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 $\Lambda_m$ appear to be inconsistent with expectations for a strong 1-1 electrolyte.

**Acknowledgment.**—The authors wish to express their appreciation to Dr. T. F. Young of the University of Chicago for interesting discussions concerning this work.

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.

RECEIVED APRIL 23, 1956

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)

---

[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.

inserted within the heater sleeve in the axial calorimetric well. The thermometer was calibrated by the National Bureau of Standards against the International Temperature Scale above 90°K., and by comparison at 19 temperatures with the Bureau's platinum thermometers[6] over the range 10–90°K. Below 10°K. we established a provisional temperature scale by fitting the constants in the equation $R = A + BT^2 + CT^5$ to the observed resistance of the thermometer at 10°K., the resistance at the boiling point of helium, and $dR/dT$ at 10°K. The temperature scale thus defined probably agrees with the thermodynamic scale to 0.1° below 10°K., 0.03° from 10 to 90°K. and 0.05° from 90 to 400°K.

TABLE I

MOLAL HEAT CAPACITY OF URANYL CHLORIDE (IN CAL. PER DEGREE)

| $T$, °K. | $Cp$ |
|---|---|
| Series I | |
| 246.58 | 24.46 |
| 256.05 | 24.74 |
| 265.76 | 25.02 |
| 275.72 | 25.24 |
| 285.61 | 25.50 |
| 295.16 | 25.69 |
| Series II | |
| 7.09 | 0.086 |
| 8.21 | 0.139 |
| 18.64 | 1.562 |
| 20.42 | 1.885 |
| 22.49 | 2.294 |
| 24.91 | 2.775 |
| 27.49 | 3.296 |
| 30.35 | 3.870 |
| 33.54 | 4.503 |
| 37.02 | 5.180 |
| 40.86 | 5.913 |
| 44.65 | 6.627 |
| 48.91 | 7.430 |
| 54.01 | 8.376 |
| 59.37 | 9.389 |
| 64.95 | 10.39 |
| 70.64 | 11.36 |
| 76.63 | 12.36 |
| 83.21 | 13.43 |
| 90.07 | 14.44 |
| 97.31 | 15.41 |
| 105.15 | 16.36 |
| 113.09 | 17.24 |
| 120.82 | 18.04 |
| 128.53 | 18.74 |
| 136.22 | 19.37 |
| 144.18 | 19.96 |
| 152.80 | 20.55 |
| 161.71 | 21.09 |
| 170.95 | 21.61 |
| 180.53 | 22.08 |
| 190.03 | 22.51 |
| 199.35 | 22.90 |
| 208.55 | 23.24 |
| 216.49 | 23.52 |
| 224.31 | 23.79 |
| 233.14 | 24.08 |
| 241.86 | 24.34 |
| 250.91 | 24.59 |
| 260.52 | 24.86 |
| 270.26 | 25.14 |
| 279.95 | 25.36 |
| 289.69 | 25.59 |
| 299.43 | 25.80 |
| 309.18 | 26.02 |
| 319.01 | 26.24 |
| 328.95 | 26.39 |
| 338.94 | 26.57 |
| Series III | |
| 5.66 | 0.057 |
| 6.40 | .059 |
| 7.46 | .095 |
| 8.46 | .169 |
| 9.45 | .265 |
| 10.47 | .367 |
| 11.50 | .487 |
| 12.55 | .590 |
| 13.72 | .750 |
| 15.03 | .944 |
| 16.46 | 1.170 |
| 18.11 | 1.457 |
| 20.04 | 1.813 |
| 22.19 | 2.234 |
| 24.46 | 2.685 |
| 26.96 | 3.189 |
| 29.77 | 3.753 |
| 32.80 | 4.360 |
| 36.26 | 5.036 |
| 40.34 | 5.813 |
| 44.84 | 6.658 |
| 254.49 | 24.69 |
| 265.33 | 25.01 |
| 276.12 | 25.25 |
| 285.80 | 25.49 |
| 295.67 | 25.74 |
| 305.67 | 25.96 |
| 315.67 | 26.18 |
| 325.64 | 26.36 |
| 335.59 | 26.58 |
| 345.55 | 26.73 |

