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The Entropies of Large Ions. The Heat Capacity, Entropy and Heat of Solution of Potassium Chloroplatinate, Tetramethylammonium Iodide and Uranyl Nitrate Hexahydrate

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An extension of our present knowledge of ionic entropies to include large sized ions is desirable from several points of view. Such information may serve as a guide in estimating unknown ionic entropies for similar ion types as well as being of aid in understanding the hydration of ions. The immediate contribution is, of course, to the thermodynamics of the particular substance chosen for study.

With these views in mind the salts, potassium chloroplatinate, K_2PtCl_6, tetramethylammonium iodide, $(CH_3)_4NI$, and uranyl nitrate hexahydrate, $UO_2(NO_3)_2 \cdot 6H_2O$, were selected for heat capacity and heat of solution studies. Such data combined with free energy of solution values have allowed the partial molal entropies of the chloroplatinate, tetramethylammonium and uranyl ions to be evaluated.

Materials.—For the preparation of the K_2PtCl_6 used in the heat capacity and heat of solution experiments scrap platinum was purified by the method of Gilchrist and Wichers.[1] The platinum metal thus obtained was dissolved in *aqua regia* and repeatedly evaporated on a water-bath with concentrated hydrochloric acid to remove entirely the nitric acid and to destroy any platinum nitrogen complex. The resulting chloroplatinic acid was dissolved in water and precipitated with potassium chloride solution. Subsequent recrystallization and drying at 100° gave a product containing the calculated amount of platinum in K_2PtCl_6 (± 0.1%) and yielding negative tests for indium, palladium and rhodium, the more likely impurities, upon repetition of the separation scheme originally used in the purification. A sample weight of 118.526 g. (*in vacuo*), 0.25317 mole, was used in the heat capacity measurements.

Tetramethylammonium iodide obtained from Eastman Kodak Company and recrystallized from water solution several times was used for the heat capacity and heat of solution measurements. After drying at 100°, analysis for iodine by precipitation with silver nitrate indicated 99.8% of the calculated amount. Precaution was taken to avoid undue light exposure and high temperature since the sample as obtained showed a yellowish tint presumably due to free iodine. A sample weight of 61.218 g. (*in vacuo*) or 0.30446 mole was used in the heat capacity measurements.

The uranyl nitrate hexahydrate used in this study was prepared from Baker C. P. $UO_2(NO_3)_2 \cdot 6H_2O$ and City Chemical UO_3, the latter being dissolved in nitric acid to form the nitrate. The absence of heavy metal impurities in the sample was evidenced by no precipitate with hydrogen sulfide in acid solution or in alkaline solution in the presence of ammonium carbonate which prevents precipitation of the uranium. The absence of an appreciable precipitate with ammonium carbonate and also with cupferron in acid solution confirmed the above conclusions. After several recrystallizations the hydrated uranyl nitrate was placed over 40% sulfuric acid until constant water content was obtained. Ignition of samples so prepared yielded the correct per cent. of volatile matter within experimental error. However, the presence of traces of lighter metals is still possible since their effect might not be so perceptible in this type of analysis.

To eliminate certain objectionable features of the first heat capacity data obtained for this compound it was found necessary to slowly crystallize the hydrate by evaporation and reserve only the middle third for heat capacity measurements. Further discussion of this precautionary measure will be included in the following section. The sample weights, *in vacuo*, for the various series listed in Table III are as follows: series I and II 103.530 g. (0.20612 mole); series IV, 108.375 g. (0.21578 mole).

Heat Capacity Measurements.—The heat capacity measurements were made in the calorimeter and cryostat described by Latimer and Greensfelder,[2] the only significant change being the replacement of the external heater thermometer type calorimeter by an internal strain free platinum thermometer heater as described by

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[1] Gilchrist and Wichers, THIS JOURNAL, **57**, 2565 (1935).

[2] Latimer and Greensfelder, *ibid.*, **50**, 2202 (1928).

