An Investigation of Conditions for Precipitation of Uranium(IV) Orthophosphate

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The precipitation of uranium as uranium(IV) orthophosphate from low concentrated acid solutions depends greatly on the possible presence of aluminium salts in the solutions. At high concentrations of aluminium ion, no precipitation is obtained. In chloride solutions consisting of uranium(IV) chloride, aluminium chloride, orthophosphoric and hydrochloric acids, the precipitation is prevented due to the formation of soluble double complexes between uranium, aluminium and phosphate ions. In sulfate solutions consisting of uranium(IV) sulfate, aluminium sulfate, orthophosphoric and sulfuric acids, the precipitate is formed only within a relatively narrow pH range around pH 1. At higher pH values, precipitation is prevented probably by the same double complexes as in chloride solutions. At lower pH values, precipitation is prevented mainly by soluble complexes between uranium and sulfate.

Some investigations were performed in order to clarify the conditions for the precipitation of uranium(IV) orthophosphate from low concentrated acid solutions. It was then proved that the presence of aluminium salts in the solutions has a great effect.

PRECIPITATION EXPERIMENTS

To perform the precipitation experiments, solutions were prepared containing 0.0017 M uranyl chloride, 0.042 M orthophosphoric acid and various amounts of aluminium chloride. The pH was adjusted to various values using hydrochloric acid. Analogous sulfate solutions were prepared from uranyl sulfate, orthophosphoric acid, aluminium sulfate and sulfuric acid. The solutions were heated to 35° C and reduced with a suitable reducing agent. The solutions were kept under slight stirring at 35° C for about 24 h. The time elapsing before a precipitate could be clearly seen was noted. After 24 h, the solutions were filtered and the amounts of uranium in the mother liquors were determined by analysis.

Fig. 1. Precipitation of uranium(IV) phosphate from chloride solutions with various concentrations of AlCl_3 . + indicates precipitation, — no precipitation.

Fig. 2. Precipitation of uranium(IV) phosphate from sulfate solutions with various concentrations of $\text{Al}_2(\text{SO}_4)_3$. (+) indicates precipitation after 5 h.

In Figs. 1 and 2, where the axes are the concentration of aluminium in the various solutions and pH, the precipitation experiments on the above mentioned chloride and sulfate solutions have been plotted. Cases where a precipitate is obtained within 5 h have been marked with + on the figures. If precipitation occurs after 5 h, this is marked with (+). Cases where no precipitation occurs within 24 h have been marked with — on the figures. The approximate boundary between precipitation and no precipitation is drawn.

Figs. 1 and 2 show that no uranium(IV) phosphate precipitates from low concentrated solutions at high aluminium concentrations. Fig. 1 shows that, in chloride solutions, the boundary between precipitation and no precipitation decreases with increasing pH. Gelin¹ has in an unpublished article given an account of precipitation experiments with uranium chloride solutions with various concentrations of aluminium chloride and phosphoric acid. In diagrams with the aluminium concentration plotted against the phosphate concentration, Gelin obtained precipitation boundaries similar to those of Fig. 1. According to Fig. 2, a boundary with a pronounced peak within pH interval 0.7—1.2 is obtained in sulfate solutions.

Precipitation experiments have been performed on sulfate solutions with an addition of sodium, magnesium or iron(II) sulfate as ionic medium, Figs. 3, 4 and 5. These additions were so calculated that, at various concentrations of aluminium sulfate, the total concentration of sulfate in the different solutions remained constant = 1.4 mole/l. The experiments were carried out as before.

Figs. 2—5 show that the area for precipitation of uranium(IV) phosphate in sulfate solutions depends greatly on the ionic medium. The difference between sodium and magnesium sulfate as ionic medium is especially remarkable.

Fig. 3. Precipitation of uranium(IV) phosphate from sulfate solutions at various concentrations of aluminium. Sulfate concentration kept at 1.4 mole/l using Na_2SO_4 .

