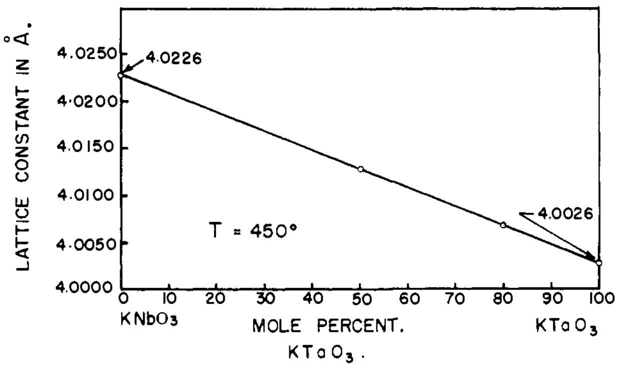

Fig. 3.—Variation of lattice constant of $KNbO_3$ with mole % $KTaO_3$ at 450°.

lum concentration. This decrease in lattice constant can only be attributed to an increase in the ionic character of the heavy metal atom–oxygen bond. Using the data of Shirane, *et al.*,[26] for cubic $KNbO_3$ at various temperatures above the Curie point, one obtains a straight line relationship between cubic lattice parameter and temperature. The extrapolated value obtained for $KNbO_3$ at room temperature is 4.0033 Å. As the $KTaO_3$ parameter is 3.9885 Å. this further substantiates the belief that the Ta–O bond is more ionic than the Nb–O bond.

A qualitative application of the Huggins relationship[27] indicates that "effective" ionic characters of the Ta–O and Nb–O bonds are essentially the same. The equation was applied, assuming that the contribution of K would be the same for both systems. What is most apparent, however, is that the combination of geometric and electronic factors is not significantly different for Ta and Nb indicating that the Goldschmidt theory[28] is extremely sensitive to this combination. Therefore one would rarely expect to encounter model behavior relationships.

Acknowledgment.—The authors wish to acknowledge the invaluable assistance given by S. Triebwasser during his many helpful discussions and to thank Miss S. Silverman for preparation of samples, and the North American Philips Company for making available equipment for several experiments.

[26] G. Shirane, R. Newnham and R. Pepinsky, *Phys. Rev.*, **96**, 581 (1954).

[27] M. L. Huggins, THIS JOURNAL, **75**, 4123, 4126 (1953).

[28] J. M. Goldschmidt, *Skrift Norske, Vid. Akad. Oslo. Mat. Nat. Kl.*, No. 8, 7 (1926).

NEW YORK, NEW YORK

[CONTRIBUTION FROM OAK RIDGE NATIONAL LABORATORY]

The Thermodynamics of Indium Sulfate Solutions[1]

BY M. H. LIETZKE AND R. W. STOUGHTON

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E.m.f. data are presented for the cell In, $In_2(SO_4)_3(m)$, Ag_2SO_4(sat), Ag for $In_2(SO_4)_3$ concentrations of 0.01 to 2.3 m and temperatures of 15 to 70°. The log of the activity of $In_2(SO_4)_3$ is approximately proportional to the molality at any given temperature. E.m.f., conductivity and solubility data all strongly indicate considerable ionic association in $In_2(SO_4)_3$ solutions.

Introduction

The cell In, $In_2(SO_4)_3(m)$, Hg_2SO_4, Hg was studied by Hattox and DeVries[2] as a function of $In_2(SO_4)_3$ concentration at 15, 25 and 35°. They calculated activity coefficients of $In_2(SO_4)_3$ on the assumption of complete dissociation into In^{+++} and SO_4^{--} ions at the lower concentrations and by making the usual extrapolation using the Debye-Hückel equation. The current study began as an attempt to extend the useful range of the In, $In_2(SO_4)_3(m)$ electrode to higher temperatures. Because of the lesser tendency of Ag_2SO_4 than Hg_2SO_4 to hydrolyze as the temperature is raised and the acidity lowered and the consequently greater reliability of the Ag, Ag_2SO_4 electrode under these conditions,[3] the cell In, $In_2(SO_4)_3(m)$, Ag_2SO_4(sat), Ag was used. The $In_2(SO_4)_3$ concentration was varied from about 0.01 to 2.3 m and the temperature from 15 to 70°. The lower limit in concentration and the upper limit in temperature were fixed by the ability to obtain reproducible results.

The relatively highly solubility of Ag_2SO_4 (0.02676 m in water at 25°) combined with the necessity of keeping it out of the In, $In_2(SO_4)_3$ electrode compartment imposed a further restriction on the lower limit of useful $In_2(SO_4)_3$ concentrations as far as interpreting the data was concerned, because of the problem of liquid junction potentials.

Experimental

The Ag_2SO_4 used in all the measurements was prepared according to the method described by Archibald,[4] while the $In_2(SO_4)_3$ was prepared by the method suggested by Hattox and DeVries.[2]

E.m.f. Measurements.—The Ag, Ag_2SO_4 electrode consisted of a pure silver wire dipping into the desired $In_2(SO_4)_3$ solution saturated with Ag_2SO_4. The indium electrode consisted of a platinum spiral plated with indium metal as previously described.[2] Both electrodes were contained in 10 mm. o.d. glass tubes which were drawn down to capillary size at the lower end and then bent up in the form of a *U*. The $In_2(SO_4)_3$ solution and electrodes were contained in a Pyrex tube fitted with a Teflon cover having holes to admit the electrode compartments. The entire electrode assembly was sealed in a steel bomb fitted with electrically insulated leads. As shown previously,[5] this type of electrode as-

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[1] This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] E. M. Hattox and T. DeVries, THIS JOURNAL, **58**, 2126 (1936).