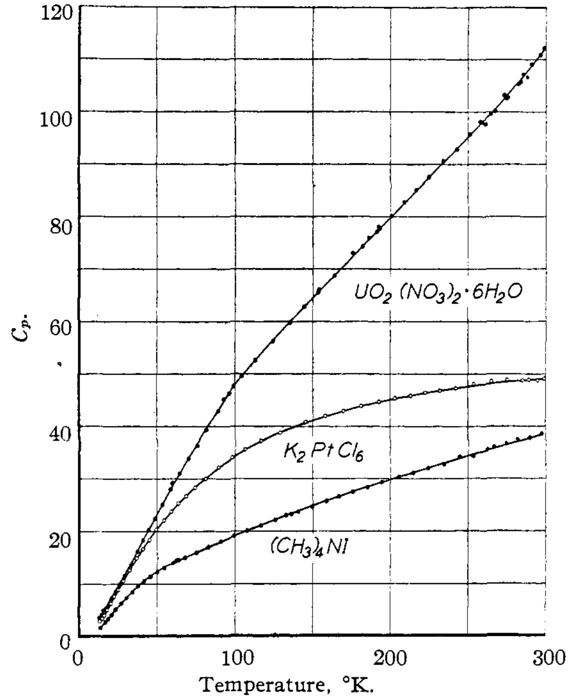

Fig. 1.—Heat capacity in cal. per degree per mole for uranyl nitrate hexahydrate, potassium chloroplatinate, and tetramethylammonium iodide.

Pitzer and Coulter.[3] The experimental data obtained are presented in Tables I, II and III and are shown graphically in Fig. 1. Smoothed values for the heat capacities appear in Table V.

TABLE I

MOLAL HEAT CAPACITY OF POTASSIUM CHLOROPLATINATE K_2PtCl_6 (MOL. WT. 486.18)

T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.
13.70	2.875	106.33	35.56
15.18	3.465	116.70	37.17
16.61	4.169	129.16	38.75
18.41	5.124	145.51	40.78
20.60	6.365	158.02	41.99
22.80	7.662	169.61	42.97
25.32	8.942	181.47	43.90
28.48	10.61	192.63	44.61
32.59	12.56	203.30	45.44
36.89	14.87	213.18	45.89
40.85	16.69	222.50	46.47
45.23	18.45	231.74	46.81
49.72	20.31	242.39	47.35
54.34	22.04	253.82	48.07
59.13	23.75	264.56	48.60
63.76	25.33	275.14	48.92
68.62	26.74	285.24	48.75
74.49	28.33	289.23	48.93
80.84	30.08	294.58	48.81
89.50	32.20	299.13	49.11
98.01	34.01		

TABLE II

MOLAL HEAT CAPACITY OF TETRAMETHYLAMMONIUM IODIDE, $(CH_3)_4NI$ (MOL. WT. 201.03)

T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.
14.10	1.714	125.83	22.23
15.68	2.186	132.54	23.03
17.41	2.757	135.17	23.25
19.23	3.377	140.60	23.79
21.20	4.157	149.60	24.70
23.83	5.136	158.59	25.74
27.32	6.337	166.95	26.60
30.68	7.369	175.87	27.50
34.17	8.487	185.34	28.41
37.89	9.677	195.32	29.40
41.71	10.61	205.27	30.30
45.88	11.48	214.53	31.11
50.22	12.33	224.28	32.00
54.82	13.11	234.53	32.79
60.27	14.02	244.75	34.18
62.33	14.47	245.59	33.82
63.86	14.62	253.37	34.40
68.09	15.05	253.42	34.47
75.10	15.96	262.18	35.54
82.77	17.01	266.49	36.02
90.82	18.04	274.54	38.74
99.26	19.10	282.09	37.49
107.66	20.12	289.99	37.80
116.50	21.16	297.53	38.54

An inspection of the heat capacity data for potassium chloroplatinate and tetramethylammonium iodide in the ice-point region reveals a bump in the smooth trend of their heat capacity. This was attributed to the presence of water in the samples. Although the decomposition temperatures of these salts are well above 100°, long drying at this temperature was avoided in preparing the samples as a precautionary measure. As estimated from the high experimental points at the ice point and a smooth curve drawn through the experimental points above and below this region the water present amounted to 0.021 g. for the chloroplatinate and 0.113 g. for the tetramethylammonium iodide. The heat capacity data and entropy calculations have been corrected on this basis

As already mentioned in the preceding section, considerable difficulty was encountered in obtaining reliable heat capacity measurements on uranyl nitrate hexahydrate because of its relative ease of thermal decomposition. After obtaining heat capacities designated by I in Table III, experimental difficulties necessitated the removal and resealing of the calorimeter. After reassembling the apparatus, measurements designated by II were made in the region 14 to 60°K.