Fig. 4. Precipitation of uranium(IV) phosphate from sulfate solutions at various concentrations of aluminium. Sulfate concentration kept at 1.4 mole/l using MgSO_4 .

PRECIPITATION YIELDS

In the above mentioned chloride solutions, the yield of precipitate is over 90 % in the greater part of the region where a precipitate is obtained. Not until the precipitation boundary is reached does the yield quickly decrease to zero. Corresponding conditions are obtained with sulfate solutions, with sodium, magnesium or iron(II) sulfate as ionic medium, on the right hand side of the peak. With magnesium sulfate as ionic medium, the following yields at pH 1.3, 1.8 and 2.5 were obtained, corresponding to the precipitation experiments shown in Fig. 4:

Al mole/l	pH 1.3	Yield, % pH 1.8	pH 2.5
0.07			93
0.11	97	94	0
0.15	72	0	
0.19	90		
0.22	35		

In sulfate solutions without an extra addition of sulphate salt, the yields of uranium decrease more slowly with increasing concentration of aluminium. The corresponding precipitation experiments are shown in Fig. 2.

Al mole/l	Yield, % pH 1.8	pH 2.5
0.07	97	96
0.15	95	66
0.30	85	40
0.45	30	
0.52	0	

On the left side of the peak in Figs. 2—5, the yields decrease slowly with increasing concentration of aluminium. In solutions without an extra addition of sulfate salt and also in solutions with magnesium sulfate, the following yields were obtained at pH 0.4. The corresponding points are found in Figs. 2 and 4.

Al mole/l	Yield, %	
	No extra addition of sulfate	With MgSO_4 as ionic medium
0.07	94	
0.15	75	92
0.30	15	45
0.45		15

PRECIPITATE ANALYSES

Examinations in a Norelco Geiger-Counter X-Ray Diffractometer and in an electron microscope ($10\,000\times$) showed the precipitate to be amorphous.

A number of precipitates deposited from solutions at pH 0.4 have been analysed. The results are shown in Figs. 6—9. By means of the chloride analyses of the precipitates and the mother liquors, the compositions of the precipitates have been corrected for the amount of enclosed mother liquor using the rough assumption that Cl^- was not adsorbed on the precipitates to any appreciable extent. In chloride solutions containing 0.0025 M uranium(IV) chloride, 2.8 M sodium chloride, orthophosphoric and hydrochloric acids, the uranium phosphate precipitates with a composition of 2.1 mole phosphate/mole

Fig. 5. Precipitation of uranium(IV) phosphate from sulfate solutions at various concentrations of aluminium. Sulfate concentration kept at 1.4 mole/l using FeSO_4 .

Fig. 6. Composition of uranium precipitates: A) The ratio $\text{PO}_4:\text{U}$ in precipitates from solutions of uranium chloride with 2.8 M NaCl and various proportions of H_3PO_4 , pH 0.4. B) The same solutions with an addition of 0.7 M FeSO_4 .

Fig. 7. The compositions of precipitates from solutions containing 0.0025 M UCl_4 , 2.8 M NaCl, 0.04 M H_3PO_4 and various concentrations of sulfate, pH 0.4. A) The ratio $\text{PO}_4:\text{U}$ in the precipitates. B) The ratio $\text{SO}_4:\text{U}$.

uranium irrespective of the phosphoric acid concentration in the solution (cf. Fig. 6). From the same chloride solutions but with an addition of ca. 0.7 M iron(II) sulfate, precipitates are obtained with a phosphate/uranium ratio which decreases as the phosphate concentration in the solution decreases. In solutions with the same phosphate concentration but with different sulfate concentrations, the precipitates according to Fig. 7 deposit, where the ratio mole phosphate/mole uranium decreases with increasing amount of sulfate in the solution. However, the ratio sulfate/uranium increases to the same extent so that the ratio (phosphate + sulfate)/uranium remains constant at 2.1.