[3] M. H. Lietzke and R. W. Stoughton, *ibid.*, **75**, 5226 (1953).

[4] E. H. Archibald, "The Preparation of Pure Inorganic Substances," John Wiley and Sons, Inc., New York, N. Y., 1932.

[5] M. H. Lietzke and J. V. Vaughen, THIS JOURNAL, **77**, 876 (1955).

sembly is very easy to remove from the bomb for the purpose of changing solution or electrodes.

The bomb containing the electrode assembly was immersed in a constant temperature bath controlled to at least ±0.05°. The e.m.f. values were measured with a Rubicon precision potentiometer which was standardized with an Eppley cell calibrated by the Bureau of Standards.

The time required for the cells to reach equilibrium varied with the temperature. At the lowest temperatures the cells were allowed to stand overnight although the potentials became steady after 3 to 4 hours. In the intermediate temperature range equilibrium was established in 2 to 3 hours, and at the higher temperatures within 2 hours.

In all cases the e.m.f. measurements were carried to as high a temperature as possible. In the most dilute solutions this was 40°, while in the more concentrated solutions 70°. Above these temperatures irreversible hydrolysis of the $In_2(SO_4)_3$ occurred. This was indicated by a sudden drop in electrode potential after which the system never recovered at lower temperatures.

It was found that the $In_2(SO_4)_3$ solutions changed slowly with time, the rate of change being a function of the $In_2(SO_4)_3$ concentration. Below 0.1 *m* it was necessary to complete the e.m.f. measurements within one day. In the range 0.1 to 0.3 *m*, the measurements could be extended to two days, while at 0.5 *m* and above the measurements could be reproduced for a week. This effect also may have been due to irreversible hydrolysis of the $In_2(SO_4)_3$ solution.

Solubility Measurements.—Aliquots of $In_2(SO_4)_3$ solutions of known concentration were saturated with Ag_2SO_4 by stirring the solutions with excess Ag_2SO_4 crystals at 25° on a magnetic stirrer. The solutions were then analyzed for silver volumetrically by means of a Dow Precision Recordomatic titrimeter. In carrying out the determinations, sample aliquots were added to an excess of HCl and the excess chloride titrated with $AgNO_3$. It was found that this method of silver analysis gave much more precise and reproducible results than a gravimetric silver determination. The densities of the solutions were measured by weighing aliquots delivered from a Normax pipet.

Conductivity Measurements.—The resistances of aliquots of the same solutions used in the Ag_2SO_4 solubility measurements (both before and after saturation with Ag_2SO_4) were measured by means of a Serfass Conductivity Bridge. A dipping conductivity cell with a cell constant of 1.08 was used. Both the solubility and conductivity measurements were carried out at 25° only.

Results and Discussion

E.m.f. Measurements.—Table I summarizes the experimental measurements of the e.m.f. of the cell In, $In_2(SO_4)_3(m)$, Ag_2SO_4(sat), Ag as a function of $In_2(SO_4)_3$ concentration and temperature.

In previous measurements of the thermodynamic properties of $In_2(SO_4)_3$ solutions,[2] a saturated Hg, Hg_2SO_4 reference electrode was used. However, Hg_2SO_4 is known to hydrolyze in weakly acid systems[6] and at higher temperatures. For example, when the cell Hg, Hg_2SO_4(sat), $H_2SO_4(m)$, Ag_2SO_4(sat), Ag was studied,[3] it was found difficult to attain the theoretical e.m.f. for the cell at 25° in acid solutions more dilute than 0.05 *m*. This effect which was even more pronounced at higher temperatures, was shown previously to be due to formation of HgO.[3] The discrepancy is in such a direction as to make the e.m.f. of the In, $In_2(SO_4)_3(m)$, Hg_2SO_4(sat), Hg cell too positive if any hydrolysis of the Hg_2SO_4 occurs.

When the e.m.f. values measured in the present work are corrected for the difference between the Ag, Ag_2SO_4 and Hg, Hg_2SO_4 electrode potentials and compared at the same concentration with the values obtained by Hattox and DeVries it is found that the e.m.f. values reported by Hattox and DeVries are more positive. The discrepancy is about 5 millivolts at 0.4 *m* and 15° and becomes increasingly larger at lower concentrations and higher temperatures, amounting to about 20 millivolts at 0.01 *m* and 15° and to about 8 millivolts at 0.4 and 35°. Thus the e.m.f. values measured by Hattox and DeVries appear to be somewhat too high because of hydrolysis of the Hg, Hg_2SO_4 reference electrode.

TABLE I

THE EFFECT OF TEMPERATURE AND $In_2(SO_4)_3$ CONCENTRATION ON THE e.m.f. (IN VOLTS) OF THE In, $In_2(SO_4)_3(m)$, Ag_2SO_4(sat), Ag ELECTRODE SYSTEM

0.009888 *m*		0.04933 *m*		0.09799 *m*		0.1957 *m*	
t, °C.	*E*	*t*, °C.	*E*	*t*, °C.	*E*	*t*, °C.	*E*
13.2	1.1048	14.5	1.0992	14.3	1.0960	24.9	1.0841
20.4	1.0977	23.9	1.0901	24.4	1.0870	36.2	1.0735
27.5	1.0905	28.3	1.0862	40.3	1.0730	44.8	1.0661
35.1	1.0837	35.6	1.0795	50.2	1.0647	50.4	1.0616
						60.3	1.0533