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(3) Pitzer and Coulter, THIS JOURNAL, **60**, 1310 (1938).

TABLE III

MOLAL HEAT CAPACITY OF $UO_2(MO_3)_2 \cdot 6H_2O$ (MOL. WT. 502.25)

	T, °K.	C_p, cal./deg.		T, °K.	C_p, cal./deg.
II	13.67	3.582	I	153.67	66.10
II	15.35	4.214	II	163.94	68.84
II	16.73	4.803	II	175.42	73.05
II	17.91	5.452	IV	181.95	74.31
II	19.48	6.158	II	185.96	75.94
II	21.53	7.297	IV	191.33	77.16
II	24.06	8.720	II	192.25	78.02
II	26.80	10.11	II	193.26	77.95
II	29.71	11.57	IV	200.48	80.19
II	33.52	13.67	IV	208.70	82.75
II	37.51	16.15	IV	216.37	85.15
II	41.25	18.30	IV	224.93	87.55
II	44.87	20.28	IV	234.08	90.61
II	48.91	22.49	IV	242.74	92.84
II	53.56	25.09	IV	251.08	95.76
II	58.83	28.02	IV	257.57	97.61
I	60.00	29.23	IV	259.07	98.01
I	64.42	31.02	I	261.33	97.63
I	70.42	33.92	IV	264.66	99.69
I	75.70	36.36	I	267.27	100.2
I	81.75	39.43	IV	273.08	103.2
I	89.24	42.98	IV	274.73	102.6
IV	92.96	45.15	I	275.53	102.8
I	96.64	46.31	IV	282.13	105.3
IV	99.32	47.72	IV	283.09	106.1
I	104.30	49.56	I	283.36	105.7
I	113.19	52.70	IV	285.31	107.1
I	124.38	56.33	I	287.63	106.6
I	135.49	59.87	IV	290.65	109.1
I	144.96	63.18	I	296.17	110.9
II	153.17	65.57	IV	298.68	112.2

TABLE IV

MOLAL HEAT CAPACITY OF $UO_2(NO_3)_2 \cdot 6H_2O$ IN THE REGION 200–250°K. SHOWING THE EFFECT OF IMPURITY

T, °K.	C_p, cal./deg.
203.86	83.08
212.14	84.73
221.47	88.12
231.40	90.94
240.90	93.29
249.96	95.40
258.70	97.56

TABLE V

SMOOTHED VALUES OF THE HEAT CAPACITY OF K_2PtCl_6, $(CH_3)_4NI$ AND $UO_2(NO_3)_2 \cdot 6H_2O$

T, °K.	C_p		
	K_2PtCl_6	$(CH_3)_4NI$	$UO_2(NO_3)_2 \cdot 6H_2O$
15	3.43	1.99	4.08
20	6.02	3.68	6.45
25	8.81	5.56	9.20
30	11.30	7.15	11.72
35	13.85	8.75	14.59
40	16.30	10.23	17.58
45	18.35	11.31	20.35
50	20.39	12.28	23.10
60	24.07	13.96	28.61
70	27.12	15.29	33.70
80	29.85	16.63	38.43
90	32.30	17.93	43.30
100	34.35	19.19	47.83
120	37.67	21.57	54.87
140	40.18	23.71	61.40
160	42.14	25.88	67.75
180	43.77	27.90	73.65
200	45.16	29.82	79.92
220	46.30	31.60	86.10
240	47.24	33.25	92.21
260	48.01	35.20	98.35
280	48.63	36.81	105.00
300	49.14	38.78	112.70

followed by measurements from 153 to 260°K. In the latter region a slight bulge in the heat capacity curve occurred in the neighborhood of 220°K. The data showing this feature do not appear in the main body of the data but are listed separately in Table IV. A repetition of the measurements in this region resulted in the same shape for the heat capacity curve. Since the irregularity occurred near the melting point of nitric acid, the sample was removed and recrystallized. A third set of measurements was then obtained resulting in the same behavior as previously observed with the additional fact that the heat capacities were now rising rapidly at room temperature and were not reproducible. In a final effort the sample was again removed, combined with additional hydrate and recrystallized. For the new sample only the middle third was reserved for the measurements as already described. At all times the sample was treated with extreme care to prevent any thermal decomposition. A fourth series of measurements were then made which did not show the characteristics observed before but instead indicated a smooth trend of the heat capacity. These measurements are designated IV in Table III.

