

625. *The Heat of Dilution of Aqueous Uranyl Acetate Solutions.*

By (MISS) B. C. L. SALMAN and A. G. WHITE.

The heat of dilution of aqueous uranyl acetate solutions at 25° has been measured over a concentration range 0.17—0.00002 molal. The results are discussed in terms of the complex-ion formation and hydrolysis processes.

THE heat of dilution of uranyl salt solutions has not previously been reported. Heats of dilution of strong electrolytes are, in general, adequately represented in dilute solutions by expressions derived from the Debye-Hückel theory.¹ For uranyl acetate, however, there is evidence² of strong complex formation between acetate and uranyl ions and, in addition, the uranyl ion is known to be extensively hydrolysed in dilute solutions.³ It was thus expected, and found, that the heats of dilution of uranyl acetate solutions differed markedly from theoretical predictions based on the theory of strong electrolytes. In dilute solutions the molar heat of dilution increases very rapidly with decreasing concentration and appears to approach the axis asymptotically at infinite dilution. In consequence it is impossible to calculate integral heats of dilution or relative apparent molal heat contents in the normal manner by reference to an infinitely dilute solution and an arbitrary standard state has to be adopted.

EXPERIMENTAL

Stock solutions were prepared from "AnalaR" uranyl acetate, and the concentrations determined by the ammonium diuranate gravimetric method and by passage of the solution through a cation-exchange column in the hydrogen form with titration of the acid in the effluent. The two methods gave excellent agreement.

¹ Gucker, *Ann. New York Acad. Sci.*, 1949, 51, 680.

² Ahrland, *Acta Chem. Scand.*, 1951, 5, 199.

³ Hearne and White, *J.*, 1957, 2081, 2168.

Water used in the preparation of the solutions and for the dilutions was doubly distilled and stored in a Pyrex container.

The calorimeter (no. 1) used first consisted of a cylindrical Pyrex Dewar vessel of 70 mm. diameter and 700 ml. capacity which was closed with a thin rubber bung. Through the bung ran a glass stirrer in a guide tube and two thin-walled glass tubes which carried a thermistor (Standard Telephones and Cables Type F 2311/300) and an electrical heater (wound from manganin) of 50 ohms resistance, severally. The glass dilution pipette, of approximately 45 ml. capacity, had ground joints at top and bottom connected internally by a length of glass rod so that both could be opened simultaneously by means of a waxed thread which was attached to the top joint and passed out of the calorimeter *via* a capillary tube inserted through the bung. A stoppered side-arm was provided for filling. The pipette was supported by means of a glass rod, passing through the bung, to which it was tied by means of waxed thread.

During the work a more satisfactory calorimeter became available (no. 2). This was constructed from a cylindrical Pyrex Dewar vessel of 90 mm. diameter and 1200 ml. capacity, to the top of which a brass flange was cemented with litharge and glycerol cement. When dry the cemented joint was protected by a coating of Durofix. The brass lid of the calorimeter rested on a rubber gasket, which was inset in the flange, and was held firmly in position, giving a watertight seal, by means of a threaded ring cap which fitted over it and screwed on to the brass flange at the top of the Dewar flask. Brass tubes were fitted externally to the lid of the calorimeter. A central tube acted as guide to the stainless-steel stirrer which rotated in a ball-race fixed to the top of this tube. A short length of Perspex rod was inserted in the stirrer shaft at the point of entry into the calorimeter in order to prevent rapid heat conduction along the metal shaft, and the lower portion of the shaft carrying the paddle was made to screw into the Perspex insert, thus allowing its ready removal for cleaning. Through two peripheral brass tubes, at opposite ends of a diameter of the lid, two glass tubes passed into the calorimeter. One of these terminated in a thin-walled portion which contained the 50 ohms manganin electrical heater; the second ended just below the lid and was cemented (with Araldite cold-setting resin) into the open end of a stainless-steel tube, the other end of which was closed. This stainless steel tube served as a thermometer pocket and contained a Standard Telephones and Cables thermistor, type F 2311/300. A metal thermometer pocket was preferable to a glass one as it provides a better indication of the mean temperature of the liquid and in the present case was found to reduce short-term random fluctuations in the thermometer bridge output by a factor of 2—3. Three further brass tubes on the lid situated on radii at 120° to one another carried the three stainless-steel lifting rods, actuated by a screw mechanism, which were used to open the dilution pipette. The lifting rods ended immediately on entry into the calorimeter and carried short lengths of Perspex rod at their ends which could be bolted to the lid of the dilution pipette. The lengths of Perspex once again served to prevent rapid heat conduction. The dilution pipette of approximately 200 ml. capacity, which was machined from stainless steel, consisted of an open-ended canister, the upper opening being of greater diameter than the lower. This was closed by a bobbin-shaped portion, the edges being ground to give a liquid-tight seal. The canister had three stainless-steel rods fixed to its upper rim which were connected via short lengths of Perspex to the brass lid of the calorimeter. The upper surface of the bobbin carried three short stainless-steel pegs, which were fixed by means of bolts to the Perspex ends of the lifting-rods mentioned above, and in addition a small screw-capped filling hole, the cap being ground to give a liquid-tight fit. The central portion of the bobbin was hollow and the stirrer shaft passed through it.

