bromides with thiosulfate ion are therefore believed to be true bimolecular substitution reactions. The important conclusions of this paper are derived from the relative heats and entropies of activation in Table VI. The rate of reaction of *n*-propyl bromide is only about half that of ethyl bromide in spite of the fact that its heat of activation is lower by about 0.5 kcal. A decrease in the entropy of activation well in excess of experimental error is responsible for the lower rate. On the other hand, the difference in rate between ethyl and *i*-propyl bromides is primarily due to a difference of 1.6 kcal. in the heats of activation of the two compounds. The difference in the entropies of activation is uncertain.

These results are in qualitative agreement with those of Seelig and Hull for the bromide ion–alkyl bromide reaction.[2c] The interesting calculations of Dostrovsky and Hughes[5] show that in the latter reaction, steric hindrance in the transition state would be equal for ethyl and *n*-propyl bromides, but would cause a rise of about 1 kcal. in the activation energy of *i*-propyl bromide. The results of the present paper show that these calculations may well be a valid explanation of the difference in rates between the primary and secondary compounds, but that no refinement of the calculation of activation energies will account for the difference in rates of reaction of ethyl and *n*-propyl bromides.

Steric hindrance and electric fields no doubt influence the entropy of activation; the only contention here is that the rate difference is not due to their influence on the energy barrier to the transition state, when a beta methyl group is added. The state of affairs is similar to that found in ester hydrolysis[15] and in the formation of semicarbazones,[10] where variations in rate are in many cases due to entropy, rather than energy differences.

Summary

The rates of reaction of thiosulfate ion with ethyl, *n*-propyl and *i*-propyl bromides have been measured at 12.50, 25.00 and 37.50° in an ethanol–water solvent (44.05% ethanol by weight) buffered with sodium acetate. Rates of solvolysis and reaction with acetate ion were also measured.

The replacement of an α-hydrogen atom of ethyl bromide by a methyl group increases the heat of activation of the first reaction by 1.6 kcal. This is the essential reason for a decrease in reaction rate. The replacement of a β-hydrogen atom also decreases the rate, but in this case the change is due primarily to a decrease of 3.0 cal./deg. in the entropy of activation.

[15] Smith and Steele, THIS JOURNAL, **63**, 3466 (1941).

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[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY]

The System Uranyl Sulfate–Water. I. Temperature–Concentration Relationships Below 300°[1]

BY C. H. SECOY

At the outset of this research it was proposed to study the phase relationships in the system uranyl sulfate–water at high temperatures and pressures. However, an inspection of the literature revealed only very meager and inconsistent information concerning the system at low temperatures. Therefore, in order to make the study complete, the work described in this paper was undertaken.

The solubility of uranyl sulfate in water at or near room temperature is reported in the earlier literature by various workers with a great lack of agreement. Mellor[2] gives values reported by de Coninck as 0.461 molal at 13°, and 0.513 molal at 16°; by Buckholz as 3.95 molal at ordinary temperature and as 5.28 molal in boiling water; by Ebelman as 5.07 molal at 21° and 8.49 molal in boiling water; and other data from which one can calculate 4.30 molal at 25°. The only other pertinent data which could be found were those of Dittrick[3] for the freezing point depression for very dilute solutions. More recently, Helmholtz and Friedlander[4] have reported the solubility at 30, 35 and 40°. Values from the last two sources are included in Table I.

Experimental Procedure

Data for the ice curve were obtained by the usual techniques of thermal analysis. Since supercooling was great, warming curves were used for the most part. Most of the analyses were done volumetrically, reducing the uranyl ion to tetravalent and trivalent uranium with zinc amalgam, oxidizing the trivalent ion to tetravalent with air, and titrating the tetravalent uranium with standard potassium permanganate solution. Many of the analyses were checked gravimetrically by ignition to U_3O_8.

The solubility of the salt above room temperature was determined by the following steps: (1) a weighed amount of water and a weighed amount of salt of known composi-

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[1] This document is based on work performed under Contract No. W-35-058-eng-71 for the Atomic Energy Project at the Clinton National Laboratory (now known as the Oak Ridge National Laboratory). Presented before the Division of Physical and Inorganic Chemistry at the 113th national meeting of the American Chemical Society, Chicago, Illinois, April 19–23, 1948.

