$\rightleftarrows$ C. Let us assume that two paths for this reaction are possible: the direct reduction of A; and the reduction of B to C, where B is an isomer of A. We may depict this mechanism thus

$$\begin{tikzcd} \mathrm{A} + \alpha_2\mathrm{e}^- \arrow[r, shift left, "k_2"] \arrow[d, shift left] & \mathrm{C} - (1 - \alpha_2)\mathrm{e}^- \arrow[l, shift left] \\ \mathrm{B} + \alpha_3\mathrm{e}^- \arrow[u, shift left, "k_1"] \arrow[r, shift left, "k_3"] & \mathrm{C} - (1 - \alpha_3)\mathrm{e}^- \arrow[l, shift left] \end{tikzcd}$$

To the system in equilibrium we can apply the "principle of microscopic reversibility"[15] to obtain

$$\overrightarrow{\mathrm{rate}_1} - \overleftarrow{\mathrm{rate}_1} = \overrightarrow{\mathrm{rate}_2} - \overleftarrow{\mathrm{rate}_2} = \overrightarrow{\mathrm{rate}_3} - \overleftarrow{\mathrm{rate}_3} = 0$$

where the nomenclature is self-evident. Substituting into these three equations the kinetic expressions for the rates, we can obtain the relationship $\overrightarrow{k_2}/\overrightarrow{k_3} = K(\overleftarrow{k_2}/\overleftarrow{k_3})$, where K is the equilibrium constant $(= \overrightarrow{k_1}/\overleftarrow{k_1})$ for the isomerization. This result is valid at all potentials. Now, if for the reaction path (1 + 3), reaction pair (1) is rate determining, we may derive the relationship: $\overrightarrow{\mathrm{rate}_1}/\overrightarrow{\mathrm{rate}_2} = \overleftarrow{\mathrm{rate}_1}/\overleftarrow{\mathrm{rate}_2}$. Or, should reaction pair (3) be the rate-determining member, we have: $\overrightarrow{\mathrm{rate}_3}/\overrightarrow{\mathrm{rate}_2} = \overleftarrow{\mathrm{rate}_3}/\overleftarrow{\mathrm{rate}_2}$. That is, in either case, if one path contributes a certain fraction to the total forward rate, then the reverse rate of that path contributes the same fraction to the total reverse rate.

The same conclusion holds for the majority of such parallel schemes. It means that an electrode reaction at any constant potential cannot proceed by a certain forward path coupled with a different reverse path. The possibility of different forward and reverse paths at different potentials is not, of course, precluded. Systems of parallel reaction paths may therefore be treated as the additive effect of the individual paths.

Appendix 2

The Condition $\phi = 1$.—The derivation of the equivalent reaction pair required the condition $\phi = [Z]^z[Y]^y[X]^x \ldots = 1$. We will now analyze the significance of this limitation. The condition will not be satisfied, except fortuitously, unless $z = y = x = \ldots = 0$. Equation 21 define these terms and shows that for the condition to be satisfied, no Class IV substance produced prior to the rate-determining pair must be consumed subsequent to it, or *vice versa*. This simply means that an equivalent reaction pair can be written in a form that involves no Class IV substance. An equivalent reaction pair containing a Class IV substance would, in any case, be valueless.

Actually. most mechanistic schemes that can be envisaged do not involve this limitation. The following is a scheme that does

$$\mathrm{Fe(CN)_6}^{---} \rightleftarrows \mathrm{Fe(CN)_5}^{--} + \mathrm{CN}^-$$
$$\mathrm{Fe(CN)_5}^{--} + \alpha\mathrm{e}^- \underset{*}{\rightleftarrows} \mathrm{Fe(CN)_5}^{---} - (1 - \alpha)\mathrm{e}^-$$
$$\mathrm{CN}^- + \mathrm{Fe(CN)_5}^{---} \rightleftarrows \mathrm{Fe(CN)_6}^{----}$$

In attempting to construct an equivalent reaction pair from this mechanism, it is found to be impossible to eliminate the CN^- ion. Therefore, unless cyanide ion is present in the bulk, this reaction scheme is not amenable to the equivalent reaction pair treatment.

URBANA, ILLINOIS

---

[15] See, for example, E. D. Eastman and G. K. Rollefson, "Physical Chemistry," McGraw-Hill Book Co., New York, N. Y., 1947, p. 396.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY]

The System UO_2CrO_4–H_2O

BY FRANK J. LOPREST, WILLIAM L. MARSHALL AND C. H. SECOY

RECEIVED MARCH 14, 1955

Phase equilibria in the system uranyl chromate–water have been studied from 0° to the ice eutectic at −0.145° and to temperatures at which hydrolytic precipitation of an uncharacterized solid phase occurs. The solubility of $UO_2CrO_4 \cdot 5^1/_2H_2O$ exhibits a marked increase with temperature from 3.11 weight per cent. of uranyl chromate at 0° to 70.4 at 66°. A transition between the $5^1/_2H_2O$ hydrate and a lower hydrate (probably $1H_2O$) occurs at 66.3°. The solubility of the latter solid exhibits practically no variation with temperature.

