ΔH° = 5.7 kcal./mole for $HOAc(HOAc) = H^+(HOAc) + OAc^-(HOAc)$, the ionization of anhydrous acetic acid.

Kolthoff and Willman[10] reported the ionization constant of anhydrous acetic acid to be 2.5×10^{-13} at 25°, and Kilpi and Puranen[15] reported 2.8×10^{-13}. Kolthoff and Willman note in their paper that e.m.f. measurements of Hall[16] and Hall and Conant[17] lead to a value of about 10^{-10} for the ionization constant. It should be pointed out that Hall and Conant worked with solutions of rather high ionic strength and with acetic acid which may have contained as much as 0.5% water (0.28 molal in H_2O). An average value, $K = 2.6 \times 10^{-13}$, is taken for the ionization constant on a volume basis at 25°. Taking the density of acetic acid as 1.044 at 25°,[18] this is corrected to $K = 2.4 \times 10^{-13} = (H^+)(OAc^-)$ on a molality basis, corresponding to a free energy of ionization of 17,210 cal./mole. Combining this with the heat of ionization, 5,700 cal./mole, one obtains $\Delta S^\circ = -38.6$ cal./deg. mole. This entropy is much more negative than the corresponding value for water, and bears out the conclusion that ionic entropies in water are higher than those of other protonic solvents.

Recent work by Smith and Elliott[19] indicates that perchloric acid is far from completely ionized in acetic acid. It may be necessary to re-interpret the results of the present investigation in light of these new findings.

Acknowledgment.—The author wishes to acknowledge Prof. Wendell M. Latimer's helpful suggestions, which were cheerfully given throughout this investigation.

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[15] S. Kilpi and M. Puranen, *Ann. Acad. Sci. Fennicae, Ser A.*, **57**, No. 10, 3 (1941); *C. A.*, **38**, 4855 (1944).

[16] N. F. Hall, THIS JOURNAL, **52**, 5115 (1930).

[17] N. F. Hall and J. B. Conant, *ibid.*, **49**, 3047 (1927).

[18] "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1928.

[19] T. L. Smith and J. H. Elliott, paper presented before Division of Physical and Inorganic Chemistry at A. C. S. Meeting, Atlantic City, Sept. 14-19, 1952; also see E. A. Evans, J. L. Huston and T. H. Norris, THIS JOURNAL, **74**, 4985 (1952).

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND METALLURGY, NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY]

Thermodynamic Properties of Indium(III) Oxide[1]

BY MORRIS F. STUBBS, JOSEPH A. SCHUFLE AND ALVIN J. THOMPSON

RECEIVED JUNE 23, 1952

The free energy and enthalpy change for the formation at 298°K. of In_2O_3 have been determined to be −196.4 and −216.8 kcal./mole, respectively, by equilibrium methods. The absolute entropy of the oxide is then calculated to be 30.1 e.u./mole. X-Ray evidence indicates the reduction of In_2O_3 with hydrogen probably takes place directly to the metal with no appreciable amounts of lower oxides being formed under the conditions studied (823–1123°K.).

This work was undertaken to determine the standard free energy and enthalpy of formation of indium oxide by thermodynamic methods. The method used was to determine the equilibrium ratios of water vapor to hydrogen in the reduction of indium(III) oxide with hydrogen over the temperature range 823–1123°K.

The enthalpy of formation of indium oxide was first determined by Ditte[2] from the heats of solution of indium and indium oxide in sulfuric acid. Ditte's value of −240 kcal./mole was used by Latimer[3] to estimate the free energy of formation of the oxide as −218 kcal./mole. Becker and Roth[4] determined the enthalpy of formation of the oxide by combustion of the metal and obtained a value of −222.5 ± 0.7 kcal./mole. These authors also estimated the entropy of the oxide to be 27.0 ± 2.5 e.u./mole. Hart,[5] in a recent survey of the periodicity of chemical thermodynamic functions, used the Becker and Roth value for the enthalpy of formation, and gave −73.5 e.u./mole for entropy of formation, and calculated a value of −200.5 kcal./mole for free energy of formation. Recently, a new value for the enthalpy of formation of In_2O_3 has been determined by Holley, Huber and Meierkord[6] by the combustion of indium metal in an oxygen bomb calorimeter. They report finding a value of −221.27 ± 0.40 kcal./mole.