[2] Mellor, "A Comprehensive Treatise on Inorganic and Physical Chemistry," Vol. XII, Longmans Green and Co., New York, N. Y., 1932, pp. 103–105.

[3] Dittrick, *Z. physik. Chem.*, **29**, 449 (1899).

[4] Helmholtz and Friedlander, Manhattan Project Report, LAMS 30.

tion were placed in a Pyrex tube; (2) permanent gases were removed from the tube by alternate freezing and thawing of the contents under vacuum; (3) the tube was sealed off and attached to a shaker in a water or oil bath the temperature of which could be slowly raised; (4) the temperature at which the last crystal dissolved was observed; and (5) the composition was checked by analysis of the contents of the tube. It is to be noted that this procedure did not give points at a constant pressure but rather each point represented the solubility when the solution was at its equilibrium vapor pressure. The temperature observation was repeated several times for each tube before it was opened for analysis and each value given in Table I represents a mean of the observed values.

TABLE I

SOLUBILITY OF URANYL SULFATE IN WATER

t, °C.	m	Solid phase	t, °C.	m	Solid phase
− 0.0705	0.03[a]	Ice	106.2	5.26	$UO_2SO_4·3H_2O$
− .1100	.05[a]	Ice	116.8	5.59	$UO_2SO_4·3H_2O$
− .200	.10[a]	Ice	118.4	5.73	$UO_2SO_4·3H_2O$
− .516	.30[a]	Ice	119.9	5.66	$UO_2SO_4·3H_2O$
− .948	.60[a]	Ice	125.2	5.90	$UO_2SO_4·3H_2O$
−17.7	2.87	Ice	134.9	6.25	$UO_2SO_4·3H_2O$
−22.9	3.33	Ice	139.0	6.51	$UO_2SO_4·3H_2O$
−38.5	3.82	Eutectic	140.7	6.55	$UO_2SO_4·3H_2O$
−27.0	3.84	$UO_2SO_4·3H_2O$	145.1	6.72	$UO_2SO_4·3H_2O$
30.0	4.135[b]	$UO_2SO_4·3H_2O$	149.6	6.89	$UO_2SO_4·3H_2O$
35.0	4.171[b]	$UO_2SO_4·3H_2O$	153.6	7.14	$UO_2SO_4·3H_2O$
40.0	4.225[b]	$UO_2SO_4·3H_2O$	168.6	7.75	$UO_2SO_4·3H_2O$
46.8	4.31	$UO_2SO_4·3H_2O$	181	8.66	Transition
57.3	4.50	$UO_2SO_4·3H_2O$	152	8.97	$UO_2SO_4·1H_2O$
71.7	4.73	$UO_2SO_4·3H_2O$	287	7.75	$UO_2SO_4·1H_2O$
80.8	4.70	$UO_2SO_4·3H_2O$	49.2	4.70	$UO_2SO_4·2H_2O$ (*m*)
90.1	5.02	$UO_2SO_4·3H_2O$	53.2	4.73	$UO_2SO_4·2H_2O$ (*m*)
93.5	5.06	$UO_2SO_4·3H_2O$	75.5	5.06	$UO_2SO_4·2H_2O$ (*m*)

[a] Dittrick, reference 3. [b] Helmholtz and Friedlander, reference 4.

Only three points were obtained on the retrograde solubility curve of the monohydrate and, therefore, the shape of this curve may be somewhat questionable. One of these points (181° and $m = 8.66$) lies very nearly on the intersection of the two curves since it could be approached with either rising or falling temperature. Temperature readings recorded for this tube are as follows:

With rising temperature: 181.0, 181.1, 181.1
With falling temperature: 180.9, 180.8, 181.0

The other two points on the monohydrate curve, one of which lies in the metastable region, were obtained with the temperature falling.