0.1990 *m*		0.3959 *m*		0.5527 *m*		0.6806 *m*	
t, °C.	*E*	*t*, °C.	*E*	*t*, °C.	*E*	*t*, °C.	*E*
15.0	1.0923	13.3	1.0915	14.6	1.0830	13.6	1.0791
20.0	1.0880	20.2	1.0838	33.2	1.0661	22.7	1.0706
25.1	1.0836	30.0	1.0747	42.45	1.0577	29.8	1.0645
		35.3	1.0701	50.5	1.0502	30.4	1.0640
		41.8	1.0644	58.3	1.0434	39.5	1.0558
		49.9	1.0576	68.9	1.0342	50.6	1.0468
		57.3	1.0518	74.6	1.0297	62.3	1.0370
		65.4	1.0450			71.5	1.0299
		70.5	1.0409				

0.9732 *m*		1.2909 *m*		2.2822 *m*	
t, °C.	*E*	*t*, °C.	*E*	*t*, °C.	*E*
24.9	1.0599	14.0	1.0588	12.5	1.0296
48.2	1.0422	19.3	1.0531	21.8	1.0225
63.4	1.0310	29.5	1.0449	23.1	1.0215
		40.8	1.0368	29.0	1.0175
		50.2	1.0306	39.4	1.0105
		60.3	1.0245	40.2	1.0102
		70.5	1.0176	49.8	1.0053
				70.5	0.9951

Since the Ag, Ag_2SO_4 electrode was shown to be less susceptible to hydrolysis than the Hg, Hg_2SO_4,[3] it seemed that the Ag, Ag_2SO_4 electrode should be a better choice as a reference electrode and that the calculations involving the thermodynamic functions of $In_2(SO_4)_3$ solutions should be more nearly correct in the present work. In both cases the results may be slightly in error due to hydrolysis of the $In_2(SO_4)_3$ which would lower the $In_2(SO_4)_3$ activity by the amount hydrolyzed. The ratio moles of acid formed per mole of Indium $(H^+)/(In^{+3})$ increases at 23° from about 0.035 at 0.2454 *m* to about 0.12 at 0.0063 *m*.[2] Since the extent of hydrolysis is relatively small and since attempts to reduce the hydrolysis by the addition of acid were unsuccessful in producing consistent e.m.f. data, no attempt was made to correct for hydrolysis in the subsequent calculations. Added acid dissolved the In metal of the In electrode so rapidly that no stable potential was obtained.

In the course of the work no attempt was made to obtain e.m.f. measurements at even temperatures. For convenience in calculating and presenting data on activity coefficients and partial molal heat contents the e.m.f. values were plotted against temperature at each experimental concentration to obtain values at 5° intervals. The e.m.f.'s at the even temperatures were also plotted as a function of $In_2(SO_4)_3$ concentration to obtain values at even concentrations.

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[6] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IV, Longmans, Green and Co., London, 1923, p. 966.

When the $In_2(SO_4)_3$ electrode is measured against the saturated Ag, Ag_2SO_4 electrode the cell reaction is

$$2In + 3Ag_2SO_4 \rightleftarrows In_2(SO_4)_{3(aq)} + 6Ag \qquad (1)$$

The e.m.f. is given by the Nernst equation in the form

$$E = E^\circ - \frac{RT}{6F} \ln a_{In_2(SO_4)_3} \qquad (2)$$

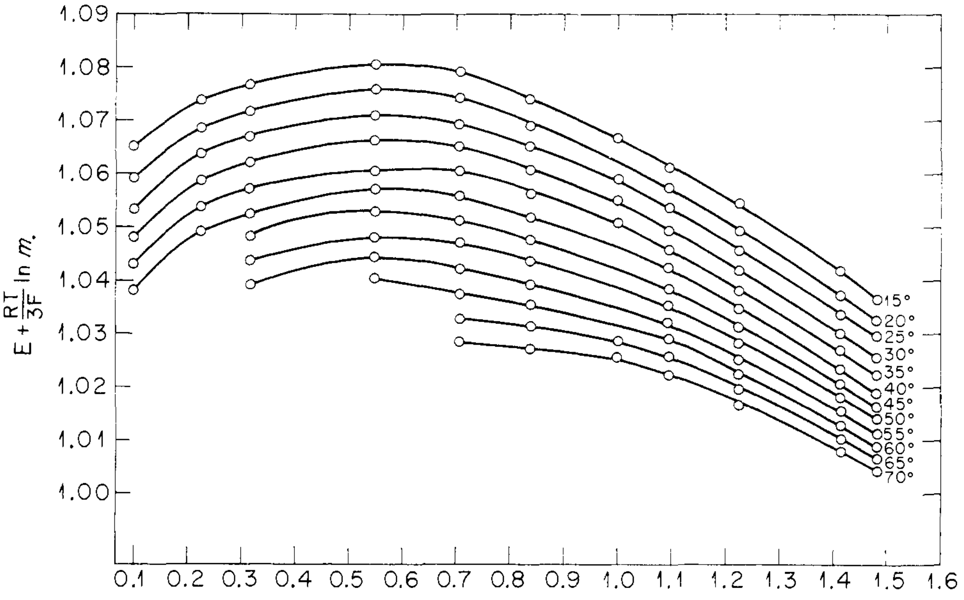

Fig. 1.—Plot of $E + RT/3F \ln m$ vs. $\sqrt{m}$ for the In, $In_2(SO_4)_3(m)$, Ag_2SO_4, Ag electrode combination.

where $a_{In_2(SO_4)_3}$ represents the thermodynamic activity of the $In_2(SO_4)_3$ solution. In order to compute activity coefficients from the e.m.f. data it is necessary to make an assumption concerning the species in solution. Three different assumptions which might be made are that $In_2(SO_2)_3$ dissociates

completely into $2In^{+++} + 3SO_4^{--}$ (a)
completely into $2InSO_4^{+} + SO_4^{--}$ (b)
completely into $InSO_4^{+} + In(SO_4)_2^{-}$ (c)

Depending on the assumption made the activity of $In_2(SO_4)_3$ would be given by (a) $108m^5\gamma^5$, (b) $4m^3\gamma^3$ or (c) $m^2\gamma^2$, respectively, where γ is the stoichiometric mean ionic activity coefficient consistent with the particular assumption made. Of course, the actual species existing in solution may not correspond to any one of the above assumed modes of dissociation, or even to a combination of them; that is, the actual predominant species may be more complex than those indicated. The hope was that by attempting to calculate the activity coefficients on one or all of the three bases mentioned, E^0 values might be obtained and by comparing the γ's with those of strong electrolytes conclusions might be drawn as to the species existing in solution.