On the basis of the above experience it appears then that the last traces of free nitric acid are removed from this salt with difficulty or that the salt was decomposed to a small extent when care was not taken in sealing the calorimeter.

The heat capacity curve for uranyl nitrate hexahydrate in Fig. 1 and the entropy calculations are based only on data listed in Table III. Although the sample for series I and II was known to be at fault, it appears reasonable to utilize the data up to 200° since in the region 153–200° and at scattered points below this region it is in agreement within experimental error with series IV.

Series I and IV are also in fair agreement from 260 to 300°K. However, in this range greater weight was given to series IV measurements for the reasons already discussed. Since the heat capacity of this compound at low temperatures is due primarily to the heavy atoms, the above procedure would appear justified for using the data in series I and II below 200°K.

The absolute temperature of the ice-point was taken to be 273.10°K. and one calorie was taken as 4.1833 int. joules.

Entropy of Potassium Chloroplatinate, Tetramethylammonium Iodide and Uranyl Nitrate Hexahydrate.—The entropy computations were made in the usual manner from plots of C_p *vs.* log T through the temperature range 14 to 298.1°K. From 0 to 14°K. the entropy contribution was estimated by means of a Debye extrapolation, in the cases of potassium chloroplatinate and tetramethylammonium iodide. A combination of Debye and Einstein functions fitting the heat capacity data up to 30°K. was necessary in extrapolating the data to 0°K. for uranyl nitrate hexahydrate. These calculations are summarized in Table VI.

TABLE VI

	ENTROPY OF K_2PtCl_6	
0°–14°K.	Debye extrapolation; $3D(105/T)$	1.05
14°–298.1°K.	Graphical integration from data	78.73
	$S°_{298.1°K.}$, cal./deg. mole	79.78±0.4
	ENTROPY OF $(CH_3)_4NI$	
0°–14°K.	Debye extrapolation; $2D(111/T)$	0.60
14°–298.1°K.	Graphical integration from data	49.10
	$S°_{298.1°K.}$, cal./deg. mole	49.7 ± 0.2
	ENTROPY OF $UO_2(NO_3)_2 \cdot 6H_2O$	
0°–14°K.	Debye and Einstein extrapolation $D(51/T) + 2E(107/T) + 2E(145/T)$	1.89
14°–298.1°K.	Graphical integration from data	118.96
	$S°_{298.1°K.}$, cal./deg. mole	120.85±0.6

Heat of Solution Measurements.—The calorimeter and the procedure employed were essentially those described by Pitzer.[4] The substitution of a new thermometer heater unit for the original silver unit was the only alteration of importance. This replacement consisted of a copper wire resistance thermometer and manganin heater wound on a varnished copper tube and water-proofed with a resin beeswax mixture. The results of the measurements are tabulated in Table VII along with the observations made by other workers on these compounds under different conditions. As no data are available for correcting the observed heats of solution of potassium chloroplatinate and uranyl nitrate to infinite dilution, the mean values listed will be used for the remaining calculations. The error therein involved as well as that arising from hydrolysis in the case of uranyl nitrate will be included in the final error estimated for the ionic entropies of $PtCl_6^=$ and UO_2^{++}. The heat of dilution of tetramethylammonium iodide was estimated from the work reported by Lange[5] on tetramethylammonium chloride.

The final volume of the solution in each experiment was 1050 cc. with the exception of the two experiments on the uranyl salt in which cases the final volume was 1060 cc.

Free Energy of Solution

K_2PtCl_6.—The solubility of K_2PtCl_6 has been measured as a function of temperature by Archibald, Wilcox and Buckley.[6] At 25° they found the solubility to be 0.0178 *M*. Although activity coefficients are not known for this salt, an estimate of 0.7 appears reasonable and in line with other salts of this type. For the free energy of solution to form the hypothetical 1 *M* solution of the ions

$$\Delta F = -RT \ln (\gamma m)^3 4 = -1363.8 \log (0.7 \times 0.0178)^3 4 = 6970 \pm 200 \text{ cal.}$$

$(CH_3)_4NI$.—Walden[7] and Hill[8] give, respectively, 0.274 and 0.262 *M* as the solubility of this salt at 25°. The latter appears to be the more reliable value and will be used in the following calculations.