Fig. 8. The ratio Al:U in the precipitates from uranium chloride solutions with 2.8 M NaCl, 0.04 M H_3PO_4 , various concentrations of AlCl_3 and pH 0.4.

Fig. 9. The ratio Fe:U in the precipitates from solutions of uranium chloride with 2.8 M NaCl, 0.04 M H_3PO_4 , various concentrations of FeSO_4 and pH 0.4.

According to Fig. 8, a larger amount of aluminium is obtained in the precipitate as the concentration of aluminium in the solution increases. With iron(II) sulfate in the solution, iron is also found in the precipitates. A comparison between washed and unwashed precipitates showed that the iron, but not the aluminium, can be removed by water.

EXTINCTIOMETRIC MEASUREMENTS

It was found that, in the greater part of the precipitation regions in Figs. 1—5, an initial opalescence or precipitation develops to complete visibility within 0.5—1.5 h. The time required has been measured from the moment when the reducing agent was added. In the chloride solutions, the precipitate shows a tendency to develop more rapidly than in the corresponding sulfate solutions. In the vicinity of the precipitation boundary, the precipitates do not become visible until after *ca.* 1.5—3.5 h.

Some preliminary complex investigations and measurements of reduction speed have been performed to find the reason for these long precipitation times. The experiments were performed in a Beckman spectrophotometer, model DU. The concentrations of the solutions were selected so that no precipitation was obtained during the reduction.

First, the extinction was measured at various wave-lengths on unreduced as well as reduced solutions containing 0.0075 M uranium chloride or uranium sulfate dissolved in 0.4 N hydrochloric acid or sulfuric acid respectively. Then the extinction was measured on the same solutions after the addition of the remaining components. The state of reduction and complexity for uranium were estimated by comparing the extinction curves obtained. These experiments were supplemented by a few measurements of the reduction speed, where the extinction was measured at 649 $m\mu$ as a function of the time elapsed from the addition of the reducing agent. In Fig. 10, where a few of the extinction curves obtained are shown, the curves A and B refer to the above mentioned reduced solutions containing uranium chloride and sulfate, respectively. Curve C is the extinction curve for the same reduced uranium chloride solution as in curve A but with an addition of 0.5 M aluminium chloride and 0.1 M orthophosphoric acid.

According to Rodden ⁴, curve A is typical for the extinction of uranium(IV) chloride in strong hydrochloric acid solutions. Not only are the extinction peaks at 429.5 $m\mu$, 549 $m\mu$ and 649 $m\mu$ characteristic but also the shape of the peak at 485—495 $m\mu$ and the small extra peak at 672 $m\mu$. The same curves are obtained with uranium(IV) perchlorate. This indicates that uranium(IV) is present mainly as free ions in the solutions.

According to Betts and Leigh ², uranium(IV) forms very strong complexes with sulfate. Curve B is characteristic for these complexes. The shape of the peak at 485—495 $m\mu$ is especially remarkable. In addition, the highest peak is lower than that for the chloride solutions and moved from 649 $m\mu$ to 651 $m\mu$. The small peak at 672 $m\mu$ was not found.

During measurements on 0.0075 M uranium(IV) chloride solutions containing 2.8 M sodium chloride, it was proved that the extinction curve typical for sulfate solutions was obtained on the addition of 0.1 M sodium sulfate. This is also evidence for no, or only weak, complexes between uranium(IV) and chloride.

Fig. 10. Extinction curves of a few uranium(IV) solutions. A) 0.0075 M UCl_4 in 0.4 N HCl. B) 0.0075 M $\text{U}(\text{SO}_4)_2$ in 0.4 N H_2SO_4 . C) 0.0075 M UCl_4 , 0.5 M AlCl_3 , 0.1 M H_3PO_4 and HCl to pH 0.4. The measurements were performed in 10 mm cuvettes.