The preparation of uranyl chromate has been described by Formánek[1] and by Orlow[2] but very few data on the solubility of this salt have been reported in the literature. Orlow gives the solubility at 15° as 7.52 parts of the trihydrate per 100 parts of water. Formánek reports the existence of $UO_2CrO_4 \cdot 5^1/_2H_2O$, but gives no quantitative solubility data. This study confirms Formánek's identification of the solid and presents solubility data over a wide temperature range.

Experimental

Uranyl chromate was prepared by dissolving at 50° a stoichiometric amount (from 50–100 g.) of pre-washed Mallinckrodt uranium trioxide, of nitrate content less than 0.1 p.p.m., in a weighed amount of a standardized 1 to 2 molar aqueous solution of Baker and Adamson C.P. chromic trioxide and crystallizing the uranyl chromate at 0°. The solid phase appeared as very small light yellow-orange needle crystals. The remaining liquid was removed from the solid by suction filtration and the solid was washed with several portions of cold water, redissolved and recrystallized. Several different batches of the solid were prepared. Determinations of the UO_3/CrO_3 ratio in samples taken from two of the batches yielded values of 0.99 and 1.00, the precision of the analysis being of the order of ±0.5%. In-

---

(1) J. Formánek, *Ann. Chem.* (*Liebig*), **257**, 102 (1890).

(2) N. A. Orlow, *Chem. Z.*, **31**, 375 (1907).

ternal checks on the purity of the various batches were provided by the reproducibility of solubility values at various temperatures using solid from different batches and using mixtures of widely varying liquid-solid ratios.

Most of the binary liquids and solids were analyzed for chromate alone, iodometrically. Uranium did not interfere with the titration and a precision of about one part per thousand was obtained.

In those samples for which determination of both chromate and uranium[3] was desired, chromate was determined by a coulometric method in which an aliquot of the sample was added to an excess of aqueous solution of a ferric salt through which a constant electrical current was passed. Ferrous ion produced at the cathode immediately reduced the chromate. The time required for the reduction of all the chromate was accurately measured, the end-point being detected potentiometrically. The precision was of the order of ±0.4%. Uranium was determined in a separate aliquot by a potentiometric titration which involved the reduction of both U(VI) and Cr(VI) with an excess of freshly prepared chromous salt solution[4] followed by titration with standard potassium dichromate solution. The volume of titrant used between the Cr(II)–Cr(III) and the U(IV)–U(VI) end-points represented the number of equivalents of uranium present.

Initially, uranium and chromate were determined in a single aliquot of the sample by separating one from the other using a Dowex 50 cation exchange resin.[5] The uranium was adsorbed on the resin column and the column was washed free of chromate which was collected and determined iodometrically. The uranium was then removed from the column with 8 *M* HCl or 4 *M* H_2SO_4 and determined either gravimetrically by evaporating to dryness and igniting, or volumetrically (in the case of the sulfuric acid solutions) using a Jones reductor and standard ceric sulfate solution.[6] This method of analysis was not used further because of the difficulty of removing uranium quantitatively from the column and because at concentrations of chromate above approximately 0.03 *M* the chromate was apparently reduced[7] introducing a variable error.

The solubility of uranyl chromate hydrate was determined by stirring liquid-solid mixtures (15–25 g.) contained in a test-tube in a liquid thermostat (±0.05°) at various temperatures from the ice eutectic to 100°. In sampling, the stirrer was removed, the tube was stoppered, and the solid was allowed to settle. An appropriate weight (about 1 g.) of the clear liquid was transferred by means of a pipet, preheated if necessary, to a tared weighing bottle, weighed and analyzed. Equilibrium was attained rapidly from undersaturation (within 2 hr.) and more slowly from oversaturation as proved by repeated analysis of the liquid phase after stirring for varying lengths of time.

The solubility at 140° was determined by equilibrating in a sealed Pyrex tube, allowing the solid phase to settle, and then transferring the tube carefully to an ice-bath whereupon the liquid phase solidified and a portion of this frozen "liquid phase" was removed and analyzed.

Experiments to determine the hydrolytic phase stability of the system were carried out by sealing unsaturated solutions of varying compositions in Pyrex tubes and rotating them from one to five days at different temperatures, between 100 and 140°. The tubes were examined periodically for solid phases which appeared in certain temperature ranges for particular solution compositions.