Employing the freezing point lowering data obtained by Lange,[9] the activity coefficient for tetramethylammonium iodide at 0.1 *M* (saturation) and 0° was calculated to be 0.693. Extrapolation to 0.262 *M* yielded the value 0.53 for the activity coefficient of this salt in the saturated solution at 25°. These calculations were made in the manner described by Lewis and Randall.[10] With one exception all of the freezing point data followed the empirical Lewis and Linhart law[11] in which the constants for this substance, α and β, as defined by Lewis and Randall,[6] were found to be 0.531 and 0.435, respectively. For the free energy change accompanying the solution of one

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[4] Pitzer, THIS JOURNAL, **59**, 2365 (1937).

[5] Lange and Streeck, *Z. physik. Chem.*, **A169**, 103 (1934).

[6] Archibald, Wilcox and Buckley, THIS JOURNAL, **30**, 747 (1908).

[7] Walden, *Z. physik. Chem.*, **55**, 68B (1906).

[8] Hill, THIS JOURNAL, **39**, 218 (1917).

[9] Lange, *Z. Elektrochem.*, **39**, 546 (1935).

[10] Lewis andRa ndall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, N. Y., 1923, p. 342.

[11] Lewis and Linhart, THIS JOURNAL, **41**, 1952 (1919).

TABLE VII

HEAT OF SOLUTION OF POTASSIUM CHLOROPLATINATE AT 25°

Sample, g.	Moles	Obsd. heat absorbed, cal.	ΔH of soln., cal.
3.0247	0.006221	83.95	13,495
3.0167	.006205	84.31	13,587
3.0135	.006198	82.81	13,361
		Mean	13,480 ± 150
Thomsen[12] (from heat of precipitation of 0.05 mole at 18°)			13,760

HEAT OF SOLUTION OF TETRAMETHYLAMMONIUM IODIDE AT 25°

Sample, g.	Moles	Observed heat absorbed	ΔH of soln., cal.	ΔH of diln., cal.	$\Delta H°$ of soln. to ∞ diln., cal.
11.0345	0.05489	551.97	10,055	− 6	10,049
8.0955	.04027	405.17	10,061	−16	10,045
8.3141	.04136	416.01	10,058	−15	10,043
7.8354	.03898	392.94	10,081	−17	10,064
12.4397	.06188	622.10	10,053	− 3	10,050
				Mean	10,050 ± 20

Walden,[13] heat of solution at 20°

Sample, g.	Final vol., cc.	Molal ΔH, cal. (not corrected to infinite dilution)
12.502	500	10,165
21.813	500	10,108

HEAT OF SOLUTION OF URANYL NITRATE HEXAHYDRATE AT 25°

Sample, g.	Moles	Observed heat absorbed, cal.	ΔH of soln., cal.
31.8095	0.06333	332.32	5,247
32.4323	.06457	339.48	5,257
			5,250 ± 20
ΔH of solution of $UO_2(NO_3)_2 \cdot 6H_2O$ at 11–12° by de Forcrand[14] (final concn. 0.25 M)			5,450
ΔH of solution by Marketos[15]			4,760

mole of solid $(CH_3)_4NI$ to form the hypothetical 1 M solution we then have

$$\Delta F = -RT \ln (\gamma m)^2 = -1363.8 \log (0.53 \times 0.262)^2$$
$$= 2340 \text{ cal.}$$

$UO_2(NO_3)_2 \cdot 6H_2O$.—From the existing solubility and freezing point lowering data on this salt only an approximate value for the ΔF of solution can be obtained. However, this will serve temporarily for the present calculations.

From a smooth curve drawn through the solubilities as a function of temperature, determined by Vasilev,[16] the solubility of $UO_2(NO_3)_2$ is 3.35 M at 25°.