On the basis of assumption (a), (b) or (c), equation 2 might be rewritten as equation 3, 4, or 5, after rearrangement of terms.

$$E + \frac{RT}{6F} \ln 108 + \frac{5RT}{6F} \ln m = E^\circ - \frac{5RT}{6F} \ln \gamma \qquad (3)$$

$$E + \frac{RT}{6F} \ln 4 + \frac{RT}{2F} \ln m = E^\circ - \frac{RT}{2F} \ln \gamma \qquad (4)$$

$$E + \frac{RT}{3F} \ln m = E^\circ - \frac{RT}{3F} \ln \gamma \qquad (5)$$

As will be shown later, the solubility data of Ag_2SO_4 in $In_2(SO_4)_3$ solutions may be interpreted on the assumption that $In_2(SO_4)_3$ behaves qualitatively like a strong 1-1 electrolyte, at the higher concentrations at least, although the evidence is not necessarily definitive. Hence, as a consistency check on the e.m.f. data, the left side of equation 5 was plotted against the square root of the $In_2(SO_4)_3$ molality to give the family of curves shown in Fig. 1. Because of the curvature of the lines at lower concentrations this type of plot is not useful for extrapolation to obtain E^0 values for the electrode combination. However, the curves do indicate the consistency of the e.m.f. data and show at each temperature the range of concentration in which the activity coefficients decrease in value then increase again.

In an effort to extrapolate the data to obtain E^0 values for the electrode combination and hence to permit the calculation of activity coefficients for the $In_2(SO_4)_3$ solutions equations 3, 4 and 5 were modified by substitution of the Debye–Hückel expression for the ln γ term and rearranged to give at 25° the expression

$$E^{\circ\prime\prime} = E + 0.009859 \left[\log k + \nu \log m - \frac{0.35999 \left(\sum_j \nu_j Z_j^2\right)^{3/2} \sqrt{m}}{1 + 1.06 \left(\sum_j \nu_j Z_j^2\right)^{1/2} \sqrt{m}} \right] \qquad (6)$$

For a 1-1 electrolyte $k = 1$, $\nu = 2$, and $\sum_j \nu_j Z_j^2 = 2$; for a 1–2 electrolyte $k = 4$, $\nu = 3$, and $\sum_j \nu_j Z_j^2 = 6$; while for a 3-2 electrolyte $k = 108$, $\nu = 5$, and $\sum_j \nu_j Z_j^2 = 30$. When the values of the constants were substituted into equation 6 for each case the curves shown in Fig. 2 were obtained. As can be seen subtraction of the Debye–Hückel term does not in any case give a function providing a linear extrapolation to infinite dilution. Hence values of

E^0 for the electrode system could not be obtained by this method.

Because it was not possible to derive values of E^0 by extrapolation, activities and activity coefficients had to be expressed as ratios and partial molal heat contents as differences. For reasons discussed in the section on conductivity measurements all ratios and differences were referred to the value at 0.1 *m*.

Figure 3 shows the variation of log $a/a_{0.1}$ for $In_2(SO_4)_3$ solutions as a function of concentration and temperature. The values of log $a/a_{0.1}$ were calculated by means of the expression

$$\log a/a_{0.1} = \frac{6F}{2.303RT}(E_{0.1} - E) \qquad (7)$$

which follows immediately from equation 2. The ratios are much more sensitive to temperature variation at the higher concentrations than at the lower. At each temperature, however, the log of the activity ratio is approximately proportional to the molality, a fact difficult to explain simply.

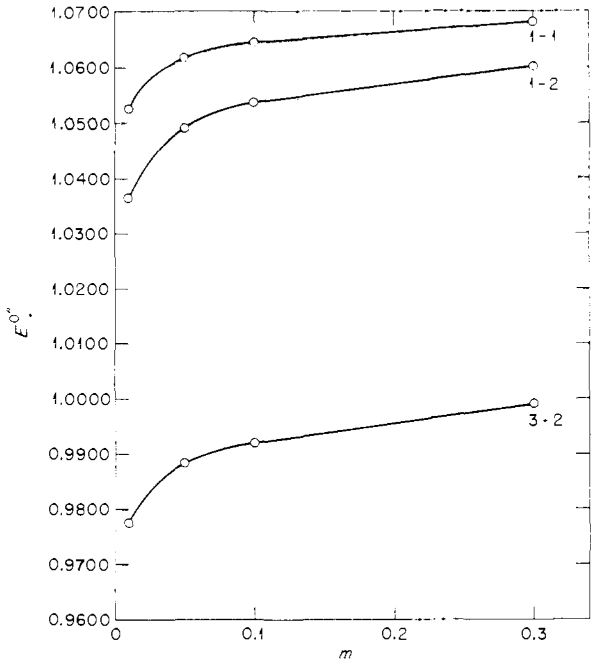

Fig. 2.—Plot of $E^{0''}$ *vs.* *m* for the In, $In_2(SO_4)_3(m)$, Ag_2SO_4, Ag electrode combination.