The composition of the solid phases was determined by separation of the phases and chemical analysis of the solids. A tube containing an excess of the salt was shaken at the desired temperature until equilibrium was assured, then quickly cooled to lower the pressure, opened, and some of the crystals isolated by quick filtration through a very porous filter. These crystals were immediately weighed and their uranium content determined by analysis. The formula of the hydrate could then be calculated. The rates of the processes involved in altering the composition of the crystals during the cooling, opening and weighing operations were sufficiently slow so that results obtained were reasonably consistent. Results of the analyses were as follows:

Anal. Calcd. for $UO_2SO_4·3H_2O$: U, 56.66. Found: U, 56.28, 56.34; moles of H_2O, 3.16, 3.13.

Anal. Calcd. for $UO_2SO_4·2H_2O$: U, 59.20. Found: U, 58.56, 58.63; moles of H_2O, 2.24, 2.22.

Anal. Calcd. for $UO_2SO_4·1H_2O$: U, 61.97. Found: U, 61.48, 61.41; moles of H_2O, 1.17, 1.20.

Experimental Results

The data obtained are summarized in Table I and shown graphically in Fig. 1. The values of Dittrick for the freezing point depression in dilute solutions are included in the table as well as those of Helmholtz and Friedlander for the solubility. These are in good agreement with the results of this work. The solubility of the trihydrate over the entire range of its stable existence is expressed by the empirical equation, $m = 2.438 \times 10^{-16} T^{6.134} + 3.731$, in which T is the absolute temperature and m the molality of the saturated solution. The mean deviation of the experimentally determined points from values calculated by the equation is 1%.

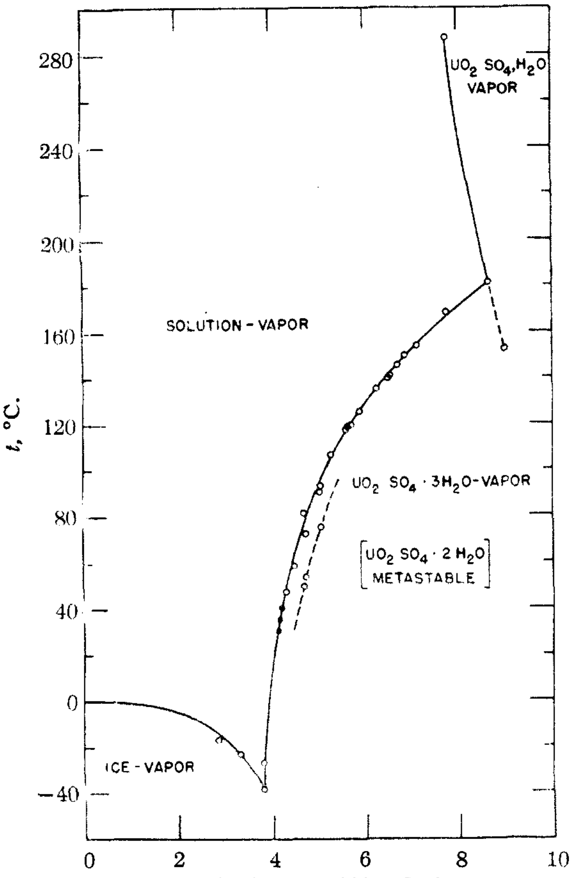

Fig. 1.—Temperature–concentration diagram for the system uranyl sulfate–water.

After having made a temperature determination, difficulty in obtaining recrystallization for a check run was often experienced. It was impossible to seed the solution and a remarkable ability to supercool was displayed. This difficulty was overcome by allowing most of the solution to flow to the lower end of the tube leaving a few drops at the upper end. This small portion of the solution was then cautiously evaporated to dryness leaving a small solid residue in one end of the tube. After this portion of the tube was cool, the solution was allowed to flow back into contact with the solid and a recrystallization slowly took place. After shaking and standing for a sufficient time the tube was ready for a check run. In most cases these check runs agreed with initial results but in some tubes the check run gave a lower solution temperature than the original value. At first these discrepancies were blamed on experimental error in the initial run, but as the data accumulated it was evident that we were getting two nearly parallel curves. Search for a transition throughout this portion of the diagram failed. Finally, analysis of the solid phases indicated that the material with the lower solubility, the stable phase, was the trihydrate while that with the higher solubility was the dihydrate which was metastable with respect to the trihydrate over the entire range of its existence. Those tubes in which the dihydrate had been formed continued to give points on the dihydrate curve on immediately repeated runs. However, if the tube were allowed to stand with a solid phase present for a period of about a week, a point on the trihydrate curve was once again obtained.