Experimental

Material, Apparatus and Procedure.—The In_2O_3 was prepared from 99.96% indium. The pure metal was dissolved in hydrochloric acid and the excess acid evaporated off on a hot-plate. The resulting $InCl_3$ was dissolved in water and hydrous indium oxide precipitated from the solution with 6 *F* ammonium hydroxide. The hydrous oxide was washed thoroughly and ignited to constant weight at 800°.

It was first necessary to establish the mechanism of the reduction of In_2O_3 with H_2. A charge of pure In_2O_3 was slowly reduced in a stream of H_2 at 600° in a porcelain boat placed in a Vycor tube in an electric furnace. Samples were removed from the boat at intervals for analysis and X-ray examination. The results obtained show only two crystalline forms, those of In_2O_3 and In metal. The reduction, therefore, probably takes place under the conditions described according to the reaction represented by the equation: $In_2O_3(s) + 3H_2(g) \rightleftarrows 2In(l) + 3H_2O(g)$ and not through the intermediate formation of InO and In_2O, as reported by Thiel and Luckmann.[7] (There is a possibility, of course, that in cooling the sample from the furnace temperature to room temperature, InO and In_2O could disproportionate to In and In_2O_3.)

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[1] Presented at the 121st Meeting, American Chemical Society, Buffalo, N. Y., March 23–27, 1952.

[2] A. Ditte, *Compt. rend.*, **72**, 858 (1871).

[3] W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1938, p. 150.

[4] W. A. Becker and G. Roth, *Z. physik. Chem.*, **159A**, 1 (1932); **161A**, 69 (1932).

[5] D. Hart, *J. Phys. Chem.*, **56**, 202 (1952).

[6] C. E. Holley, E. J. Huber, Jr., and E. H. Meierkord, THIS JOURNAL, **74**, 1084 (1952).

[7] A. Thiel and H. Luckmann, *Z. anorg. allgem. Chem.*, **172**, 353 (1928).

The equilibrium data were secured in a dynamic system as shown in Fig. 1. Electrolytic tank hydrogen was passed through a "Deoxo" catalytic purifier (A), a pressure regulator (C), a flowmeter (D), drying tubes, (B) and (E), then bubbled through a water saturator (F) held at constant temperature by means of a water-bath. By regulating the temperature of the saturator, gas mixtures of various hydrogen–water vapor ratios could be obtained. The charge of 10–12 g. of pure In_2O_3 was suspended on washed and ignited asbestos and placed in the Vycor reaction tube (G) in the electric furnace (H). The furnace temperature was regulated to ±1° of the desired temperature. Temperatures were recorded with a chromel–alumel thermocouple connected to a General Electric thermocouple potentiometer type P.J.–1B4. The thermocouple was calibrated against U.S. Bureau of Standards metals.

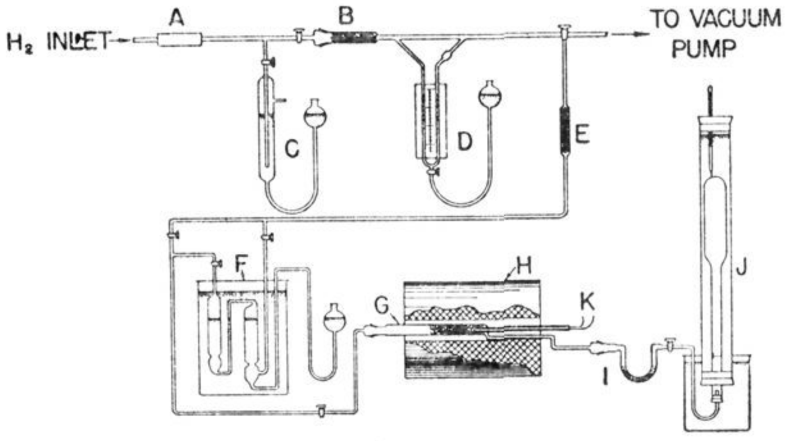

Fig. 1.

