value for ΔH_5. The results are given in Table I.

$$Na_2MoO_4(c) = \text{soln. I} \quad \Delta H_4 \quad (4)$$

$$MoO_3(c) + 2NaOH(0.531\ M) = Na_2MoO_4(c) + H_2O \quad \Delta H_5 = \Delta H_2 - \Delta H_4 \quad (5)$$

From our value for ΔH_5, Snyder's heat of formation of MoO_3[4] and the Bureau of Standards[1] heat of formation of NaOH (0.531 M) and H_2O(l), we calculate the standard heat of formation of Na_2MoO_4(c) to be −350.4 kcal./mole. Mixter[9] has previously studied the heat of the reaction of Mo(c) with Na_2O_2(c) to give Na_2MoO_4, but we be-

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[3] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, "Applied Inorganic Analysis," Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 307.

[4] B. A. Staskiewicz, J. R. Tucker and P. E. Snyder, THIS JOURNAL, **77**, 2987 (1955).

[5] G. Åkerlöf and G. Kegeles, *ibid.*, **62**, 620 (1940).

[6] G. F. Hüttig and B. Kurre, *Z. anorg. Chem.*, **126**, 167 (1923).

[7] L. Pissarjewsky, *ibid.*, **24**, 108 (1900).

[8] E. Pechard, *Ann. chim. phys*, **28**, 537 (1893).

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

TABLE I

HEATS OF SOLUTION OF MoO_3 AND Na_2MoO_4 (ALL ΔH VALUES GIVEN IN KCAL./MOLE)

Pair	ΔH_2	ΔH_4	ΔH_5	Moles Mo × 10^2
1	−18.52	−1.91	−16.61	4.531
2	−18.70	−2.20	−16.50	2.459
3[10]	−18.75	−2.19	−16.56	4.074
4	−18.69	−2.10	−16.59	3.143
5	−18.66	−2.26	−16.40	2.622

Av. ΔH_5 = −16.53 kcal./mole. Av. dev. 0.07 kcal./mole.

lieve our heat of formation is to be preferred to that calculated from his results.[1,2]

The heat of solution of Na_2Mo_4 in water and in extremely dilute aqueous NaOH was measured at several concentrations. Results of these experiments are given in Table II. The starred heats indicate heats of solution in pure water and the others refer to solution in dilute NaOH. We have extrapolated these heats to infinite dilution in order to obtain $\Delta H^\circ = -2.4$ kcal./mole for the heat of solution of Na_2MoO_4(c). From this heat of solution, the heat of formation of Na^+(aq)[1] and our previously determined heat of formation of Na_2MoO_4(c), we calculate the standard heat of formation of $MoO_4^=$(aq) to be −238.2 kcal./mole.

TABLE II

HEAT OF SOLUTION OF Na_2MoO_4

Moles Na_2MoO_4/ 950 ml. soln.	ΔH(kcal./mole)	Moles Na_2MoO_4/ 950 ml. soln.	ΔH(kcal./mole)
0.02459	−2.26	0.02474	−2.19
.03143	−2.10	.03587	−2.23
.04074	−2.19	.02174	−2.24*
.05031	−2.03*	.01155	−2.24*

The heat of formation of $MoO_4^=$(aq) and Latimer's[11] estimate of the partial molal entropy enable us to calculate the standard free energy of formation of $MoO_4^=$(aq) to be −201.8 kcal./mole. This free energy leads to 0.92 volt for the standard potential of the Mo–$MoO_4^=$ couple (6).

$$\mathrm{Mo} + 8\mathrm{OH}^- = \mathrm{MoO_4}^{=} + 4\mathrm{H_2O} + 6e^- \quad E^\circ = 0.92 \qquad (6)$$

Discussion of Results

Because our heat and free energy of formation of $MoO_4^=$(aq) are considerably different from the old values, it is desirable to have an independent check on one or the other of these quantities. Two recent investigations on $CaMoO_4$ make available the necessary data for a calculation of the free energy of $MoO_4^=$(aq).

Gerasimov[12] has studied the reduction of $CaMoO_4$ to CaO and Mo by hydrogen. From his data we calculate the free energy of the reduction reaction to be 38.8 kcal./mole at 25° which leads to −347 kcal./mole for the free energy of formation of $CaMoO_4$. The solubility of $CaMoO_4$ in water has been determined by Spitsyn and Savich.[13] We have estimated the small activity coefficient and hydrolysis of $MoO_4^=$ corrections in order to calculate from the solubility data that the thermodynamic solubility product is about 1×10^{-8} and the free energy of solution is 11 kcal./mole. The free energy of formation and free energy of solution, together with the free energy of Ca^{++}(aq),[1] lead to −204 kcal./mole for the free energy of formation of $MoO_4^=$(aq). This is in satisfactory agreement with our free energy but is 15 kcal. more positive than the value calculated by Latimer[11] from the Bureau of Standards heat of formation.

It should be pointed out that Ketchen and Wallace[14] have recently published a calculation, based on the results of their earlier calorimetric work, of the standard heat of formation of aqueous NaOH. On the basis of their heat of formation and heats of dilution from the Bureau of Standards tabulation[1] the heats of formation we have reported could be revised slightly.

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CHARLOTTESVILLE, VIRGINIA

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[10] The third pair of heat of solution determinations was carried out in 1.062 *M* NaOH rather than in 0.531 *M* NaOH as was used for all of the other determinations.

[11] W. M. Latimer, "Oxidation Potentials," Second Edition, Prentice-Hall, Inc., New York, N. Y., 1952, p. 251.

[12] Y. I. Gerasimov, "Koklady Mezhdunarod. Kongr. Teoret. Priklad. Khim. XIII Kongr.," 77–131 (Stockholm, Sweden, 1953).

[13] V. I. Spitsyn and I. A. Savich, *J. Gen. Chem. U.S.S.R.*, **22**, 1323 (1952) (English translation).

[14] E. E. Ketchen and W. E. Wallace, THIS JOURNAL, **76**, 4736 (1954).