Curve C, Fig. 10 is characteristic for the soluble uranium(IV) phosphate complexes that were obtained in connection with the precipitation experiments. Especially notable is the double peak at 479 and 498 $m\mu$ and the great decrease in the peak at 650 $m\mu$. In those cases where it was impossible to determine whether the change in the extinction curves was due to incomplete reduction or complex formation, measurements were performed on solutions where the uranium was reduced before as well as after the addition of the remaining components. If the extinction curves from solutions reduced *before* the addition of remaining components agree with those from solutions reduced *after* the addition, then any differences between these extinction curves and the corresponding curves from solutions *without* addition cannot be caused by incomplete reduction. The difference must then be due to complex formation in the solutions.

The important results from experiments on precipitation of uranium as uranium(IV) orthophosphate from acid solution can be summed up as follows:

a) In the solutions used for precipitation experiments according to Figs. 1—5, uranium(IV) is reduced completely or almost completely to uranium(IV) even in the cases where no precipitate is obtained.

b) The long times for precipitation are due not to the rate of reduction but to difficulties of precipitate development.

c) In chloride solutions, the extinction curves typical for the actual uranium(IV) phosphate complexes are found in the region where, according to Fig. 1, no precipitate is formed.

d) In sulfate solutions, the uranium is complex-bound in the region for no precipitation on the right hand side of the peak in Figs. 2—5, in the same way as in chloride solutions. However, on the left hand side of the peak, the uranium in sulfate solutions mainly exists as soluble uranium(IV) sulfate complexes.

CALCULATION OF THE PRECIPITATION BOUNDARY IN FIG. 1 VALID FOR CHLORIDE SOLUTIONS

Figs. 1 and 2 show that the precipitation conditions are simpler in chloride solutions than in corresponding sulfate solutions. The extinction curves obtained do not indicate that uranium(IV) forms complexes with chloride. However, uranium does form very strong complexes with sulfate². When calculating the complex ratio of uranium in chloride solutions, the possible presence of uranium(IV) chloride complexes may therefore be disregarded, whereas the complexes between uranium(IV) and sulfate must be considered when calculating the ratio in sulfate solutions. Only the conditions in chloride solutions are discussed here. The calculations below should give an explanation of the form of the precipitation boundary in Fig. 1 as well as of the precipitation yield, which is over 90 % within the whole precipitation region except for a small section near the precipitation boundary where the yield quickly decreases to zero.

The calculations have been based upon the assumption that soluble double complexes between uranium(IV), aluminium and phosphate prevent the uranium phosphate from precipitating.

In the calculations, consideration has been taken only of possible complexes between uranium, aluminium and phosphate, while all the possible complexes with remaining ions are neglected. No consideration has been taken of activity factors, hydrolysis (the actual pH-range is below 2) or of the fact that the salt concentrations have not been kept constant in the experiments in Fig. 1 with which the calculated precipitation boundaries are compared.

The following complexes between uranium and phosphate are conceivable: With one uranium ion in each complex, such as $U(H_2PO_4)_n$, $U(HPO_4)_n$ and $U(PO_4)_n$, with several uranium ions such as $U_m(H_2PO_4)_n$, $U_m(HPO_4)_n$ and $U_m(PO_4)_n$ or mixed complexes such as $U_m(H_2PO_4)_n(HPO_4)_n'(PO_4)_n''$. The complexes found in the solutions can be designated by the formula $U_m(H_pPO_4)_n$ where $m = 1, 2, 3, \dots$, $n = 1, 2, 3, \dots$ and p is continuously variable between 0 and 2. The total concentration is denoted here by $\Sigma[U_m(H_pPO_4)_n]$.

The corresponding complexes between aluminium and phosphate are conceivable and may be collected together in the general formula $Al_q(H_iPO_4)_r$. The total concentration of these complexes is written $\Sigma[Al_q(H_iPO_4)_r]$.