Landolt-Börnstein[17] give the value 0.66 for the activity coefficient of this salt at 1 M which was calculated from freezing point lowering data obtained by Dittrich[18] and Vasilev.[16]

An extension of the calculation to the eutectic concentration 1.92 M by means of known cryoscopic data[16] followed by extrapolation to 3.35 M did not appear permissible in this case either because of the quality of the data or neglect of thermal terms in the calculation[19] or both.

As a consequence a series of vapor pressure measurements by the static method were made on solutions at several concentrations from which a series of values proportional to the activity coefficients were obtained. The data are tabulated in Table VIII.

TABLE VIII

VAPOR PRESSURE OF URANYL NITRATE SOLUTIONS AT 25°

Moles/1000 g. H_2O	Vap. press. of soln., mm.	a_1
3.11	17.2	0.724
1.98	18.7	.786
1.257	21.8	.918
0.578	23.0	.968

Employing the usual procedure for such calculations[20] the activity coefficient of $UO_2(NO_3)_2$ at

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[12] Thomsen,' 'Thermochemische Untersuchungen," Verlag Johann Barth, Leipzig, 1883, Vol. 3, p. 420.

[13] Walden, *Z. physik. Chem.*, **58**, 479 (1907).

[14] De Forcrand, *Ann. chim.*, [9] **3**, 5 (1915); *Compt. rend.*, **156**, 1207, 1954 (1913).

[15] Marketos, *ibid.*, **155**, 210 (1912).

[16] Vasilev, *J. Russ. Phys.-Chem. Soc.*, **42**, 570 (1910).

[17] Landolt-Börnstein, "Physikalisch-chemische Tabellen," 2nd Sup. Vol., part 2, p. 1128.

[18] Dittrich, *Z. physik. Chem.*, [7] **29**, 449 (1899).

[19] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw Hill Book Co., New York, N. Y., 1923, pp. 341–364.

[20] Lewis and Randall, "Thermodynamics and Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, N. Y., 1923, p. 331.

3.35 *M* and 25° was found to be 4.3. Considering the accuracy of the data and certain approximations made in the calculation, this value is to be considered only as an approximate one.

Knowing the solubility and activity coefficient of the salt at 25° and the activity of the water in the saturated solution (0.72), we have for the free energy of solution of the hydrate

$$\Delta F = -RT \ln (\gamma m)^3 4\, a^6_{H_2O} = -1363.8 \log \frac{(4.3 \times 3.4)^3}{4(0.72)^6}$$
$$= -4400 \pm 1000 \text{ cal.}$$

Entropy of Chloroplatinate, Tetramethylammonium and Uranyl Ions.—Combining the above values for the heat and free energy of solution of K_2PtCl_6 one obtains 21.8 E. U. for the entropy of solution at 25°. This value combined with the entropy of the solid and the previously determined value for $\bar{S}^\circ_{K^+}$[21] results in the following for $\bar{S}^\circ_{PtCl_6} =$

$$\bar{S}^\circ_{PtCl_6} = \Delta S_{\text{soln.}} + S^\circ_{K_2PtCl_6} - 2\bar{S}^\circ_K = 21.8 + 79.8 - 48.4$$
$$= 53.2 \pm 2 \text{ cal./degree mole}$$

From the already determined heat and free energy of solution of tetramethylammonium iodide the entropy of solution at 25° is found to be 25.9 cal./deg. mole. The calculation of the partial molal entropy of $(CH_3)_4N^+$, involving the entropy of solution, the entropy of solid $(CH_3)_4NI$ and the entropy of I^-,[22] may now be computed as follows:

$$\bar{S}^\circ_{(CH_3)_4N^+} = \Delta S_{\text{soln.}} + S^\circ_{(CH_3)_4NI} - \bar{S}^\circ_{I^-}$$
$$= 25.9 + 49.7 - 25.3 = 50.3 \pm 1 \text{ cal./deg. mole}$$

Proceeding as in the above two cases the entropy of solution of uranyl nitrate hexahydrate at 25° is 32.5 cal./deg. mole. For the partial molal entropy of UO_2^{++} we then have $\bar{S}^\circ_{UO_2^{++}} = \Delta S_{\text{soln.}} + S_{UO_2(NO_3)_2 \cdot 6H_2O} - 2\bar{S}^\circ_{NO_3^-}$[23] $- 6S^\circ_{H_2O}$[24] $= 32.5 + 120.9 - 70.0 - 100.5 = -17 \pm 5$ cal./deg. mole.