In both calorimeters the stirrer was rotated at 150 r.p.m. by means of a Drayton type RQR induction motor. Tests with permanganate solutions and glass vessels of the same internal dimensions as the calorimeter indicated that in both calorimeters complete mixing of the solutions occurred within 30 seconds of opening the dilution pipettes.

Temperature measurements were made with the Thermistor in a bridge circuit as described previously.⁴ The output from the bridge was taken to a D.C. amplifier, of the galvanometer-photocell type, of variable gain, and the amplified output was then fed into a Honeywell-Brown potentiometer recorder, thus providing an automatic temperature-time record.

The electrical calibration heater in the calorimeter was supplied from a constant-current source and automatic timing unit which switched the constant-current supply from a dummy load to the calorimeter heater for any preselected time from 0.5 to 5 min. (in 0.5 min. steps).

⁴ Hutchison and White, *J. Sci. Inst.*, 1955, **32**, 309.

The current was checked by measuring the potential drop across a 10 ohms standard resistor. The timing unit was also arranged to switch, simultaneously with the current, the output from a 500 c./sec. valve-maintained tuning fork to a cold cathode-scaling unit to provide a precise determination of the time interval.

The calorimeters were immersed in a water-bath, the temperature of which was held constant within $\pm 0.01^\circ$ of its nominal setting of 25° . After loading and transfer to the bath the calorimeter was brought almost to bath-temperature by means of its heater and was then left to attain thermal equilibrium, for 24 hr. in the case of calorimeter no. 1 and 48 hr. in the case of no. 2. A series of blank tests with water in both the calorimeter and the dilution pipette showed that after these times no detectable temperature change occurred on mixing.

RESULTS AND DISCUSSION

Table 1 presents the results of the dilutions carried out with calorimeter no. 1 and Table 2 those made with calorimeter no. 2.

Integral heats of dilution are normally calculated with reference to the infinitely dilute solution as a standard state, and it is necessary for this purpose to be able to extrapolate the experimental data to zero concentration. Table 2 shows that the molar heat of dilution is becoming rapidly more positive as the solution is made more dilute and appears to be approaching the axis tangentially. This fact combined with the relative crudeness of the data available in the most dilute solutions makes it impossible to carry out any

TABLE 1. *Heat of dilution of uranyl acetate solutions at 25.0° (data obtained with calorimeter no. 1).**

	Molality		Heat evolved (cal./mole)	Molality		Heat evolved (cal./mole)	Molality		Heat evolved (cal./mole)		
	Initial	Final		Initial	Final		Initial	Final			
1	0.1713	0.1577	-21.9	3	0.0352	0.00296	-210	7	0.1156	0.00741	-614
	0.1577	0.1439	-24.6		0.0352	0.00305	-204		0.1156	0.00752	-611
	0.1439	0.1322	-24.2		4	0.0896	0.0821	-27.6	8	0.0929	0.00610
	0.1322	0.1210	-24.9	0.0821		0.0748	-24.0	0.0929		0.00604	-562
	0.1210	0.1113	-25.5	5	0.0598	0.00362	-402	9	0.0482	0.00318	-315
0.1113	0.1023	-25.3	0.0598		0.00369	-374	0.0482		0.00316	-319	
2	0.0858	0.0784	-25.1	6	0.1725	0.01102	-710	10	0.01729	0.001590	+167
	0.0784	0.0716	-30.2		0.1725	0.01118	-697		0.01729	0.001130	+193
	0.0716	0.00590	-448								
	0.0716	0.00593	-460								

* Braces indicate series of experiments.