Conceivable complexes between uranium, aluminium and phosphate may be collected together in the general formula:

which is shortened below to $U-Al-PO_4$. The total concentration of these complexes is written $\Sigma[U-Al-PO_4]$. The complexity constants are obtained from the formula:

$$[U-Al-PO_4] / [U^{4+}]^x \cdot [Al^{3+}]^y \cdot [H_zPO_4^{-3+z}]^w = K_{x,y,w} \quad (1)$$

According to Fig. 6, uranium(IV) precipitates from a chloride solution as phosphate with a composition approximately corresponding to the formula $U(HPO_4)_2$. Hence we obtain the following equation for the solubility product L :

$$[U^{4+}] \cdot [HPO_4^{2-}]^2 = L \quad (2)$$

If the complexity constants for the aluminium phosphate complexes are denoted by $k_{q,r}$, the following equation is obtained:

$$[Al_q(H_iPO_4)_r] = k_{q,r} \cdot [Al^{3+}]^q \cdot [H_iPO_4^{-3+i}]^r \quad (3)$$

If the total concentrations of uranium, aluminium and phosphoric acid are written C_U , C_{Al} and C_{PO_4} , respectively, the following formulas are obtained:

$$C_U = [U^{4+}] + \Sigma m[U_m(H_2PO_4)_n] + \Sigma x[U-Al-PO_4] \quad (4)$$

$$C_{Al} = [Al^{3+}] + \Sigma q[Al_q(H_2PO_4)_r] + \Sigma y[U-Al-PO_4] \quad (5)$$

$$C_{PO_4} = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] + \Sigma r[Al_q(H_2PO_4)_r] + \Sigma n[U_m(H_2PO_4)_n] + \Sigma w[U-Al-PO_4] \quad (6)$$

In uranium(IV) chloride solutions not containing aluminium, the uranium phosphate precipitates almost to 100 %. In sulfate solutions not containing aluminium, a complete yield is also obtained within a favourable pH range. According to Betts and Leigh², uranium(IV) forms very strong complexes with sulfate. Consequently the solubility product must be very small and the concentration of soluble uranium phosphate complexes must be low. In eqn. (4), $[U^{4+}]$ and $\Sigma m[U_m(H_2PO_4)_n]$ may be disregarded in comparison with the double complexes. Since it cannot be determined from the empirically found precipitation boundary whether one or several uranium ions are found in each double complex, it may be assumed that only one uranium ion is present in each complex, consequently $x = 1$. The low uranium concentrations in the solutions are in evidence for this assumption. It may further be assumed that one of the double complexes present is so dominant that the remainder can be overlooked. On applying these simplifications we obtain:

$$C_U \approx [U-Al-PO_4] \quad (7)$$

Similarly, one of the aluminium phosphate complexes present in the solutions may be assumed so dominant that the remainder can be neglected. This complex is assumed as simple as possible, i. e. $AlHPO_4^+$. Eqn. (3) is then:

$$\Sigma [Al_q(H_2PO_4)_r] \approx [AlHPO_4^+] = k_{1,1} \cdot [Al^{3+}] \cdot [HPO_4^{2-}] \quad (8)$$

In eqn. (6), $[HPO_4^{2-}]$ and $[PO_4^{3-}]$ may be neglected since the pH range is below 2.5. The uranium phosphate complexes may be neglected for the same reason as in eqn. (3). On applying these simplifications the following equations are obtained:

- 1) For soluble complexes of the type $UAl_y(PO_4)_w^{+4+3y-3w}$:

$$C_{Al} = \left(\frac{C_U}{K_{1,y,w} \cdot L} \right)^{\frac{1}{y}} \cdot [HPO_4^{2-}]^{\frac{2-w}{y}} \cdot (1 + k_{1,1} \cdot [HPO_4^{2-}]) \cdot \left(\frac{k_s'''}{[H^+]} \right)^{\frac{y}{w}} + yC_U \quad (9)$$