Several points in the ternary system, UO_3–CrO_3–H_2O, were obtained by preparing an accurate mixture of the components by weighing them in a Pyrex tube, the CrO_3 being introduced as a standard solution containing between 55 and 60 weight per cent. of CrO_3. The solid weighed was either UO_3 or UO_2CrO_4 of known water content. The tubes were sealed and agitated by rotating on a wheel in a liquid thermostat for about five days after which the liquid phase was sampled for analysis.

The ice curve and also the hydrate transition at 66.30 ± 0.30° were obtained by standard cooling curve methods using an iron–constantan thermocouple connected to a Leeds and Northrup K-2 potentiometer for temperature measurement. The ice curve data are precise and accurate to ±0.015° while the hydrate transition temperature is within ±0.30° precision and accuracy as verified with a Bureau of Standards certified thermometer.

Discussion

Complete data for the system are given in Table I and are plotted in the binary, condensed, phase diagram, Fig. 1.

The solubility curves of the two binary solids formed in this system intersect at a temperature very close to 66°. The solubility curve of the $5^1/_2$ hydrate undergoes a reversal in curvature at a temperature of about 40° indicating the possibility of a solid phase transition. However, no detectable break in cooling curves occurred in the temperature range from about 60 to 30°. It therefore appears that there is no transition below that which occurs at 66.3°. It may be mentioned that a plot of the solubility expressed in mole fractions against the temperature does not exhibit as marked a reversal in curvature as does the weight per cent.–temperature plot. The curvature of the solubility curve of the $5^1/_2$ hydrate suggests the possibility of the proximity of a submerged two-liquid region. This is interesting because of the two-liquid regions appearing (although at higher temperatures) in the corresponding sulfate and fluoride systems.[8,9] The solubility of the high temperature binary solid, which contains between 0 and 3 moles of water per mole of uranyl chromate, shows no detectable variation with temperature.

In Fig. 1 are included points (region r to s) indicating the temperature range within which a dark brick-red solid phase was observed to precipitate in five solutions unsaturated with respect to the normal chromate. This solid was not characterized but is probably a basic uranyl chromate and therefore not a part of the binary system.

That the system is binary at least to the transition at 66.3° is indicated by the results of analyses of liquid phases for both uranium and chromium at 25, 45 and 55°, the UO_3/CrO_3 ratios obtained being 1.01, 1.01 and 1.00 ± 0.005, respectively.

The lower temperature hydrate was found to be $UO_2CrO_4 \cdot 5^1/_2H_2O$ (theoretical, 79.58% UO_2CrO_4) confirming the report of Formánek.[1] Preliminary experiments had indicated that the composition of the solid lay between that of the pentahydrate (UO_2CrO_4 = 81.09%) and that of the hexahydrate (UO_2CrO_4 = 78.13%). Samples of solids that had been equilibrated at three temperatures, 0, 25 and 40°, were allowed to dry in air at room temperature (23°). These solids contained an average percentage of UO_2CrO_4 of 80.59 with an average deviation of 0.21. A sample of solid equilibrated at 40.0° was removed and rapidly dried with filter paper, weighed and analyzed. It contained 77.59% UO_2CrO_4. That the solid was actually the $5^1/_2H_2O$ hydrate was proved by desiccating a sample of the

---

[3] These analyses were carried out by P. F. Thomasen and W. D. Shults of the Analytical Division of ORNL.

[4] C. J. Rodden, Editor-in-Chief, "Analytical Chemistry of the Manhattan Project," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 62.

[5] H. O. Day, Jr., J. S. Gill, E. V. Jones and W. L. Marshall, *Anal. Chem.*, **26**, 611 (1954).

[6] C. Sill and H. Peterson, *ibid.*, **24**, 1175 (1952).

[7] O. Samuelson, "Ion Exchangers in Analytical Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 74.

[8] C. H. Secoy, THIS JOURNAL, **72**, 3343 (1950).

[9] W. L. Marshall, J. S. Gill and C. H. Secoy, *ibid.*, **76**, 4279 (1954).

wet equilibrated solid (40.0°) at room temperature using a lower hydrate of uranyl chromate as the desiccant. If the desiccant contains a sufficient quantity of the next lower hydrate, then it will dry the wet solid without decomposing it.[10] The wet sample of the solid was allowed to come to constant weight in a small desiccator and it was then analyzed. The results of two such experiments yielded values of the percentage of UO_2CrO_4 of 79.57 and 79.68. The composition of the desiccant, which weighed 5–10 times as much as the sample, was determined after equilibration and it was found to have a water content (10.8%) less than that of the $5^1/_2H_2O$.

