the concentration range 0.1 to 10.75 moles per liter, were measured at 25°.

The apparent molal heat capacity is a linear function of $c^{1/2}$ (or $m^{1/2}$ or $N_2^{1/2}$) only up to about a 1.5 molal solution, above which the relation found by Randall and Rossini fails. A hyperbolic second degree equation for the apparent molal heat capacity as a function of the square root of the volume concentration reproduces the specific heats with an average deviation of

$\pm 0.0075\%$. Values of the partial molal heat capacity of the salt at round concentrations were calculated from an equation previously derived and values of the partial molal heat capacity of the water were calculated from a new equation which is generally applicable to all molal quantities. These values are tabulated, along with those of the specific heats of the same solutions.

The Thermodynamics of Aqueous Indium Sulfate Solutions[1]

BY ERWIN M. HATTOX AND THOS. DE VRIES

Very little work has been done on the activity coefficients and other thermodynamic properties of aqueous solutions of the ter-bivalent salts. Hovorka and Rodebush[2] determined the freezing point lowering of dilute solutions of lanthanum sulfate, and from these data calculated the activity coefficients. Since their results dealt only with dilute solutions, it seemed desirable to study the behavior of indium sulfate in aqueous solutions over a wider range of concentrations and at several temperatures. E. m. f. measurements were made on cells of the type In (s) | In$_2$(SO$_4$)$_3$ (m) | Hg$_2$SO$_4$–Hg at 0, 15, 25 and 35°, and freezing point lowerings were determined for a few dilute solutions of indium sulfate. The degree of hydrolysis was also determined at room temperature.

Materials and Apparatus

All materials used in this investigation were very carefully purified. The water used for making the solutions and for making ice was prepared by double distillation of the ordinary laboratory distilled water. The first distillation was made from alkaline permanganate and the second from barium hydroxide. The water thus purified was stored in glass-stoppered Pyrex bottles.

Commercially pure indium (98.9%), obtained from W. S. Murray, Ithaca, New York, was purified in the following manner. The metal was dissolved in concentrated nitric acid, the solution diluted, and precipitated as indium hydroxide with dilute ammonium hydroxide. This was washed several times and dissolved in dilute hydrochloric acid. Spongy indium was plated out from

this solution, using platinum electrodes and a current of about 0.3 ampere. The washed, spongy mass then served as an anode in another dilute hydrochloric acid solution, the indium being redeposited by electrolysis on a platinum cathode.[3] Indium sulfate was prepared from this indium by slowly evaporating a strong sulfuric acid solution of it at about 50°, washing the crystals that separated out with glacial acetic acid, and then heating in a furnace to a temperature of 450–500° for six hours.[4] By gravimetric analysis the product was shown to be anhydrous indium sulfate.

The mercury was purified by washing for several days with dilute nitric acid and distilling twice under reduced pressure in a current of air.

Mercurous sulfate was prepared by electrolysis from dilute sulfuric acid using a mercury anode and a platinum cathode, and a current density of 0.5 ampere per square decimeter. In order to prevent the formation of a yellow basic salt due to hydrolysis, the mercurous sulfate, along with the finely divided mercury mixed with it, was washed first with alcohol, then with ether. The product was dried and kept in a desiccator until ready for use.

The most concentrated indium sulfate solution was made up by weight from the prepared anhydrous salt. All the solutions of lower concentrations were made by successive weight dilutions, using an analytical balance of 2-kg. capacity.

After experimenting with complicated cells in which the air could be replaced by hydrogen, a simple cell was developed, made by sealing a platinum wire in the bottom of a 16-mm. Pyrex tube, and having a side-arm in which the indium electrode was placed.

The thermostat temperatures were maintained within $\pm 0.01°$. A two-liter size Dewar flask with crushed ice served very satisfactorily for the 0° bath. All temperatures were established with standard thermometers.

Electromotive forces of the cells were measured on a Leeds and Northrup Type K potentiometer.

Apparatus for the freezing point measurements was

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(2) Hovorka and Rodebush, THIS JOURNAL, 47, 1614 (1925).

(3) Baxter and Alter, ibid., 55, 1943 (1933).

(4) Seward, ibid., 55, 2740 (1933).

essentially the same as that described by Hovorka and Rodebush,[2] the only change being that the two Dewar flasks were not sealed together. A twelve-junction thermel, carefully calibrated, and having a potential change of 461 microvolts per degree at 0°, was used for the determinations of the temperature differences. A very sensitive galvanometer set-up was arranged by making use of a lens of 1.22 meters focal length and focusing a straight edge image from the galvanometer mirror onto a ground glass plate. The distance from light source to the galvanometer, the same as that from the galvanometer to the plate, was 3.2 meters. The scale on the glass plate was calibrated and it was found that readings could be made with a precision of about 0.0001°. A White potentiometer, with the lower dials marked in 10 and 1 microvolts, was used to measure the voltage of the thermel.