- 2) For soluble complexes of the type $UAl_y(HPO_4)_w^{+4+3y-2w}$:

$$C_{Al} = \left(\frac{C_U}{K_{1,y,w} \cdot L} \right)^{\frac{1}{y}} \cdot [HPO_4^{2-}]^{\frac{2-w}{y}} \cdot (1 + k_{1,1} \cdot [HPO_4^{2-}]) + yC_U \quad (10)$$

- 3) For soluble complexes of the type $UAl_y(H_2PO_4)_w^{+4+3y-w}$:

$$C_{Al} = \left(\frac{C_U}{K_{1,y,w} \cdot L} \right)^{\frac{1}{y}} \cdot [HPO_4^{2-}]^{\frac{2-w}{y}} \cdot (1 + k_{1,1} \cdot [HPO_4^{2-}]) \cdot \left(\frac{k_s''}{[H^+]} \right)^{\frac{w}{y}} + yC_U \quad (11)$$

$[HPO_4^{2-}]$ is obtained from the equation:

$$k_{1,1} \cdot \left(\frac{\{H^+\}^2}{k_s' \cdot k_s''} + \frac{\{H^+\}}{k_s''} \right) \cdot [HPO_4^{2-}]^2 + \left(\frac{\{H^+\}^2}{k_s' \cdot k_s''} + \frac{\{H^+\}}{k_s''} + k_{1,1} \cdot (C_{Al} - C_{PO_4} + wC_U - yC_U) \right) \cdot [HPO_4^{2-}] = C_{PO_4} - wC_U \quad (12)$$

where $k_s' = \{H^+\} \cdot [H_2PO_4^-] / [H_3PO_4]$, $k_s'' = \{H^+\} \cdot [HPO_4^{2-}] / [H_2PO_4^-]$,
 $k_s''' = \{H^+\} \cdot [PO_4^{3-}] / [HPO_4^{2-}]$ and $-\log\{H^+\} = \text{pH}$.

From eqns. (9)–(12), $C_{Al} = f([H^+])$ is obtained by inserting various values for y and w at constant concentrations of uranium and phosphate. In Figs. 13–15, precipitation boundaries with 0% yields are shown, calculated with $C_U = 0.0017$ mole/l and $C_{PO_4} = 0.042$ mole/l. In eqns. (9)–(12), the complexity constant for aluminium phosphate is included. Bjerrum and Dahm⁸ have examined complex formations in acid solutions with low concentrations of aluminium, an excess of phosphate and low salt concentrations. From the complexity constants obtained, $k_{1,1}$ is calculated to be 7.2×10^7 l/mole. A determination in solutions containing 2.8 M sodium chloride as ionic medium, made for the calculations mentioned below, gave $k_{1,1} = 3.3 \times 10^7$ l/mole. In the precipitation experiments according to Fig. 1, the salt concentrations in the solutions varied between the concentrations used in the two determinations of $k_{1,1}$ mentioned above. Thus the average value 5×10^7 l/mole is used here.

The dissociation constant of the orthophosphoric acid k_s' was taken to be 8×10^{-2} l/mole, k_s'' to be 6×10^{-8} l/mole and k_s''' to be 5×10^{-13} l/mole.

In eqn. (12), the factors wC_U and $(w-y) \cdot k_{1,1} \cdot C_U$ can be neglected. In this equation, C_{Al} is included as a correction factor. These values of C_{Al} at various pH values are taken from Fig. 1. Such a correction is not accurate in cases where the calculated precipitation boundary does not agree with the experimental one but this is of course of no importance here.

The factor $(C_U/K_{1,y,w} \cdot L)^{\frac{1}{y}} = a_{y,w}$ included in eqns. (9)–(11) is calculated from these equations at $C_{Al} = 0.31$ mole/l, $C_{PO_4} = 0.042$ mole/l and pH = 0.4 corresponding to point A in Figs. 13–15.