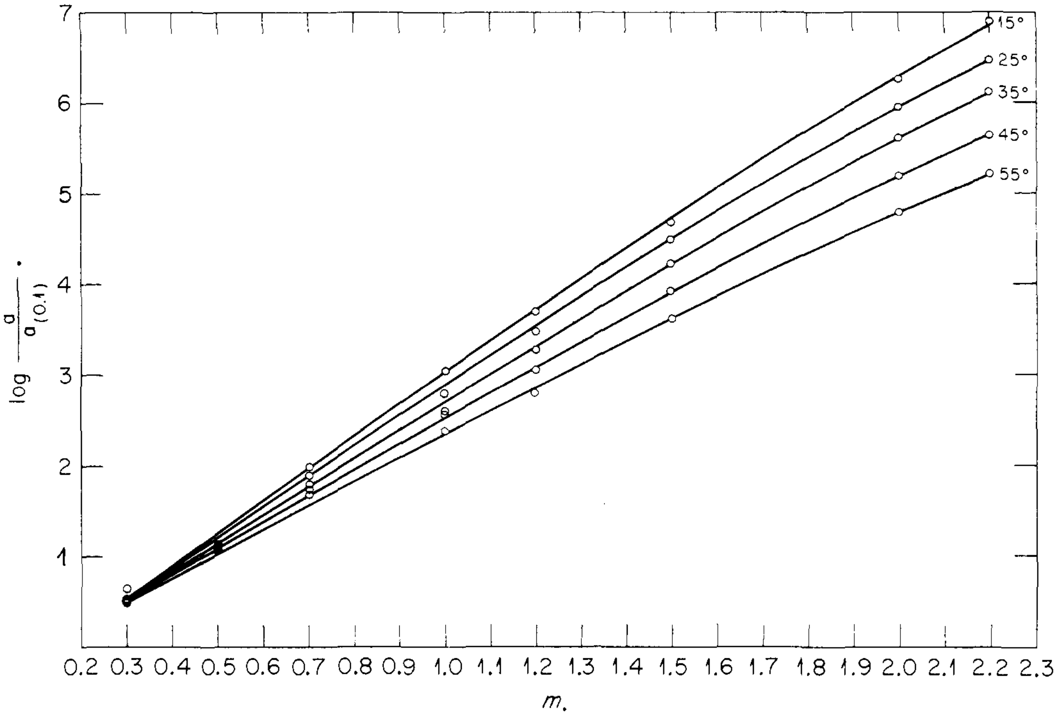

Fig. 3.—The variation of log $a/a_{0.1}$ for $In_2(SO_4)_3$ solutions as a function of concentration and temperature.

Activity coefficient ratios $\gamma/\gamma_{(0.1)}$ were calculated for $In_2(SO_4)_3$ on the basis of a 1-1, a 1-2, and a 3-2 electrolyte at 25° using the general equation

$$\log \gamma/\gamma_{(0.1)} = \frac{6F}{2.303\nu RT}(E_{(0.1)} - E) - \log \frac{m}{0.1} \qquad (8)$$

The values of $\gamma/\gamma_{(0.1)}$ as a function of *m* are given in Table II. The values of $\gamma/\gamma_{(0.1)}$ for the case of the 1-1 electrolyte increase more rapidly with *m* at the higher concentrations than do those of any known 1-1 electrolyte. This may be considered as evidence against any conclusion that $In_2(SO_4)_3$ behaves like a strong 1-1 electrolyte throughout any large concentration range.

Values of $\bar{L}_2 - \bar{L}_{2(0.1)}$ were calculated directly from Fig. 3 showing the variation of log $a/a_{(0.1)}$ with concentration and temperature. Since

$$\left(\frac{\partial \log a/a_{(0.1)}}{\partial T}\right)_m = -\frac{\bar{L}_2 - \bar{L}_{2(0.1)}}{2.303RT^2} \qquad (9)$$

$$\bar{L}_2 - \bar{L}_{2(0.1)} = -2.303RT^2\frac{\Delta \log a/a_{(0.1)}}{\Delta T} \qquad (10)$$

Table III shows the temperature and concentration

TABLE II

$\gamma/\gamma_{(0.1)}$ VALUES FOR $In_2(SO_4)_3$ SOLUTIONS CALCULATED ON THE BASIS OF A 1-1, A 1-2 AND A 3-2 ELECTROLYTE AT 25°

m	$\gamma/\gamma_{(0.1)}$ 1-1	1-2	3-2
0.3	0.5976	0.4919	0.4210
.5	0.7310	.4745	.3357
.7	1.224	.5983	.3374
1.0	2.509	.8570	.3629
1.2	4.625	1.213	.4154
1.5	11.89	2.113	.5303
2.0	47.37	4.786	.7755
2.2	77.22	6.471	.8904
2.3	123.5	8.718	1.046

dependence of $\bar{L}_2 - \bar{L}_{2(0.1)}$ values calculated by means of equation 10, from the table it is evident that the $\bar{L}_2 - \bar{L}_{2(0.1)}$ values become more temperature dependent at higher concentrations of $In_2(SO_4)_3$.