Exit gases were analyzed by passing through a weighing tube (I) containing anhydrous magnesium perchlorate to remove water, and collecting the remaining H_2 gas in a gas buret (J) over water. The connecting tubes between the saturator (F) and the furnace, and the drying tube (I) and the furnace, were wrapped with asbestos cord and heated by means of Nichrome wire to prevent condensation of water vapor. At each temperature studied the equilibrium was approached from both sides with varying hydrogen–water vapor ratios and with varying rates of flow of the gases. Table I gives equilibrium data for runs at 873°K. for the system $^1/_3\ In_2O_3(s) + H_2(g) \rightleftarrows {}^2/_3\ In(l) + H_2O(g)$.

TABLE I

RESULTS OF EQUILIBRIUM DETERMINATIONS AT 873°K.

Inlet mixture V_{H_2O}/V_{H_2}	Rate of flow, ml./min.	Exit totals H_2O, g.	Exit totals H_2, ml. S.T.P.	$K_e = P_{H_2O}/P_{H_2}$
Pure H_2	8.3	0.291	229.9	0.158
Pure H_2	8.7	.289	229.9	.157
Pure H_2	6.1	.257	227.7	.140
Pure H_2	7.2	.270	227.0	.148
Pure H_2	6.6	.282	227.0	.155
Pure H_2	7.2	.276	229.7	.150
Pure H_2	7.2	.283	227.7	.155
Pure H_2	7.9	.273	227.7	.149
Pure H_2	7.9	.279	225.4	.154
Pure H_2	7.4	.281	225.4	.155
Pure H_2	7.4	.286	225.4	.158
Pure H_2	8.4	.282	225.3	.156
Pure H_2	6.0	.278	223.8	.155
0.166	7.8	.277	229.3	.150
.166	8.0	.281	229.3	.153
.222	8.0	.270	226.8	.148
.222	8.9	.270	226.8	.148
.222	8.4	.272	226.8	.149
.125	7.1	.278	230.3	.150
.125	5.8	.284	227.4	.155
.125	5.6	.296	227.4	.162
.125	7.8	.276	227.7	.151
.125	7.6	.280	226.4	.154
.125	7.4	.273	226.4	.150

The values of the equilibrium constant listed in column 5 of Table I are calculated from the ratio of the volumes of the two gaseous substances corrected to standard conditions. However, since the reactions were carried out at one atmosphere total pressure and since the standard state for free energy calculations is the real gas at unit fugacity, usually at pressures near one atmosphere, the activity coefficients are essentially one, and the volume ratio is practically equal to the ratio of partial pressures.

Table II gives the average values of K_e obtained at the six temperatures studied. The deviations listed in column three are standard deviations.

TABLE II

SUMMARY OF EXPERIMENTAL RESULTS

Temp., °K.	Number of determinations	P_{H_2O}/P_{H_2}	ΔF/mole In_2O_3, cal.
823	15	0.083 ± 0.004	12,215
873	24	.153 ± .005	9,771
923	17	.235 ± .004	7,969
973	19	.353 ± .021	6,040
1023	11	.567 ± .018	3,460
1123	14	.891 ± .039	772

A plot of $1/T$ *vs.* log K gives a straight line as shown in Fig. 2, indicating a fairly constant value of the enthalpy of reaction. If one assumes that this value remains the same down to 298°K., the standard enthalpy of formation of indium oxide at 298°K. can be calculated as −216.4 kcal./mole.