In Fig. 11, some precipitation boundaries for uranium(IV) orthophosphate, based on point A and under the assumption of a few simple soluble double complexes of the type $UAl_y(HPO_4)_w^{+4+3y-2w}$, are found. The figure shows that soluble complexes of this type give a boundary close to the experimental one

Fig. 11. A few calculated precipitation boundaries under assumption of soluble complexes of the type $UAl_y(HPO_4)_w^{+4+3y-2w}$.

I) $UAl(HPO_4)_4^-$; II) $UAlHPO_4^{5+}$; III) $UAl_2(HPO_4)_3^{4+}$; $UAl(HPO_4)_2^{3+}$; IV) $UAl_3(HPO_4)_2^{7+}$; V) By Fig. 1; VI) $UAl(HPO_4)_3^+$, $UAl_y(HPO_4)_{y+2}^{+y}$.

Fig. 12. A few precipitation boundaries calculated under the assumption of soluble complexes of the type $UAl_y(PO_4)_w^{+4+3y-3w}$.

I) $UAl_8(PO_4)_6^{4+}$; II) $UAl(PO_4)_3^{2-}$; III) $UAlPO_4^{4+}$; IV) $UAl_2PO_4^{7+}$; V) $UAl_2(PO_4)_2^{4+}$; VI) $UAl_3(PO_4)_3^{4+}$; VII) $UAl(PO_4)_2^+$.

Fig. 13. A few precipitation boundaries calculated under the assumption of soluble complexes of the type $\text{UAl}_y(\text{H}_2\text{PO}_4)_w^{+4+3y-w}$. I) $\text{UAl}(\text{H}_2\text{PO}_4)_2^{+2}$; II) $\text{UAl}(\text{H}_2\text{PO}_4)_3^{+1}$; III) $\text{UAl}(\text{H}_2\text{PO}_4)_4^{+0}$; IV) $\text{UAl}(\text{H}_2\text{PO}_4)_5^{-1}$.

Fig. 14. A few calculated boundaries for 90 % precipitate yield (dashed curves). The continuous line is the experimentally found boundary for a 0 % yield.

if $w \approx y + 2$, i. e. the following complex: $\text{UAl}_y(\text{HPO}_4)_{y+2}^{+y}$. If $w > y + 2$, the curve increases too rapidly with decreasing pH compared with the experimental one while, if $w < y + 2$, it increases too slowly.

If a different point than point A in Figs. 11—13 is chosen as basis for the calculations, only a parallel shift of the calculated precipitation boundary is obtained.

In Fig. 12, the precipitation boundaries for uranium phosphate have been calculated under the assumption of a few soluble complexes of the type $\text{UAl}_y(\text{PO}_4)_w^{+4+3y-3w}$. The figure shows, that complexes of this type give a precipitation boundary close to the experimental one for the following cases: a) when $y = 1$, $w = 1$, i. e. $\text{UAl}(\text{PO}_4)_2^{+2}$, b) when $y = w \geq 3$ and c) for higher values of y and w when $y \approx w$, i. e. the following complexes: $\text{UAl}_y(\text{PO}_4)_y^{+4}$.

According to eqn. (11), the following equation applies for soluble complexes of the type $\text{UAl}_y(\text{H}_2\text{PO}_4)_w^{+4+3y-w}$:

$$C_{\text{Al}} = \beta_{y,w} [\text{HPO}_4^{2-}]^2 \cdot (1 + k_{1,1} [\text{HPO}_4^{2-}]) \cdot ([\text{HPO}_4^{2-}] \cdot \{\text{H}^+\})^{-\frac{w}{y}} + yC_{\text{U}} \quad (13)$$

$$\text{where } \beta_{y,w} = (C_{\text{U}}/K_{1,y,w} \cdot L)^{\frac{w}{y}} = \text{a constant.}$$

In eqn. (13), the expression $[\text{HPO}_4^{2-}]^2 \cdot (1 + k_{1,1} [\text{HPO}_4^{2-}])$ increases rapidly with increasing pH. However, the expression $([\text{HPO}_4^{2-}] \cdot \{\text{H}^+\})^{-\frac{w}{y}}$ increases slowly with pH. In order that C_{Al} in eqn. (13) shall decrease with increasing pH, it is necessary that quotient w/y should be large. In Fig. 13, curve a shows the calculated precipitation boundary for $w/y = 2$, curve b for $w/y = 4$, curve c

for $w/y = 6$ and curve d for $w/y = 8$. It is seen that soluble complexes of the type $\text{UAl}_y(\text{H}_2\text{PO}_4)_w^{+4+3y-w}$ cannot give a precipitation boundary similar to the experimental one.