Calculations and Discussion

Freezing point data provide a means of calculating activity coefficients for the solute. Since information is lacking concerning the heat of dilution and its temperature coefficient the calculation was made neglecting these effects. It has been shown[5] that the logarithm of the mean activity coefficient, log γ', is given by the expression

$$\log \gamma' = \int_0^m -j \, d \log m - j/2.303 + 0.00025/\nu \int_0^m \theta/m \cdot d\theta \qquad (1)$$

in which ϑ is the observed freezing point lowering in a solution containing m moles of solute per 1000 g. of water and ν is the number of ions into which one molecule of salt is dissociated. The quantity j is defined by $j = 1 - \theta/\nu\lambda m$. λ is the molal lowering of the freezing point at infinite dilution.

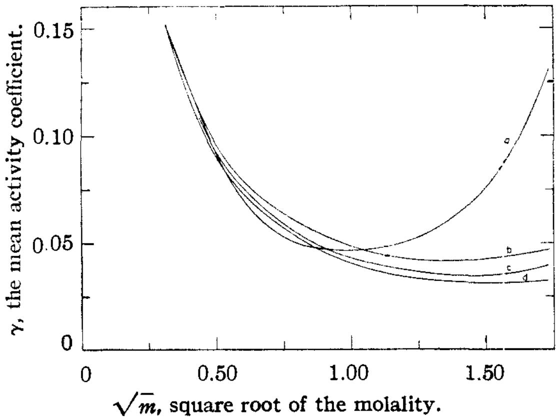

Fig. 2.—Mean activity coefficients of bivalent metal sulfates at 25°: a, UO_2SO_4; b, $MgSO_4$; c, $ZnSO_4$; d, $CdSO_4$.

The integral quantities in equation (1) were evaluated graphically, and values of γ' so obtained were then adjusted to $\gamma' = 0.150$ at $m = 0.1$ for comparison with the activity coefficients for other bivalent metal sulfates taken from the literature.[6]

TABLE II

THE MEAN ACTIVITY COEFFICIENTS OF URANYL SULFATE AT 25°

m	γ'	m	γ'
0.1	0.150	1.0	0.047
.2	.108	1.5	.053
.3	.080	2.0	.066
.4	.066	2.5	.090
.5	.056	3.0	.131
.7	.049	3.5	.274

For concentrations up to one molal, the agreement is good considering the approximation made in calculating γ'. However, at higher concentrations, the activity coefficient of uranyl sulfate rises much more rapidly than those of the other salts. In this respect the behavior of uranyl sulfate more nearly resembles that of sulfuric acid and monovalent metal sulfates. Figure 2, in which γ is plotted against $\sqrt{m}$, indicates clearly the anomalous behavior of uranyl sulfate at the higher concentrations. Experiments have been planned in this laboratory by which independent methods can be used to verify these results.

Preliminary Work at High Temperatures.—A one molal solution of uranyl sulfate in water undergoes no visible change until, at about 300°, a second liquid phase appears. This may be molten anhydrous uranyl sulfate saturated with water. The aqueous phase undergoes critical transformation at or very near the critical temperature of pure water indicating that the solubility of uranyl sulfate has reached a very low value at that temperature. The liquid salt phase remains unaltered. Further work on this system in this temperature range will be described in a later paper.

Summary

The temperature–concentration diagram for the system uranyl sulfate–water has been presented and the results discussed. The stable hydrates are the trihydrate and monohydrate. A dihydrate, metastable with respect to the trihydrate, was formed under certain conditions.

Activity coefficients for uranyl sulfate, calculated from the freezing point data without benefit of heat capacities, agree well with those of other bivalent metal sulfates at concentrations below one molal but rise more rapidly than those for other sulfates above this concentration.

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(5) Lewis and Randall, "Thermodynamics," p. 347.

(6) Harned and Owen give an excellent summary of such data in their book, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York, N. Y., 1943, p. 427.