While the entropies of chloroplatinate and tetramethylammonium ions are quite reasonable, the entropy of uranyl ion (−17) seems rather small when compared with a large, simple bipositive ion such as barium ($S^\circ_{Ba^{++}} = 3$). This latter case invites some discussion. Let us assume for the moment that the usual representation, UO_2^{++}, for uranyl ion in solid or solution phase is correct. From the low entropy value one is then forced to conclude that uranyl ion holds water molecules with stronger or more specific forces than an ion like barium. This might arise from hydrogen bonding to the oxygen atoms of the uranyl ion or bonding of the oxygen of water to the uranium or both.

Another possibility is that uranyl ion in solution or hydrated crystals is $U(OH)_4^{++}$. Support for this formula is offered by the great difficulty of removing the last water (assuming the UO_2^{++} formula) for some uranyl salts. The entropy on the basis of $U(OH)_4^{++}$ is +16 cal. per degree ($\bar{S}^\circ_{U(OH)_4^{++}} = \bar{S}^\circ_{UO_2^{++}} + 2S^\circ_{H_2O}$) which seems considerably more reasonable.

For ordinary thermodynamic calculations it is of course immaterial whether the formula UO_2^{++} with the entropy −17 or the formula $U(OH)_4^{++}$ and the entropy +16 is used.

Free Energy of Formation of $PtCl_6^=$ and UO_2^{++}.—Knowing the value for $\bar{S}^\circ_{PtCl_6^=}$ it is now possible to calculate the free energy of formation of $PtCl_6^=$. According to Bichowsky and Rossini[25] the ΔH of formation at 18° of $PtCl_6^=$ from the elements is −165,600 cal. The entropy change for this reaction is $\Delta S = 53.2 - 10 - (3 \times 53.3) - 31.2 = -147.9$. Using this entropy change and the ΔH of formation at 18° uncorrected, the free energy of formation of $PtCl_6^=$ at 25° is −121,500 cal. The free energy of formation of solid K_2PtCl_6, which involves the free energies of formation of $PtCl_6^=$ and K^+ [26] (−67,430) and the free energy of solution of K_2PtCl_6, is calculated to be −263,300 cal.

With an ionic entropy value now available for UO_2^{++}, we may revise the calculations by Latimer[27] involving the uranyl ion.

$$U(c) + 2H_2O(liq) + 2H^+(aq) = UO_2^{++}(aq) + 3H_2(g) \qquad \Delta H = -106{,}300$$

$$\Delta S = \bar{S}^\circ_{UO_2^{++}} + 3S^\circ_{H_2} - S^\circ_U - 2S^\circ_{H_2O} - 2\bar{S}^\circ_{H^+} =$$
$$-17 + 93.7 - 11.1 - 32.5 - 0 = 33 \text{ cal./deg.}$$

ΔF is then −116,100 cal. and for the half reaction

$$2H_2O + U = UO_2^{++} + 4H^+ + 6e^-; \quad E^\circ = 0.84 \text{ v.}$$

For the free energy of formation of UO_2^{++} we then have −229,200 cal.

Summary

The heat capacity of potassium chloroplatinate, tetramethylammonium iodide and uranyl nitrate hexahydrate have been determined from 14 to

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[21] Latimer, Pitzer and Smith, THIS JOURNAL, **60**, 1829 (1938).

[22] Latimer, Pitzer and Smith, THIS JOURNAL, **60**, 1829 (1938).

[23] Latimer, Pitzer and Smith, *ibid.*, **60**, 1829 (1938).

[24] Giauque and Stout, *ibid.*, **58**, 1144 (1936).

[25] Bichowsky and Rossini, "Thermo-chemistry of Chemical Substances," Reinhold Publishing Corporation, New York, N. Y., 1936.

[26] Latimer, "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1938.

[27] Latimer, *ibid.*, p. 238.

300°K. The following entropy values at 298.1 were calculated: 79.8 cal./deg. mole for potassium chloroplatinate, 49.7 cal./deg. mole for tetramethylammonium iodide and 120.9 cal./deg. mole for uranyl nitrate hexahydrate.

The heats of solution of each of these three salts has been determined at 25°.