TABLE 2. *Heat of dilution of uranyl acetate solutions at 25.0° (data obtained with calorimeter no. 2).**

	Molality		Heat evolved (cal./mole)	Molality		Heat evolved (cal./mole)	
	Initial	Final		Initial	Final		
11	0.00957	0.00245	+23.7	18	0.1569	0.0395	-420.4
	0.00957	0.00246	+25.6		0.0395	0.01025	-279.0
	0.00957	0.00243	+25.7		0.01025	0.00267	—
12	0.000638	0.0001663	+412	19	0.00267	0.000698	+293
	0.0001663	0.0000438	+777		0.000698	0.0001822	+435
13	0.000968	0.0002482	+221	20	0.1569	0.0399	-419.7
	0.0002482	0.0000652	+749		0.0399	0.01038	-273.4
14	0.0000652	0.0000171	+2180	21	0.01038	0.002714	+24.6
	0.000968	0.0002522	+279		0.002714	0.000705	+264
15	0.000968	0.0002529	+226	22	0.000705	0.0001831	+423
	0.000968	0.0002486	+298		0.0552	0.01419	-336
16	0.0002486	0.0000644	+416	23	0.01419	0.00369	-39.4
	0.00957	0.002409	+25.6		0.00369	0.000965	+203
17	0.002409	0.000624	+280	24	0.000965	0.000250	+338
	0.000624	0.0001613	+317		0.1613	0.0411	-429.9
18	0.0001613	0.0000421	+967	25	0.0411	0.0305	-101.8
	0.0000421	0.0000110	+1910		0.0305	0.0226	-70.5
19	0.0000110	0.00001644	+338	26	0.0226	0.01663	-57.0
	0.000630	0.0001644	+338		0.01663	0.01235	-41.4
					0.01235	0.00914	-24.9

* Braces indicate series of experiments.

reasonable extrapolation to $m = 0$ (where m is the molality). This being so, an arbitrary standard state of molality $m^* = 0.1713m$ (the initial molality of the first determination in series 1) has been selected and integral heats of dilution, $\Delta H_D'$, for the change $m^* \rightarrow m$ have been computed. The resulting integral heats of dilution are plotted in Fig. 1 as a

FIG. 1. Integral heat of dilution, $\Delta H_D'$, of uranyl acetate solutions at 25°. (Numbers indicate the series to which the points belong.)