Experimental

Mercury was placed in the bottom of the completely dried cell, and was then covered with a thin layer of the dry mercurous sulfate. The solution was poured down the side arm until it reached a height of about 2.5 cm. in the arm. After the cell had been tightly stoppered, it was allowed to stand for a period of from twenty-four to forty-eight hours in order for equilibrium to be reached. This time was found by experiment. When this time had elapsed, an indium electrode was prepared by plating a thin layer of the metal on a platinum spiral sealed in the end of a glass tube, using a current of about 0.2 ampere. After the electrode was washed and dried in a stream of air, it was placed in position in the side-arm, and held there by means of a rubber tubing which also served to keep the cell closed to the atmosphere. The cell was then placed in the 15° thermostat and allowed to reach equilibrium at that temperature, which usually required from three to six hours. After all the needed data at 15° had been recorded, the cell was transferred successively to the 25 and 35° thermostats. A separate cell was prepared for the measurements at 0°, but the procedure followed was the same.

The experimental technique used by Hovorka and Rodebush[2] was employed for the freezing point determinations.

Discussion of the Results

The molalities of the solutions used and the corresponding e. m. f.'s observed at the different temperatures are given in Table I. Two or more values were obtained for each concentration at each temperature. The voltages were reproducible to ±0.2 mv. in the concentrated solutions, but the deviations in the dilute solutions were about ±0.3 mv. The e. m. f.'s of the individual cells usually remained constant for eight to ten hours or longer.

In order to determine the absolute value of the activity coefficients, E_0 must be evaluated. This requires an extrapolation to infinite dilution, and the voltages of the dilute solutions are less reliable than those of the concentrated solutions. Evi-

TABLE I

ELECTROMOTIVE FORCE OF CELLS
In(s), In$_2$(SO$_4$)$_3$(m), Hg$_2$SO$_4$-Hg

m $\dfrac{\text{Moles In}_2(\text{SO}_4)_3}{1000 \text{ g. H}_2\text{O}}$	0°	15°	25°	35°
0.4231		1.0473	1.0427	1.0382
.3132		1.0500	1.0456	1.0410
.2454		1.0528	1.0483	1.0439
.1676	1.0627	1.0560	1.0515	1.0470
.0999		1.0597	1.0553	1.0508
.0526	1.0700	1.0631	1.0591	1.0551
.0378		1.0673	1.0632	1.0590
.0281	1.0749	1.0698	1.0658	1.0617
.0221		1.0718	1.0677	1.0636
.0158	1.0800	1.0742	1.0703	1.0664
.0100	1.0838	1.0782	1.0744	1.0705
.00631	1.0885			

Values of E_0

E_0	0.974	0.962	0.954	0.946

dently, then, an extremely accurate value of E_0 cannot be expected. However, from freezing point measurements the activity coefficients can be determined with considerable accuracy. Due to the formation of a precipitate resulting from hydrolysis it was possible to obtain only one point of any significance from such measurements. A 0.00631 molal solution gave a depression of 0.0316°, but solutions of 0.00198 molal and less developed precipitates upon standing. The one point that we were able to determine fits the data of Hovorka and Rodebush within the limits of experimental error. Assuming that indium sulfate and lanthanum sulfate give identical freezing point curves in very dilute solutions, which seems to be logical, we used 0.150 as the activity coefficient in 0.01 molal solution[5] and calculated E_0 to be 0.9747 volt at 0°. This agrees well with 0.974 obtained by an extrapolation from e. m. f. data.

The electromotive force of the cell at any temperature T may be given by the equation

$$E = E_0 - (RT/6F) \ln 108\gamma^5 m^5 \qquad (1)$$

which may be written

$$k \log \gamma = E_0 - E - 0.4067k - k \log m \qquad (2)$$

In dilute solutions the logarithm of the activity coefficient may also be expressed by $\log \gamma = -6A\sqrt{\mu} + B\mu$ in which A and B are constants and μ is the ionic strength. When this relation is used in (2), the following expression is obtained

$$E + 0.4067k + k \log m - 6kA\sqrt{\mu} = E_0 - kB\mu \qquad (3)$$

Designating the left side of this equation as E_0', and plotting it against m, a curve is obtained for each temperature which may be extrapolated to

(5) Rodebush, THIS JOURNAL, 48, 709 (1926).