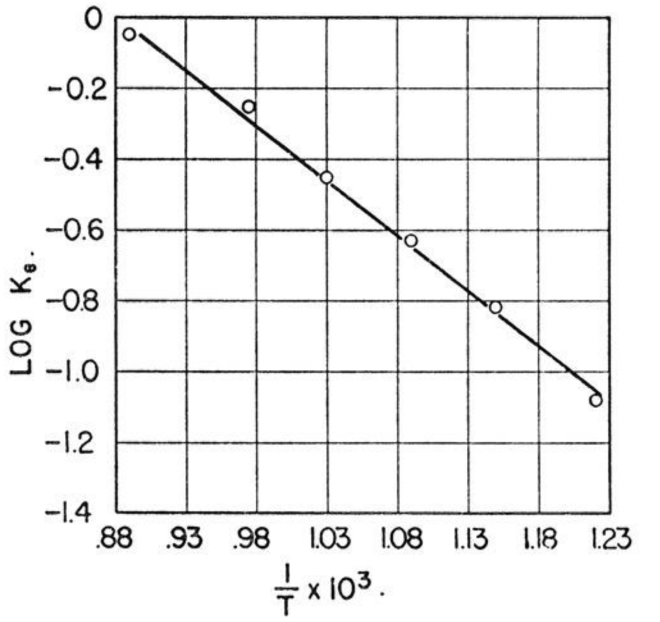

Fig. 2.

The enthalpy of reaction as a function of temperature can be calculated from heat capacity data. The heat capacities as a function of temperature were taken from Kelley[8] for In(l), In(s), $H_2O(g)$ and $H_2(g)$. The heat capacity of $In_2O_3(s)$ was obtained from "Selected Values of Chemical Thermodynamic Properties."[9] Enthalpy and free energy of the reaction: $In_2O_3(s) + 3H_2(g) \rightleftarrows 2In(l) + 3H_2O(g)$ were found to be given by the equations

$$\Delta H = 46{,}005 - 5.05T + 2.67 \times 10^{-3}T^2 + 1.2 \times 10^4T^{-1}$$

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[8] K. K. Kelley, "Contributions to Data on Theoretical Metallurgy," Bull. 476, U. S. Department of Interior, 1949, pp. 77 and 82.

[9] National Bureau of Standards, Washington, D. C., Table I, 29, Dec., 1948.

$$\Delta F = 46{,}005 + 5.05\ T \ln T - 2.67 \times 10^{-3}T^2 + 6 \times 10^3T^{-1} - 72.81T$$

From these equations for the above reaction are calculated ΔH_{298} = 44,777 cal.; ΔF_{298} = 32,885 cal. From these values one can calculate the standard enthalpy and free energy of formation of indium oxide at 298°K. as −216.8 and −196.4 kcal./mole, respectively. The value of −57.8 kcal./mole, given by Bichowsky and Rossini,[10] was used for the standard enthalpy of formation of H_2O(g), and −0.67 kcal./mole for the enthalpy of transition at 298°K. from In(l) to In(s), calculated from data given by Kelley.[8] The entropy of formation of indium oxide at 298°K. is then calculated to be −68.4 e.u./mole, using data given in reference 9, and the absolute entropy at 298°K. to be 30.1 e.u./mole.

The value of the enthalpy of formation of In_2O_3 given in this paper is possibly less accurate than the value of Holley and collaborators,[6] since our method is an indirect one depending in part for its accuracy on heat capacity data from the literature. The value for the free energy of formation of In_2O_3, however, is the first reported value obtained from direct experimental data, other values given in the literature being estimated. Moreover, the close agreement between calorimetric and equilibrium values for the enthalpy of formation of In_2O_3 is believed to be evidence for the direct reduction of In_2O_3 to indium with no appreciable amounts of lower oxides being formed under the conditions of reduction studied (823–1123°K.).

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[10] F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936, p. 20.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY, METAL HYDRIDES INC., AND THE DEPARTMENT OF CHEMISTRY, TUFTS COLLEGE]

Metal-Hydrogen Systems. III. The Uranium-Hydrogen System

BY THOMAS R. P. GIBB, JR.,[1] JAMES J. MCSHARRY AND HENRY W. KRUSCHWITZ, JR.