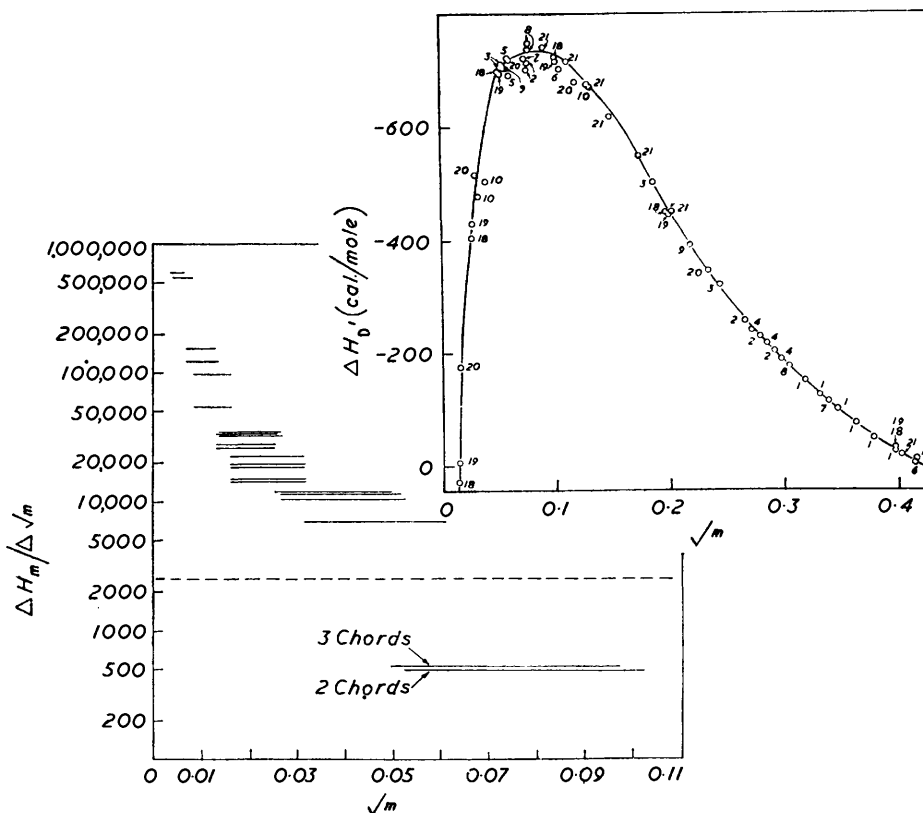


FIG. 2. Chord plot for dilute-solution data obtained with calorimeter no. 2. (The broken line represents the Debye-Hückel limiting value.)

function of \sqrt{m} . In view of the different standard states the values of $\Delta H_D'$ will differ from the normal integral heats of dilution ΔH_D by a constant amount, for :

$$-\Delta H_D = \phi_L = \phi_H - \phi_H^0$$

$$-\Delta H_D' = \phi_L' = \phi_H - \phi_H^*$$

$$\text{and } \Delta H_D - \Delta H_D' = \phi_L' - \phi_L = \phi_H^0 - \phi_H^*$$

where ϕ_L = relative apparent molal heat content of solute in solution, ϕ_H = apparent molal heat content of solute in solution, ϕ_H^0 = apparent molal heat content of solute in infinitely dilute solution, and ϕ_H^* = apparent molal heat content of solute in 0.1713m-solution. This fact should be noted in any comparison with data for other compounds.

The relative partial molal heat content L_2 of the solute is related to the integral heat of dilution by the expression :

$$\bar{L}_2 = -\Delta H_D - \frac{1}{2}\sqrt{m} \left(\frac{d\Delta H_D}{d\sqrt{m}} \right)$$

By using this expression, values of \bar{L}_2' (based on the standard state adopted for this work) have been calculated from $\Delta H_D'$ at rounded values of \sqrt{m} . The differential term was obtained graphically from a large-scale plot of $\Delta H_D'$ against \sqrt{m} . The results are set out in Table 3.

TABLE 3. *Relative partial molal heat content of uranyl acetate.*

\sqrt{m}	$d\Delta H_D'/d\sqrt{m}$	$\frac{1}{2}\sqrt{m}(d\Delta H_D'/d\sqrt{m})$	$-\Delta H_D'$	\bar{L}_2'	\sqrt{m}	$d\Delta H_D'/d\sqrt{m}$	$\frac{1}{2}\sqrt{m}(d\Delta H_D'/d\sqrt{m})$	$-\Delta H_D'$	\bar{L}_2'
0.4	1330	265	18	-247	0.12	1530	92	702	611
0.35	1650	289	92	-197	0.1	682	34	726	692
0.3	2060	309	182	-127	0.08	0	0	732	732
0.25	2670	333	298	-35	0.06	-1140	-34	720	754
0.2	3390	339	450	111	0.04	-11,800 †	-236	600	836
0.15	3170	238	620	382	0.02	-33,300 †	-333	216	549

† The slope of the $\Delta H_D-\sqrt{m}$ curve in this region is so great that these values are rough approximations only.

In dilute solutions the heats of dilution of electrolytes can normally be expressed by an equation of the form :