TABLE III

VALUES OF $\bar{L}_2 - \bar{L}_{2(0.1)}$ IN KCAL. FOR $In_2(SO_4)_3$ SOLUTIONS AS A FUNCTION OF CONCENTRATION AND TEMPERATURE

m/t	20°	30°	40°	50°
0.5	2.0	2.5	2.7	2.9
1.0	6.3	7.6	8.1	8.1
1.5	9.0	12.0	13.5	14.3
2.0	14.2	13.9	19.3	19.1
2.2	14.9	15.1	20.6	20.6

Conductivities of $In_2(SO_4)_3$ and $In_2(SO_4)_3$–Ag_2SO_4 Solutions.—The conductivities of $In_2(SO_4)_3$ solutions both saturated with Ag_2SO_4 and without Ag_2SO_4 were measured in order to get some idea of the conditions under which liquid junction potentials might be expected to be appreciable[7] and in order to elucidate the degree of dissociation of $In_2(SO_4)_3$. Table IV shows the conductivities of the solutions as a function of $In_2(SO_3)_3$ concentration. It is seen that below about 0.1 *m* $In_2(SO_4)_3$ the conductivities of the solutions vary considerably depending on whether or not Ag_2SO_4 is present (at saturation). In this range it was felt that the liquid junction potential between two solutions of $In_2(SO_4)_3$, one containing saturated Ag_2SO_4 and the other not, may well become appreciable; and even the change in this potential with indium concentration may become comparable in magnitude with the change in observed e.m.f. Hence, any interpretation of the e.m.f. data in this range may be meaningless. At higher concentrations of $In_2(SO_4)_3$ the conductivities depend very little on the presence or absence of Ag_2SO_4, and it has been assumed that liquid junction potentials could be neglected without serious error. At 0.1 *m* $In_2(SO_4)_3$ the effective equivalent conductance of the Ag_2SO_4 (calculated from the difference in conductivity with the silver present and absent) was about what might be expected on the assumption that neither salt greatly influenced the ionic concentrations resulting from the other.

The "equivalent" conductances of pure $In_2(SO_4)_3$ solutions were plotted against the square root of the molar concentration on the bases of one, two and six equivalents per mole (*i.e.*, on the bases of dissociation as 1-1, 1-2 and 3-2 electrolytes). These curves are plotted in Fig. 4 along with the curves[8] of other electrolytes for comparison. Of the latter none except strong acids and alkalies shows equivalent conductances greater than about 200 cm.^{2} ohm^{-1} equiv.$^{-1}$ at the lower concentrations. None of them decreases as rapidly with increasing concentration as does the $In_2(SO_4)_3$ conductivity if this electrolyte is assumed to dissociate as a 1-1 or 1-2 electrolyte. Also none shows as low conductivity as does $In_2(SO_4)_3$ on the basis of complete dissociation as a 3-2 salt.

If $In_2(SO_4)_3$ were assumed to dissociate into about three ions (*e.g.*, $2InSO_4^+$ and SO_4^{--}) at 0.01 *m* and to dissociate less and less with increasing concentration, then its equivalent conductance based on the assumed ion concentrations would show a behavior qualitatively similar to that of the other salts. The conductivity data are therefore interpreted as evidence against complete dissociation of $In_2(SO_4)_3$ into In^{+++} and SO_4^{--} ions in the concentration range studied. These data also imply a decreasing degree of dissociation with increasing concentration, as might be expected.

TABLE IV

THE CONDUCTIVITIES OF $In_2(SO_4)_3$ SOLUTIONS AT 25°

m	Conductivities (ohm^{-1} cm.$^{-1}$) Without $AgSO_4$	With Ag_2SO_4(sat.)
0.01	0.00242	0.00600
.03	.00527	.00777
.1	.0128	.0159
.3	.0267	.0282
1.0	.0347	.0340

Solubility of Ag_2SO_4 in $In_2(SO_4)_3$ Solutions.—The solubility of Ag_2SO_4 as a function of $In_2(SO_4)_3$ concentration at 25° is shown in the first two columns of Table V. The solubility shows an increase with increasing $In_2(SO_4)_3$ concentration rather than a decrease as expected from the common ion effect.

TABLE V

THE SOLUBILITY OF Ag_2SO_4 IN $In_2(SO_4)_3$ SOLUTIONS AT 25°

$m_{In_2(SO_4)_3}$	Exptl. solubility $m_{Ag_2SO_4}$	Calcd. Solubility Basis (a)	Basis (b)	Basis (c)
0	0.02676[a]	...	...	0.0263
0.0096	.02675	0.0248	0.0252	(0.02675)
.0294	.0272	.0222	.0231	.0277
.0494	.0285	.0207	.0240	.0287
.0989	.0294	.0178	.0196	.0305
.3020	.0341	.0134	.0157	.0353
.9809	.0373	.0092	.0118	.0428

[a] G. Åkerlöf and H. C. Thomas, THIS JOURNAL, 56, 593 (1934).

Since the effect of increasing the ionic strength is to increase the solubility, the net effect of increasing the ionic strength and the common ion concentration was estimated on the two bases of $In_2(SO_4)_3$ dissociation previously given as (a) and (b). The Ag_2SO_4 was assumed to be completely dissociated into silver and sulfate ions under all conditions. The solubility product was calculated on a molality basis for the pure Ag_2SO_4 solution and the change of

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[7] See G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., New York, N. Y., 1923, pp. 389–99.

[8] B. W. Conway, "Electrochemical Data," Elsevier Publ. Co., New York, N. Y., 1952, p. 142.

