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The Solubility of Uranyl Oxalate and the Existence
of Undissociated Uranyl Oxalate in Solution

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Abstract

The solubility of the solid, $\text{UO}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, was measured at various acid and uranyl nitrate concentrations. The results of the measurements prove the existence of the uranyl oxalate complex $\text{UO}_2\text{C}_2\text{O}_4$ in solutions containing excess UO_2^{+2} .

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The Solubility of Uranyl Oxalate and the Existence of Undissociated Uranyl Oxalate in Solution

The solubility of $\text{UO}_2\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ was measured at several nitric acid concentrations and several uranyl nitrate concentrations. From the limited influence of acid concentration and uranyl nitrate concentration on solubility it was concluded that nearly all of the oxalate in solution was in the form of the uranyl oxalate complex, $\text{UO}_2\text{C}_2\text{O}_4$ (or $(\text{UO}_2\text{C}_2\text{O}_4)_n$).

The composition of the solid phase (uranyl oxalate) present in the solubility measurements was determined. The precipitate was obtained from a solution 0.5 M in uranyl nitrate, 1.0 M in HNO_3 and 0.05 M in $\text{H}_2\text{C}_2\text{O}_4$. The solid was sucked dry on a sintered glass filter and then dissolved in 6-7 M HNO_3 . Equal aliquots were taken for oxalate titration with Ce^{+4} (see below) and for ignition to U_3O_8 . In the third experiment the precipitate was washed with a solution 1.0 M in HNO_3 and 0.5 M in $\text{H}_2\text{C}_2\text{O}_4$ before dissolving. The results are given in Table 1. They indicate that the solid phase is $\text{UO}_2\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$. (The only hydrate listed in the literature is the trihydrate).

Quantitative titration of the total oxalate* present in solution was used to measure the solubility of uranyl

*Total oxalate includes that in any uranyl oxalate complexes as well as $\text{H}_2\text{C}_2\text{O}_4$, etc..

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TABLE 1

COMPOSITION OF URANYL OXALATE PRECIPITATE

Expt. No.	Mgms. U_3O_8 per 5 cc. solution	$\text{C}_2\text{O}_4^{2-}$ conc. moles/l.	Ratio		Remarks
			moles UO_2^{+2}	moles $\text{C}_2\text{O}_4^{2-}$	
1	117.5	0.0774	1.073		This solution exposed to day- light for sev- eral hours.
2	63.4	0.04241	1.065		
3	47.2	0.03461	0.973		Precipitate washed with $\text{HNO}_3\text{-H}_2\text{C}_2\text{O}_4$ solution.

oxalate. Cerio titrimetry as proposed by G. F. Smith⁽¹⁾ proved applicable. A satisfactory titration is obtained by adding an excess of standard ammonium hexanitratocerate solution, heating at 50-60°C. for 10-15 minutes, and back titrating the excess cerate at room temperature with standard ferrous ammonium sulfate solution. Nitro-ortho-phenanthroline ferrous sulfate (nitro ferroin) gives an easily discernible color change in the presence of 0.2 M uranyl nitrate, which was the maximum end-point concentration of UO_2^{+2} used. The direct titration of oxalate with ammonium hexanitratocerate in the presence of uranyl ion gave a fading end point. This was at least partially due to an appreciable amount of reducing material in the uranyl nitrate. This reducing material necessitated corrections in all calculations. The blank titrations were similar in every respect to the usual titration except that no oxalate was added.

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The ceric solution was made 1.5 M in HNO_3 as directed by G. F. Smith⁽²⁾ to ensure stability. Sodium oxalate was used as a primary standard. The ferrous solution was checked daily against the standard ceric solution.

The solutions under investigation ($0.25-1.0 \text{ M } \text{UO}_2^{+2}$, $0.5-2.0 \text{ M } \text{HNO}_3$, $0.015-0.020 \text{ M } \text{H}_2\text{C}_2\text{O}_4$) decompose when exposed to light. It was experimentally verified that four hours exposure to very strong artificial light was sufficient to reduce the titer 5-10% in a solution 0.5 M in $\text{UO}_2(\text{NO}_3)_2$, 1.0 M in HNO_3 , and 0.020 M in $\text{H}_2\text{C}_2\text{O}_4$. No decomposition was observed on a duplicate sample left in the dark for seven hours before titration. In some of the early experiments the samples withdrawn for analysis were exposed to light for some time before being titrated. All values from samples that had more than an hour and a half of exposure were discarded. Thereafter, All solutions were left in the dark while awaiting titration, allowing about ten minutes exposure during withdrawal. This precaution eliminated the fluctuations previously observed and brought the deviations down to less than 0.5% on later samples. No precautions were taken to shield the solutions in the thermostat, since the rate of decomposition due to exposure to light is very small compared to the rate of solution of the uranyl oxalate.

To be certain that equilibrium was established, the solubility was determined both from the supersaturated and the unsaturated side. The uranyl nitrate and the nitric

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acid were first mixed and brought to the correct temperature. Then either oxalic acid or solid uranyl oxalate was added in order to approach the equilibrium by precipitation or by solution of the solid phase. Solid uranyl oxalate was prepared by precipitation from a solution similar to that in which it was to be used.