$$-d\Delta H_D/d\sqrt{m} = d\phi_L/d\sqrt{m} = S^0 + B\sqrt{m} + Cm$$

in which the value of S^0 can be calculated from the Debye-Hückel theory.¹ Hence, in dilute solutions the chords $-\Delta H_m/\Delta\sqrt{m}$, for the molar heat of dilution ΔH_m from m_1 to m_2 , should approach S^0 in the limit at $\sqrt{m} = 0$. A chord plot for the data obtained in dilute solutions, and recorded in Table 2, is given in Figure 2, in which it has been necessary to use a logarithmic scale for the chords. It will be seen that far from approaching the theoretical limit (of 2480 for a 2:1 electrolyte at 25°) the chords appear to increase indefinitely. It is of interest to compare this behaviour with that of other salts showing apparent disagreement with the theoretical limit, those which have been most thoroughly studied being the halides of cadmium,⁵ the sulphates of calcium, magnesium, cadmium, zinc, and copper,⁶ and lanthanum chloride and sulphate.⁷ In the case of the cadmium halides and of calcium, magnesium, and cadmium sulphates there is good evidence for the existence of a maximum or minimum in the chord plot at very low concentrations and of an eventual return towards the limiting value^{5,6} although in no case is the experimental value in the most dilute solutions closer than 2-3 times the theoretical. The evidence for such a maximum for zinc and copper sulphate is more doubtful though indications of such behaviour exist,⁶ while the lanthanum salts show no trace of a conformity with the theoretical limit even at concentrations of 10^{-4} - 10^{-5} molal. The data for lanthanum sulphate are analogous to those obtained in the present work,⁷ the chord measured at the lowest concentration having 17 times the theoretical slope whereas this ratio for uranyl acetate is approximately 220.

Qualitatively such behaviour is not difficult to explain, as all these metals form complex ions with the anions present and in some cases the salts hydrolyse. Two limiting types of behaviour may be envisaged, the first that of a metal which forms complex ions but whose salts are not hydrolysed: on dilution there will be a heat effect due to the dissociation of some of the complex ions which will probably be large compared with the true heat of dilution; as the concentration is lowered, however, the extent of association decreases and the contribution to the observed heat of dilution from this cause is reduced and eventually becomes insignificant. In this case the chord plot would be expected to show a maximum or minimum (according to the sign of the heat of dissociation of the complex) at some concentration depending on the dissociation constant of the complex ion: the smaller the dissociation constant the lower is the value of the concentration. The second type is that of a metal which forms no complexes with the anion but whose salts are

⁵ Robinson and Wallace, *Chem. Rev.*, 1942, **30**, 195.

⁶ *Idem*, *J. Amer. Chem. Soc.*, 1941, **63**, 1582.

⁷ Nathan, Wallace, and Robinson, *ibid.*, 1943, **65**, 790.

hydrolysed. Hydrolysis will then increase as the dilution increases, so that the measured heat effect will contain an increasing contribution from the heat of hydrolysis as the concentration is decreased. The chord plot would show an indefinite increase or decrease (depending on the sign of the heat of hydrolysis) and approach the axis asymptotically.

The salts of calcium, magnesium, and cadmium previously examined would be expected to approach the first types closely and their chord plots are in agreement with this: the dissociation constants of the sulphates are similar⁸ and the maxima occur at about the same concentrations. Copper, zinc, and lanthanum salts on the other hand are hydrolysed only slightly,⁹⁻¹¹ and the metal ions form complexes with their respective anions: their behaviour should thus be intermediate between the first and the second type and this may account for the absence of a maximum or minimum in the chord plot. Lanthanum sulphate provides the largest deviations from the theoretical although it is less strongly hydrolysed than copper and zinc salts, and it is noteworthy that in this case the dissociation constant of the sulphate complex¹⁰ is 20 times smaller than those for copper and zinc.⁹ With uranyl acetate not only is there strong complex-formation of the uranyl ion with acetate ion,² but in dilute solutions hydrolysis is extensive, being very much greater³ than for any of the metals previously studied;¹¹ hence its dilute solution behaviour would be expected to tend markedly to that of the second type, as found.

We are indebted to Mr. E. W. Pulsford of Electronics Division, A.E.R.E., for the design and construction of the D.C. amplifier, constant-current source, and automatic timing unit.

CHEMISTRY DIVISION, ATOMIC ENERGY RESEARCH ESTABLISHMENT,
HARWELL, NEAR DIDCOT, BERKS.

[Received, February 22nd, 1957.]

⁸ Harned and Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, 1943, p. 147.

⁹ Owen and Gurry, *J. Amer. Chem. Soc.*, 1938, **60**, 3074.

¹⁰ Jones and Monk, *Trans. Faraday Soc.*, 1952, **48**, 929.

¹¹ Davies, *J.*, 1951, 1256.