TABLE I

THE SYSTEM UO_2CrO_4–H_2O

Temp., °C.	Wt. % UO_2CrO_4
Ice + soln. + vapor	
−0.00	0.00
− .02	0.099
− .03	0.242
− .03	0.496
− .06	1.044
− .09	1.967
− .12	2.452
Ice + $UO_2CrO_4 \cdot 5^1/_2H_2O$ + soln. + vapor	
−0.15[a]	3.07
$UO_2CrO_4 \cdot 5^1/_2H_2O$ + soln. + vapor	
0.0	3.11
4.98	4.61
9.88	6.66
10.06	6.78
15.01	10.24
20.33	15.85
20.65	16.27
24.7	23.41
$UO_2CrO_4 \cdot 5^1/_2H_2O$ + soln. + vapor	
25.05[b]	23.24
30.00	32.87
35.00	42.69
37.50	47.36
40.03	51.62
41.96	53.70
45.06	56.75
47.64	58.80
50.10	60.05
55.14	64.76
60.18	66.84
$UO_2CrO_4 \cdot 5^1/_2H_2O$ + $UO_2CrO_4 \cdot XH_2O$ + soln. + vapor	
66.3	70.04
$UO_2CrO_4 \cdot XH_2O$ + soln. + vapor	
70.30	70.50
80.45	69.97
90.61	70.70
100.88	70.24
140	70.95

[a] Extrapolated value.
[b] Density = 1.246.

An attempt was made to determine the state of hydration of the high temperature saturating binary phase by fixing tie-lines in the appropriate region of the system UO_2CrO_4–CrO_3–H_2O at 75° and determining at what H_2O/UO_2CrO_4 ratio they intersected the 0% CrO_3 side of the ternary diagram. The tie-lines were fixed by two ternary composition points, the total composition of the mixture and the equilibrium liquid phase composition.[11] The data are listed in Table II. The point of intersection of the tie-lines with the 0% CrO_3 side of the diagram was calculated by algebraic extrapolation. It is readily seen from Table II that the data are not sufficiently accurate to determine the state of hydration. If one assumes that the same saturating solid phase was present in each of the nine experiments then there may conceivably be some significance in the average value which is 94.9% UO_2CrO_4 at 0% CrO_3 which represents a mole ratio of water to uranyl chromate of 1.15.

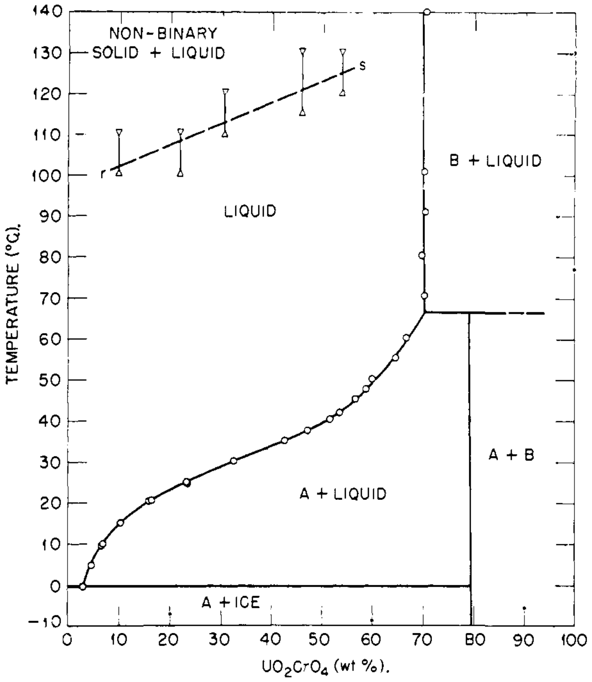

Fig. 1.—The system UO_2CrO_4–H_2O, where A = $UO_2CrO_4 \cdot 5^1/_2H_2O$, B = $UO_2CrO_4 \cdot xH_2O$.

TABLE II

UO_2CrO_4–CrO_3–H_2O AT 75°

No.	Total mixture, wt. % UO_2CrO_4	Total mixture, wt. % CrO_3	Liquid phase, wt. % UO_2CrO_4	Liquid phase, wt. % CrO_3	Wt. % UO_2CrO_4 at 0% CrO_3
1	68.84	3.06	62.18	3.83	95
2	67.93	3.44	60.98	4.48	91
3	64.71	5.02	59.37	5.86	97
4	64.09	5.37	59.65	6.13	96
5	66.74	5.85	54.85	8.74	91
6	62.88	7.87	57.69	9.00	99
7	69.42	7.94	56.01	11.96	96
8	62.34	11.84	57.62	13.60	94
9	71.01	10.38	58.19	15.95	95

The marked change in solubility from the 0° value of 3.11 weight per cent. to the 70° value of 70.5 weight per cent. is unique among uranyl salts. Uranyl chromate can be purified easily and it may conceivably be of value in separations involving uranyl systems.

OAK RIDGE, TENN.

---

[10] J. E. Ricci, "The Phase Rule and Heterogeneous Equilibrium," D. Van Nostrand Co., Inc., New York, N. Y., 1951, pp. 138–142.

[11] A. E. Hill and J. E. Ricci, THIS JOURNAL, **53**, 4305 (1931).