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infinite dilution to give a value for E_0. Harned and Ehlers' values[6] of A were used in evaluating E_0'. Curves of this type were drawn for the four temperatures. Although these were nearly straight lines and the curves did not have to be extrapolated very much, E_0 was not evaluated closer than 1 mv. The values are given in Table I. These were used in equation (1) to calculate the activity coefficients. Because of the uncertainty as to the degree of hydrolysis of indium sulfate, it is not feasible to determine the "true" activity coefficients. The "stoichiometrical activity coefficients"[7] were therefore determined. They are collected in Table II. The values, including those calculated by Rodebush[5] from the freezing point data for lanthanum sulfate, lie on a smooth curve when log γ is plotted against $\sqrt{m}$. Since Halpern[8] questions the reliability of the La Mer, Gronwall and Greiff extension of the Debye–Hückel theory[9] to unsymmetric valence type of electrolytes, no attempt was made to make the Debye–Hückel equations fit the data. When extrapolated values of the La Mer, Gronwall and Greiff formulas were used, a value of about 5 Å. was obtained for "a," the mean distance of approach of the ions.

TABLE II
ACTIVITY COEFFICIENTS OF INDIUM SULFATE

m	0°	15°	25°	35°
0.4231		0.015	0.015	0.014
.3132		.018	.017	.017
.2454		.020	.020	.019
.1676	0.025	.025	.025	.024
.0999		.035	.035	.034
.0526	.056	.056	.055	.054
.0378		.064	.063	.063
.0281	(.081)	.076	.075	.075
.0221		.088	.088	.087
.0158	.111	.110	.109	.108
.0100	.145	.143	.142	.141
.00631	.181			

The normal potential of the In, In^{+++} electrode at 25° is $+0.340$ if the value -0.614 is used for the $Hg–Hg_2SO_4$, $SO_4^=$ electrode.[10]

The Partial Molal Heat Content

The partial molal heat content relative to the 0.01 M solution was computed by the Gibbs–Helmholtz equation

$$(\overline{H}_m - \overline{H}_{0.01}) = NF(E - TdE/dT) \qquad (4)$$

(6) Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933).
(7) Brönsted, ibid., **42**, 761 (1920).
(8) Halpern, J. Chem. Phys., **2**, 85 (1934).
(9) La Mer, Gronwall and Greiff, J. Phys. Chem., **35**, 2245 (1931).
(10) Shrawder, Cowperthwaite and La Mer, THIS JOURNAL, **56**, 2348 (1934).

The temperature coefficient of the cell was nearly constant. Since an error of ± 0.01 mv. in the temperature coefficient means an error of approximately ± 100 calories, the values given in Table III are merely good approximations. Because of insufficient data it was not possible to calculate $\overline{L}_2$, the relative partial molal heat content.

TABLE III
PARTIAL MOLAL HEAT CONTENT OF INDIUM SULFATE RELATIVE TO THE 0.01 M SOLUTION

| m	$(\overline{H}_m - \overline{H}_{0.01})$ 0°	15°	Cal./mole 25°	35°
0.4231		−4280	−4390	−4470
.3132		−3900	−3990	−4080
.2454		−3520	−3610	−3680
.1676	−2920	−3070	−3170	−3250
.0999		−2560	−2640	−2730
.0526	−1910	−2090	−2120	−2130
.0378		−1510	−1550	−1590
.0281	(−1230)	−1160	−1190	−1220
.0221		− 890	− 930	− 950
.0158	− 530	− 550	− 570	− 570

Hydrolysis of Indium Sulfate

The pH values of nine solutions were determined at room temperature, 23°, using a quinhydrone electrode with a 0.1 N calomel cell as reference electrode.

Two series of hydrolysis constants were calculated from the pH values found at various molalities. These are designated in Table IV as K_h and K_h'. The K_h' was calculated on the assumption that the hydrolysis of In^{+++} may be represented

$$In^{+++} + H_2O \rightleftharpoons InO^+ + 2H^+ \qquad (5)$$
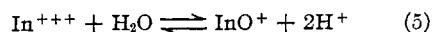
The computed values of K_h' vary considerably at the different concentrations. If, however, the hydrolysis reaction is written

$$In^{+++} + H_2O \rightleftharpoons In(OH)^{++} + H^+ \qquad (6)$$
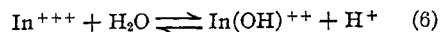
and the constant calculated for this reaction, a much nearer approach to a constant value is obtained. The values headed K_h are the results

TABLE IV
HYDROLYSIS OF INDIUM SULFATE

m	pH	$K_h' \times 10^4$	$K_h \times 10^4$
0.2454	1.77	5.1	6.6
.0999	2.01	2.4	5.1
.0526	2.20	1.2	4.0
.0378	2.29	0.93	3.7
.0281	2.36	.79	3.7
.0221	2.41	.72	3.8
.0158	2.57	.34	2.5
.0100	2.69	.21	2.2
.00631	2.83	.14	2.0

obtained. The results are not constant, but such could hardly be expected, since molalities instead of activities were used. There is indication, however, that a constant value will be approached in a very dilute solution.