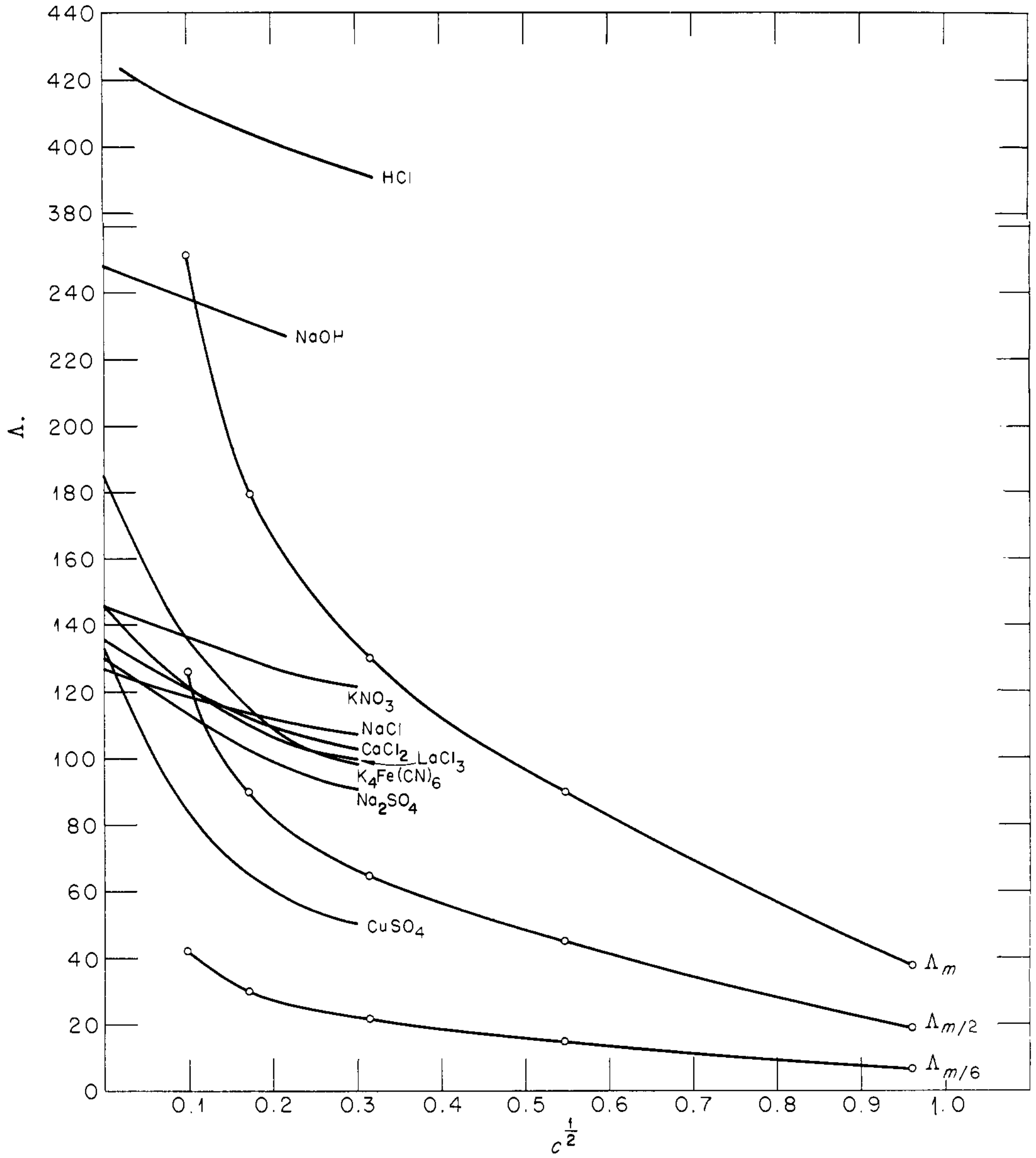

Fig. 4.—The "equivalent conductances" of $In_2(SO_4)_3$ solutions.

this product with ionic strength on bases (a) and (b) was determined using the modified Debye–Hückel equation for the log of the activity coefficient of an ion γ_i as shown in equation 11

$$\log \gamma_i = \frac{-0.509 Z_i^2 I^{1/2}}{1 + 1.5 I^{1/2}} \quad (11)$$

In this equation Z_i is the charge of the ion in question and I is the ionic strength. The constant 1.5 in the denominator was suggested to the authors by Scatchard[9]; the equation in this form gives a rough average value of the activity coefficient of an ion of a strong electrolyte out to about an ionic strength of unity, as can be verified by a plot of $(1/Z_+Z_-)$ $\log \gamma \pm$ *vs.* $I^{1/2}$ for various strong electrolytes.

Using the molality solubility products calculated in this manner, solubilities were calculated on bases (a) and (b) and these are presented in the third and fourth columns, respectively, of Table V. The solubilities calculated on both bases show a decrease with increasing $In_2(SO_4)_3$ concentration. Hence, it may be concluded from the solubility results that $In_2(SO_4)_3$ under the conditions reported is dissociated into fewer SO_4^{--} ions than indicated by basis (b). Although equation 11 is only approximate, most electrolytes known to be completely dissociated deviate at the higher ionic strength values in such a manner as to make the activity coefficients larger than the calculated values. Consequently, we do not feel that deviations from equation 11 which would invalidate our conclusion are likely to occur.

It was then assumed that $In_2(SO_4)_3$, at least at the higher concentrations, dissociates only into complex sulfate ions and hence causes no common ion effect. Using basis (c), equation 11, and the experimental solubility at 0.0096 *m* $In_2(SO_4)_3$ the Ag_2SO_4 solubilities in the other solutions were calculated; the calculated values are given in the fifth column of Table V. As can be seen, the agree-

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(9) G. Scatchard, private communication.

ment between the calculated and experimental Ag_2SO_4 solubilities is surprisingly good. This may be interpreted as evidence in favor of the validity of basis (c) for the dissociation of $In_2(SO_4)_3$ at the higher concentration, although actually one can only conclude that the magnitude of the ionic strength is consistent with basis (c).