The solubility data are presented in Table 2. Indicated with each oxalate concentration is the elapsed time between the start of the experiment and withdrawal of the sample. The average oxalate concentration for each experiment is given along with the average deviation.

In all experiments samples were removed from the solutions at varying times until no further change of solubility was observed. It can be seen in Table 2 that equilibrium is rapidly reached from the unsaturated side and is fairly rapidly established in the supersaturated solution after crystallization begins. Crystallization in the first experiment actually commenced between 2 and 3 hours after mixing of the solutions. Further, it is seen that true equilibrium was obtained as both sets of data approach the same value for the solubility.

In Table 3 the solubility values obtained in each pair of experiments (starting from opposite sides of equilibrium) are averaged. The results are arranged to show the effect of uranyl nitrate concentration, nitric acid concentration and temperature.

The results shown in part I of Table 3 lead to the surprising conclusion that over a four fold change in the

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TABLE 2

SOLUBILITY OF URANYL OXALATE

UO ₂ ²⁺ conc. at equilib. moles/l.	HNO ₃ conc. moles/l.	Temp. °C.	Uranyl oxalate precipitated to attain equilibrium			Uranyl oxalate dissolved to attain equilibrium		
			Stoichio- metric ox- alate conc. moles/l.	Time for equilib. hrs.	Average oxalate conc. moles/l.	Stoichio- metric ox- alate conc. moles/l.	Time for equilib. hrs.	Average oxalate conc. moles/l.
0.49	1.00	24.95 ±0.02	0.01724	6	0.01708	0.01703	1	0.01704
			0.01724	7	±0.1%	0.01699	2	±0.4%
			0.01692	9		0.01698	149	
			0.01715	55		0.01627*	176	
			0.01671	176		0.01720	176	
0.24	1.00	24.95 ±0.02	0.01722	149	0.01717	0.01716	1	0.01721
			0.01721	176	±0.4%	0.01711	3	±0.4%
			0.01706	218		0.01715	125	
			0.01671*	218		0.01729	151	
						0.01722	242	
0.49	2.00	24.95 ±0.02	0.01594	123	0.01591	0.01581	142	0.01583
			0.01506	123	±0.4%	0.01571	167	±0.5%
			0.01581	147		0.01593	290	
			0.01604	270		0.01587	290	
			0.01591	270				
0.40	0.50	24.95 ±0.02	0.01783	140	0.01779	0.01814	23	0.01809
			0.01784	140	±0.3%	0.01805	143	±0.2%
			0.01773	164		0.01803	143	
			0.01773	164				
0.99	1.00	24.95 ±0.02	0.01670	140	0.01664	0.01699	20	0.01670
			0.01672	140	±0.6%	0.01671	141	±0.6%
			0.01651	163		0.01672	141	
0.49	1.00	32.5 ±0.2	0.02015	136	0.02018	0.01675	163	
			0.02016	164		0.02032	136	0.02042
			0.02022	164		0.02048	164	
0.49	1.00	50.0 ±0.2	0.03115	73.5	0.03124	0.0312	73.5	0.03104
			0.03134	73.5	±0.3%	0.03084	73.5	±0.6%

*Not included in average due to large deviation.

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TABLE 3

SUMMARY OF UO_2O_4 SOLUBILITY EXPERIMENTS

I.	Effect of Uranyl Nitrate Concentration				
(HNO_3)	1.00 moles/l.				
Temp.	$24.95^\circ \pm 0.02^\circ C.$				
(UO_2^{+2})	0.24	0.49	0.99	moles/l.	
(Total oxalate)	0.0172	0.0170	0.0167	moles/l.	

II.	Effect of HNO_3 Concentration				
(UO_2^{+2})	0.49 moles/l.				
Temp.	$24.95^\circ \pm 0.02^\circ C.$				
(HNO_3)	0.50	1.00	2.00	moles/l.	
(Total oxalate)	0.0179	0.0170	0.0159	moles/l.	

III.	Effect of Temperature				
(UO_2^{+2})	0.49 moles/l.				
(HNO_3)	1.00 moles/l.				
Temp.	24.95 ± 0.02	33.5 ± 0.2	50.0 ± 0.2	$^\circ C.$	
(Total oxalate)	0.0170	0.0203	0.0312	moles/l.	

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uranyl nitrate concentration the solubility of uranyl oxalate varied by less than three percent. Also, a four fold change in nitric acid concentration produced only a 18% change in the solubility. These facts seem best explained by the assumption that nearly all of the oxalate in solution is tied up by uranyl ions as a uranyl oxalate complex of the formula $\text{UO}_2\text{C}_2\text{O}_4$ (or $(\text{UO}_2\text{C}_2\text{O}_4)_n$); if this is case, the nitric acid and uranyl concentrations would have no effect on the solubility except for ionic strength effects.

The stability of this uranyl oxalate complex is remarkable, but it should be remembered that the solution always contained a large excess of uranyl ions. At smaller concentrations of uranyl ions, the complex would tend to dissociate; at high oxalic acid concentrations and low acidity, higher complexes would probably form.

It is interesting to note that the high solubility of undissociated uranyl oxalate sets a rather high limit to the minimum total solubility of the compound in aqueous solution. Thus at 25°C., under any conditions, the solubility must be at least 0.017 moles/liter if the same solid phase as used in the above experiments is present. A search of the literature reveals this to be the case except for small deviations due to salt effects.

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