TABLE II

MOLAL THERMODYNAMIC FUNCTIONS OF URANYL CHLORIDE

| $T$, °K. | $Cp$, cal./deg. | $S^0$, cal./deg. | $(H^0 - H^0_0)$, cal. | $-(F^0 - H^0_0)/T$, cal./deg. |
|---|---|---|---|---|
| 10 | 0.312 | 0.104 | 0.78 | 0.026 |
| 15 | 0.939 | 0.338 | 3.77 | .087 |
| 20 | 1.803 | 0.723 | 10.56 | .195 |
| 25 | 2.792 | 1.231 | 22.04 | .350 |
| 30 | 3.798 | 1.829 | 38.52 | .545 |
| 35 | 4.794 | 2.490 | 60.00 | .776 |
| 40 | 5.746 | 3.193 | 86.36 | 1.034 |
| 45 | 6.690 | 3.924 | 117.45 | 1.314 |
| 50 | 7.631 | 4.678 | 153.26 | 1.613 |
| 60 | 9.506 | 6.234 | 238.90 | 2.252 |
| 70 | 11.25 | 7.832 | 342.79 | 2.935 |
| 80 | 12.90 | 9.444 | 463.71 | 3.648 |
| 90 | 14.42 | 11.054 | 600.5 | 4.382 |
| 100 | 15.74 | 12.643 | 751.4 | 5.129 |
| 110 | 16.90 | 14.198 | 914.8 | 5.882 |
| 120 | 17.94 | 15.715 | 1089.1 | 6.639 |
| 130 | 18.86 | 17.189 | 1273.2 | 7.395 |
| 140 | 19.66 | 18.616 | 1465.9 | 8.146 |
| 150 | 20.36 | 19.997 | 1666.0 | 8.890 |
| 160 | 21.00 | 21.332 | 1872.9 | 9.626 |
| 170 | 21.56 | 22.622 | 2085.7 | 10.353 |
| 180 | 22.06 | 23.869 | 2303.9 | 11.070 |
| 190 | 22.52 | 25.073 | 2526.8 | 11.774 |
| 200 | 22.92 | 26.239 | 2754.0 | 12.469 |
| 210 | 23.30 | 27.367 | 2985.1 | 13.152 |
| 220 | 23.64 | 28.458 | 3219.8 | 13.823 |
| 230 | 23.97 | 29.517 | 3457.8 | 14.483 |
| 240 | 24.28 | 30.544 | 3699.1 | 15.131 |
| 250 | 24.57 | 31.540 | 3943.4 | 15.766 |
| 260 | 24.85 | 32.509 | 4190.5 | 16.392 |
| 270 | 25.12 | 33.452 | 4440.3 | 17.006 |
| 280 | 25.36 | 34.370 | 4692.7 | 17.610 |
| 290 | 25.60 | 35.265 | 4947.5 | 18.205 |
| 300 | 25.82 | 36.136 | 5204.7 | 18.787 |
| 350 | 26.82 | 40.194 | 6521.6 | 21.561 |
| 273.16 | 25.19 | 33.745 | 4519.8 | 17.199 |
| 298.16 | 25.78 | 35.977 | 5157.2 | 18.680 |

Measurements of temperature and of electrical energy were made with an autocalibrated White double potentiometer. A timer, operated by an electrically driven 240-cycle tuning fork and amplifier, automatically indicated the duration of the energy input. Three independent determinations of the heat capacity of the empty calorimeter have been made over the entire temperature range. The accuracy of the calorimeter was ascertained by measuring the heat capacity of a standard sample of benzoic acid.

## Results

The experimental values of the molal heat capacity of uranyl chloride are presented in Table I. The results include small corrections for curvature[7] and also for slight differences in the amounts of helium and solder between the full and the empty calorimeter. The temperature increments of the individual determinations can be inferred from the adjacent mean temperatures. The data are expressed in terms of the defined thermochemical

---

(6) H. J. Hoge and F. G. Brickwedde, *J. Research Natl. Bureau Standards*, **22**, 351 (1939).

(7) N. S. Osborne, H. F. Stimson, C. S. Sligh and C. S. Cragoe, *Bur. Standards Sci. Papers*, **20**, 65 (1925).

calorie equal to 4.1840 absolute joules. The ice point is taken to be 273.16°K., and the molecular weight of $UO_2Cl_2$ as 340.98 g. A 190.623-g. (*in vacuo*) sample of $UO_2Cl_2$ was used.

The molal heat capacity and thermodynamic functions derived by numerical quadrature from the heat capacity are listed at rounded temperatures in Table II. The heat capacity values were read from a smooth curve through the experimental points, and they are estimated to have a probable error of 0.1% above 25°K., 1% at 10°K. and 8% at 5°K. A Debye $T^3$ extrapolation was used to obtain values of the thermodynamic functions below 10°K. This formulation yielded heat capacities consistent with the experimental data below 10°K. and assumes the absence of significant thermal anomalies in the extrapolation region below 5.2°K. The effects of nuclear spin and isotope mixing are not included in the entropy and the free energy function. We estimate a probable error in the entropy, heat content and free energy function of 0.1% above 100°K., but in order to make Table II internally consistent, some of the values are given to one more digit than is justified by the estimated probable error.