Summary and Conclusions

The e.m.f. of the cell In, $In_2(SO_4)_3(m)$, Ag_2SO_4(sat), Ag was studied as a function of $In_2(SO_4)_3$ concentration and temperature. Since it did not appear feasible to extrapolate to zero concentration to obtain E^0 values relative activities only were obtained based on the value at 0.1 *m*. The log of these ratios was approximately proportional to the concentration at any one temperature. No unique interpretation in terms of solute species could be made. E.m.f., conductivity and solubility data all indicate that $In_2(SO_4)_3$ is not completely dissociated into In^{+++} and $SO_4^{=}$ ions in any part of the concentration range studied. The conductivity and solubility data are qualitatively consistent with dissociation of $In_2(SO_4)_3$ into $InSO_4^+$ and $In(SO_4)_2^-$ ions at the higher concentrations and with further dissociation of these species in the more dilute range. On the other hand, at the highest concentrations the rapid change of the activity coefficient of $In_2(SO_4)_3$ on a 1-1 electrolyte basis with *m* and the low magnitude of Λ_m appear to be inconsistent with expectations for a strong 1-1 electrolyte.

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OAK RIDGE, TENNESSEE

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MICHIGAN]

Heat Capacity and Thermodynamic Functions of Uranyl Chloride from 6 to 350°K.[1]

BY ELLIOTT GREENBERG AND EDGAR F. WESTRUM, JR.

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The heat capacity of pure anhydrous uranyl chloride was measured from 6 to 350°K. and the entropy, enthalpy and free energy function calculated from these data. At 298.16°K., the molal values of C_p, S^0 and $H^0 - H^0_0$ are 25.78 ± 0.04 cal./deg., 35.98 ± 0.05 cal./deg., and 5157 ± 8 cal., respectively. There was no detectable evidence of anomalous heat capacity behavior or significant magnetic contributions to the thermal properties.

Despite the increasing scientific and technological interest in uranium chemistry, the chemical thermodynamic data on important uranium compounds are in many instances inconsistent, estimated or unknown. Furthermore, the thermodynamic functions based on thermal data are frequently rendered insecure by the possibility of substantial magnetic contributions at temperatures below those of the heat capacity measurements. The heat capacity of anhydrous, crystalline uranyl chloride (UO_2Cl_2) was determined as part of a continuing study of the thermodynamic properties of the compounds of the actinide elements. The data and functions derived herein should prove of considerable utility in chemical calculations when supplementary thermochemical data become available.

Experimental

Preparation of Uranium Tetrachloride.—Uranyl nitrate hexahydrate (500 g., Mallinckrodt A.R. grade, No. 8640) was treated with a large excess (850 ml.) of concentrated hydrochloric acid, and the mixture was evaporated to dryness. The resulting uranyl chloride was refluxed for an hour at 150° with four times the stoichiometric quantity (1 kg.) of hexachloropropene.[2,3] The supernatant liquid was then drawn off through a sintered-glass filter stick, and the uranium tetrachloride was washed repeatedly with carbon tetrachloride until the washings were colorless. This procedure was carried out in a closed system in order to protect the uranium tetrachloride from atmospheric moisture. Most of the remaining carbon tetrachloride was removed by evacuation, and the last traces by heating to 250–300° under high vacuum for several hours. The anhydrous material was sublimed twice under high vacuum in a Pyrex glass tube at about 495°. Ignition in air of the sublimed dark-green crystals indicated 62.38 and 62.62% uranium (theoretical 62.67%). Gravimetric analysis for chloride, by precipitation with silver nitrate, indicated 37.26 and 37.27% (theoretical 37.33%).

Preparation of Uranyl Chloride.—Finely ground uranium tetrachloride was converted to uranyl chloride (UO_2Cl_2), in a system protected from moisture, by reaction at 300–350° with oxygen dried over anhydrous magnesium perchlorate. Attempts to minimize sintering by gradually increasing the temperature were unsuccessful; consequently, the procedure of grinding and treating with oxygen was twice repeated in order to effect complete conversion of the sample. The bright yellow product was analyzed by the methods already indicated, and found to contain 69.68 and 69.83% uranium (theoretical 69.82%), and 20.65 and 20.72% chlorine (theoretical 20.79%).

Throughout the course of this work all transfers of hygroscopic material were performed in a dry box.

Cryogenic Technique.—The Mark I adiabatic cryostat used for these measurements has been developed previously.[4]

The calorimeter (Laboratory Designation W-9) is similar in design and dimensions to W-6[5] except for two modifications: only four conduction vanes were used, and protection against possible corrosion was achieved by a 0.03 mm. gold plate on the interior surfaces. Apiezon T vacuum grease was used to provide thermal conduction in the thermocouple sleeve and in the thermometer-heater well. The calorimeter contained 2.0 cm. helium pressure to improve thermal conduction to the sample. A 150-ohm constantan, glass-fiber insulated wire was bifilarly wound in a conforming double thread in the heater sleeve.

Temperatures were measured with a capsule-type platinum resistance thermometer (Laboratory Designation A-3)

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(1) Adapted from a portion of the thesis of Elliott Greenberg, submitted to the Graduate School of the University of Michigan in partial fulfillment of the requirements of the Ph.D. degree. This work was supported in part by the U. S. Atomic Energy Commission, Division of Research, Sub-Contract AT(11-1)-70, No. 5.

(2) Reported in: J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, pp. 468–470.

(3) J. J. Katz, private communication.

(4) Edgar F. Westrum, Jr., and A. F. Beale, Jr., to be published.

(5) E. Benjamins and E. F. Westrum, Jr., to be published.