The following partial molal entropy values have been determined: 53.2 cal./deg. mole for $PtCl_6^=$, 50.3 cal./deg. mole for $(CH_3)_4N^+$ and −17 cal./deg. mole for UO_2^{++}. Suggestions have been offered accounting for the apparent deviation of the ionic entropy of UO_2^{++} from an expected value.

The free energies of formation of $PtCl_6^=$ and UO_2^{++} have been obtained.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, DUKE UNIVERSITY]

The Electric Moments of Some Substituted Benzoic Acids

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Introduction

The direction of the group moment associated with the carboxyl group apparently has never been determined. The present measurements of the electric moments of chlorobenzene, bromobenzene, benzoic acid, *m*- and *p*-chlorobenzoic acid and *m*- and *p*-bromobenzoic acid were carried out because the approximate direction of this group moment was necessary in connection with a systematic study of the acids[1] that is being conducted in this Laboratory. The acids are normally associated even in dilute (10^{-3} mole fraction) solutions of benzene and similar substances. Therefore dioxane was used as the solvent as it apparently will inhibit the acid association because of the formation of a hydrogen bond between the acid monomer and the oxygen of the dioxane. Another interest in connection with these measurements was whether resonance of the carboxyl group with the ring inhibited free rotation about the C–C linkage. The meta compounds were measured with this in mind. A further purpose was to determine whether deviations from additivity were encountered when the resonating halogen and carboxyl group were located para to each other. Deviations of this type have been observed in the case of *p*-nitroaniline and have been explained by Pauling[2] as due to the resonance phenomenon.

Materials and Procedure

Dioxane.—Carbide and Carbon Chemicals Co. dioxane essentially free from peroxides was dried with calcium chloride and then distilled from sodium through a 180-cm. Dufton column. The middle fraction boiling at 101.25–101.45° (cor.) was used.

Chlorobenzene.—Eastman Kodak Co. highest purity chlorobenzene was dried with "Drierite" and then distilled through a 40-cm. Widmer column. The middle fraction boiling at 132.10–132.12° (cor.) was used.

Bromobenzene.—Eastman highest purity product was dried overnight with phosphorus pentoxide and then distilled through a 40-cm. Widmer still. The fraction boiling at 156.17–156.18° (cor.) was used.

Benzoic Acid.—Sublimed benzoic acid was recrystallized from anhydrous benzene; melting point by cooling curve 121.8–121.9°.

***p*-Chlorobenzoic Acid.**—Eastman highest purity product was recrystallized from a one to one mixture of dioxane and benzene. A sharp m. p. at 240° was unchanged by further recrystallization.

***p*-Bromobenzoic Acid.**—Eastman highest purity product was recrystallized from a one to one mixture of dioxane and benzene. The m. p. at 254° was unchanged by further recrystallization.

***m*-Chlorobenzoic Acid.**—Eastman best grade was recrystallized from benzene; melting point by cooling curve 154.8–154.9°.

***m*-Bromobenzoic Acid.**—Eastman best grade was recrystallized from a one to one mixture of dioxane and benzene and then twice from anhydrous benzene. The m. p. of 156° was unchanged by further recrystallization.

The procedure has been described previously.[3] The average density of the dioxane at 30° was 1.0207. Its dielectric constant at 30° was taken as 2.2310.[4]

Calculations and Data

The calculation of the polarization per gram of solute, p_2, was made with the following equation.[1]

$$p_2 = \frac{1}{\epsilon_{12} + 2}\cdot\frac{1}{d_{12}}\left\{\epsilon_{12} - 1 + \frac{W_1}{W_2}[(0.7091)(\Delta\epsilon) - (1.206)(\Delta d) - (0.285)(\Delta\epsilon)(\Delta d)]\right\}$$

In this expression ϵ_{12} is the dielectric constant of

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(1) Pohl, Hobbs and Gross, *Annals of the New York Academy of Science*, Dielectrics, in press (1940).

(2) L. Pauling, "Nature of the Chemical Bond," 1st edition, Cornell University Press, Ithaca, N. Y., 1939, p. 204.

(3) De Bruyne, Davis and Gross, THIS JOURNAL, **55**, 3936 (1933).

(4) Ulich and Nespital, *Z. physik. Chem.*, **B16**, 229 (1932).