As a test of the over-all accuracy of the calorimetric process and of the enthalpy increment obtained by integration of the heat capacity, direct determinations of the enthalpy increment were made by measuring the temperature change produced by continuous input of electrical energy. Heating the sample from 47.16 to 79.21°K. required 321.4 cal. deg.$^{-1}$ mole$^{-1}$ and from 78.33 to 249.63°K. required 3492.0 cal. deg.$^{-1}$ mole$^{-1}$. The values calculated by numerical quadrature of the heat capacity *versus* the temperature yielded 321.2 and 3491.8 cal. deg.$^{-1}$ mole$^{-1}$, respectively, in excellent agreement with the direct determination.

## Discussion

The thermodynamics of the formation of uranyl chloride from the elements at 298.16°K.

$$U(c,\alpha) + O_2(g) + Cl_2(g) \longrightarrow UO_2Cl_2(c)$$

may be evaluated from the standard entropies of uranium,[8] oxygen and chlorine,[9] and the molal free energy of formation of $UO_2Cl_2$ given by Bozic and Gal.[10] The molal values for $UO_2Cl_2(c)$ at 298.16°K. are

$$\Delta S^\circ_f = -78.34 \pm 0.08 \text{ cal./deg.}$$
$$\Delta F^\circ_f = -277 \text{ kcal.}^{10}$$
$$\Delta H^\circ_f = -300 \text{ kcal.}$$

**Acknowledgment.**—The support of the U. S. Atomic Energy Commission, the assistance of Mr. George E. Grenier in making the measurements, and of Mrs. Emilia R. Martin with the calculations are gratefully acknowledged.

(8) Reported in: J. J. Katz and E. Rabinowitch, ref. 2, p. 146.

(9) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Govt. Printing Office, Washington, D. C., 1952.

(10) B. I. Bozic and O. Gal, *Z. anorg. allgem. Chem.*, **273**, 84 (1953). This value is given without any indication of origin or probable error.

Ann Arbor, Michigan

---

[Contribution from the Monsanto Chemical Company, Research Department, Inorganic Chemicals Division]

# Structure and Properties of the Condensed Phosphates. XI. Hydrolytic Degradation of Graham's Salt

By J. F. McCullough, J. R. Van Wazer and E. J. Griffith

Received April 6, 1956

The initial rate of formation of end groups and of orthophosphate in 1% solutions of Graham's salt, both in the presence and absence of 0.5 *M* NaBr as swamping electrolyte, was measured as a function of *p*H and temperature. Chromatograms run on a series of samples taken during hydrolysis at controlled *p*H values of 4, 7 and 10 were used to help interpret the data. According to the picture developed here, hydrolytic degradation in neutral and alkaline solution consists primarily of scission at the ends of the long chains with concomitant formation of rings (nearly all trimetaphosphate). In acidic solution there is also some random scission along the chain. The presence of rings larger than the tetrametaphosphate and of occasional branching points in Graham's salt is discussed.

A considerable body of evidence[1] has now been built up to show that the vitreous sodium phosphates for which the $Na_2O/P_2O_5$ mole ratio $\geqslant 1.00$ consist of a distribution[2] of various sized phosphate molecule–ions—for the most part straight chains—with the average chain length increasing as $Na_2O/P_2O_5$ approaches unity. The term "Graham's Salt" is applied to those glasses (containing large-sized straight-chain phosphates) for which $Na_2O/P_2O_5$ is exactly one. The exact chain length (number of phosphorus atoms per chain = $\bar{n}$) of a given sample of Graham's salt depends on the residual water left in the $Na_2O{\cdot}P_2O_5$ glass, since $(\bar{n} + 2)/\bar{n} = (Na_2O + H_2O_{\text{compn.}})/P_2O_5$. Hence, the term Graham's salt refers to a series of glasses exhibiting average chain lengths ranging from a lower value of 30–40 to several hundreds.

This study of the hydrolytic degradation of Graham's salt is a continuation of our more detailed work[3] on the degradation of the pyro- and tripolyphosphates; and, for the most part, identical experimental techniques were used in both investigations. However, this study is not as detailed as

---

(1) C. F. Callis, J. R. Van Wazer and P. G. Arvan, *Chem. Revs.*, **54**, 785 (1954).

(2) A quantitative distribution theory and some supporting evidence are given by J. R. Van Wazer, This Journal, **72**, 644, 647 (1950), to show that a random reorganization distribution of straight-chain phosphates with an additional small amount of rings gives a first approximation fit to the size distribution of phosphate glasses for which $Na_2O/P_2O_5$ is approximately unity. Also see paper XII in this series.

(3) J. R. Van Wazer, E. J. Griffith and J. F. McCullough, *ibid.*, **77**, 287 (1955).