RECEIVED MARCH 24, 1952

The dissociation pressure of hydrogen over uranium hydride has been studied as a function of temperature and composition of the solid solution in regions where the isotherms show a marked upward inflection. Observations are reported for the range 500–4900 cm. at temperatures from 357 to 650° for compositions ranging from $UH_{2.85}$ to $UH_{3.00}$. The equation for $UH_{3.00}$ is: $\log P_{\text{cm.}} = (-1730/T) + 5.78$, where T is absolute temperature. Withdrawal of hydrogen from the solid phase causes a marked decrease in the dissociation pressure. After removal of several tenths of a mole of hydrogen, the solid phase reverts to normal behavior, showing a heat of dissociation of 20.5 kcal./mole H_2, and ΔF_{298} = 11.8 kcal./mole H_2.

The dissociation of uranium hydride has been studied by Newton,[2,3] Spedding, *et al.*,[4] and Flotow and Abraham,[5] whose data are in reasonable agreement. These workers employed low pressure equipment and were therefore restricted to temperatures below 450°. The single isotherm reported by Spedding was at 357° and showed a marked upward inflection as the composition of the solid phase approached $UH_{3.0}$. All three workers evidently used measurements made in the horizontal plateau regions of isotherms for preparation of log P *vs.* $1/T$ plots. The formation and properties of the compound UH_3 have been studied by Burke and Smith,[6] Driggs,[7] and Gueron and Yaffe.[8]

A tentative structure of UH_3 has been described by Rundle,[9] and the theoretical implications of this structure have been discussed by Pauling.[10]

Studies at Low Pressure.—Preliminary studies at low pressure were made in this Laboratory according to Spedding's technique, but employing the low pressure equipment described in a previous paper.[11] A 357° isotherm was observed which corresponded very well with that of Spedding except that hysteresis was slightly more pronounced. The same dip was noted in the descending arm of the hysteresis loop at composition $UH_{2.94}$. This isotherm is shown in Fig. 3, but neither the dip nor the minor deviation from Spedding's isotherm are perceptible because of the scale required for inclusion of the other isotherms. Attainment of equilibrium in this range is very slow unless an absolutely constant temperature may be maintained.

A second isotherm at 375° was attempted, and the data obtained indicated a much larger dip near the inflection at composition $UH_{2.40}$. There was sufficient drifting of the measurements, however, to cause some doubt that true equilibrium values were obtained. This drift was also noted in a 400° isotherm. Only the descending arm of the hysteresis loop was observed, and the low pressure experiments were discontinued because of the apparent difficulty of obtaining true equilibrium data. An overpressure is noted when samples of UH_3 are heated above 400°. This overpressure develops rapidly and is for the most part reversible on cooling slightly below 400°, but the latter stages of reabsorption are extremely slow. A possible explanation is that a small temperature increase may cause the plateau pressure of the sample to change to the much higher pressure of the ascending portion of the isotherm at the increased temperature. In any

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[1] Department of Chemistry, Tufts College, Medford 55, Mass.

[2] A. S. Newton, *et al.*, MDDC 1585 12 pp. decl. Dec. 16, 1947.

[3] A. S. Newton, U. S. Patent 2,446,780 (August 10, 1948).

[4] F. H. Spedding, A. S. Newton, J. C. Warf, O. Johnson, R. M. Nottorf, I. S. Johns and A. H. Doane, *Nucleonics*, **4**, 4 (1949).

[5] H. E. Flotow and B. Abraham, AECD 3074; *cf. Nuclear Science Abstracts*, 5,445 (1951).

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[7] F. H. Driggs, U. S. Patents 1,816,830 (August 4, 1930); 1,834,024 (Dec. 8, 1930).

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[9] R. E. Rundle, THIS JOURNAL, **69**, 1719 (1947).

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[11] T. R. P. Gibb, Jr., and H. W. Kruschwitz, Jr., *ibid.*, **72**, 6365 (1950).