Summary

1. Using cells of the type In(s), $In_2(SO_4)_3$-(m), Hg_2SO_4–Hg electromotive force measurements have been made at 0, 15, 25 and 35°.

2. The freezing points of dilute solutions of indium sulfate were investigated.

3. Calculations have been made of the activity coefficients of indium sulfate in aqueous solution, and of the partial molal heat contents relative to the 0.01 M solution.

4. pH values of solutions of indium sulfate have been determined at room temperature, using the quinhydrone electrode.

5. The constant for the hydrolysis of indium sulfate has been calculated assuming the reaction to be

$$In^{+++} + H_2O = In(OH)^{++} + H^+$$
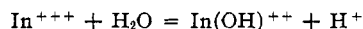
LAFAYETTE, INDIANA   RECEIVED AUGUST 1, 1936

The Presence of Free Radicals in the Thermal Decomposition of Diethyl Ether

BY C. J. M. FLETCHER AND G. K. ROLLEFSON

The decomposition of diethyl ether is a reaction for which a chain mechanism involving free radicals has been postulated.[1] The experimental results of previous investigations,[2-6] except for the recent results on the inhibition of the rate of reaction by small quantities of nitric oxide,[7] do not enable any decision to be made between the alternative theories of molecular rearrangement and such a chain mechanism. The present investigation provides definite evidence for the presence of free radicals since small amounts of ether are found to catalyze the decomposition of acetaldehyde. Quantitative estimations of the aldehydes, which are formed as intermediates, and a more detailed study of the kinetics of the over-all reaction have enabled the kinetics of the ether decomposition to be separated from those of secondary reactions.

Experimental Details.—The thermal reactions were studied in a Pyrex bulb, approximately 500 cc. in volume, placed in an electrically heated furnace. Fluctuations of the voltage were reduced by the use of Radiatron ballast tubes (U. V. 886 and 876), and the temperature was controlled by hand to within one degree. Pressures greater than 20 mm. were measured on a mercury manometer made from capillary tubing and heated by nicrome wire to prevent the condensation of organic vapors. The dead-

space outside the furnace did not amount to more than 2% of the volume of the bulb. Pressures of less than 20 mm. were measured with a sulfuric acid manometer separated from the reaction by a click-gage. It was found that pressure equilibrium between the bulb and click-gage was not established instantaneously, so that the time lag was estimated with different pressures of air and a correction applied.

The reaction vessel was evacuated through a liquid air trap by a mercury vapor pump and oil pump to pressures of less than 10^{-3} mm. If at any time air was admitted to the reaction vessel, it was well washed out with the vapor of the substance in use.

The substances used were stored, if liquids, in small bulbs attached to the system; if gases, in a reservoir over mercury. Mixtures were made in a reservoir over mercury, and could be thoroughly mixed by changing the mercury level.

Gas analyses were carried out according to the micro methods of Blacet and Leighton.[8] The greater part of any aldehyde or ether present was removed in a trap at −70°. As it was found that the beads slowly absorb other gases than that for which they are used (e. g., fuming sulfuric acid slowly absorbs carbon monoxide), the times of contact were carefully controlled.

In order to determine the amounts of aldehydes present the gas was withdrawn, shaken with water and (a) the total aldehydes found by titration with sodium bisulfite; (b) the formaldehyde estimated by the potassium cyanide method.[9] The bisulfite solution was stabilized with ethyl alcohol and frequently standardized against iodine. Blank experiments with acetaldehyde showed that it also slowly reacts with potassium cyanide for which interaction a correction was applied. Experiments with undecomposed acetaldehyde vapor withdrawn from the furnace showed the bisulfite method to be accurate.

(1) F. O. Rice and Herzfeld, THIS JOURNAL, **56**, 284 (1934).

(2) Hinshelwood, *Proc. Roy. Soc.* (London), **A114**, 84 (1927).

(3) Newitt and Vernon, *ibid.*, **A135**, 307 (1932).

(4) Steacie and Solomon, *J. Chem. Phys.*, **2**, 503 (1934).

(5) O. K. Rice and Sickman, THIS JOURNAL, **56**, 1444 (1934).

(6) Steacie, Hatcher and Rosenberg, *J. Chem. Phys.*, **4**, 220 (1936).

(7) Staveley and Hinshelwood, *Proc. Roy. Soc.* (London), **A154**, 335 (1935).

(8) Blacet and Leighton, *Ind. Eng. Chem., Anal. Ed.,* **3**, 266 (1931).

(9) Romijn, *Z. anal. Chem.*, **36**, 19 (1897).