In Figs. 11–13, the precipitation boundaries are calculated so that precipitation just begins for the appropriate solution or *i. e.* so that the yield is 0 %. In the following, the boundary is calculated on the basis of a yield of 90 %.

In Fig. 1, the yield is more than 90 % for the precipitation region and decreases rapidly near the boundary to zero. When calculating the HPO_4^{2-} concentration at various pH, C_{Al} is included only as a term of correction. Hence, during the calculation of the precipitation boundary, the same HPO_4^{2-} concentrations can be used in eqns. (9)–(11) independent of the yield.

If the total uranium(IV) concentration in the solutions at a certain precipitate yield is denoted by C'_U , the corresponding α -value by $\alpha'_{y,w}$ and the corresponding values at 0 % yield by C_U^{tot} and α_U^{tot} , respectively, the following equation is obtained from the relation $\alpha_{y,w} = (C_U/K_{1,y,w} \cdot L)^{1/y}$:

$$\alpha'_{y,w} = \left(\frac{C'_U}{C_U^{\text{tot}}} \right)^{1/y} \cdot \alpha_{y,w}^{\text{tot}} \quad (14)$$

The precipitation boundary at a certain yield is obtained from eqn. (10):

$$C'_{\text{Al}} = \alpha'_{y,w} [\text{HPO}_4^{2-}]^{2-w/y} (1 + k_{1,1} \cdot [\text{HPO}_4^{2-}]) + yC'_U \quad (15)$$

If the aluminium concentration in the solutions at 0 % yield is denoted by $C_{\text{Al}}^{\text{tot}}$, one obtains:

$$C_{\text{Al}}^{\text{tot}} = \alpha_{y,w}^{\text{tot}} \cdot [\text{HPO}_4^{2-}]^{2-w/y} \cdot (1 + k_{1,1} \cdot [\text{HPO}_4^{2-}]) + yC_U^{\text{tot}} \quad (16)$$

From eqns. (14), (15) and (16) one obtains the expression:

$$C'_{\text{Al}} = (C_{\text{Al}}^{\text{tot}} - y \cdot C_U^{\text{tot}}) \cdot \left(\frac{C'_U}{C_U^{\text{tot}}} \right)^{1/y} + yC'_U \quad (17)$$

If eqn. (9) or (11) is used instead of eqn. (10), it is seen that eqn. (17) is true for the three complex types $\text{UAl}_y(\text{PO}_4)_w^{+4+3y-3w}$, $\text{UAl}_y(\text{HPO}_4)_w^{+4+3y-2w}$ and $\text{UAl}_y(\text{H}_2\text{PO}_4)_w^{+4+3y-w}$.

At a 90 % precipitation yield the following values apply at the concentrations used in the experiments: $C_U^{\text{tot}} = 0.0017$ mole/l and $C'_U = 0.00017$ mole/l. $C_{\text{Al}}^{\text{tot}}$ at various pH values is obtained from Fig. 1.

Eqn. (17) shows that the greater the number of aluminium ions in the double complexes the closer the boundary for 90 % precipitate yield approaches the boundary for 0 % yield. In Fig. 14 the boundary for a 90 % yield is calculated for complexes with 1, 2, 4 and 8 aluminium ions. Complexes with 6–8 aluminium or more correspond best with the experimentally found precipitate yields.

According to Figs. 11 and 12, both $\text{UAl}_y(\text{HPO}_4)_w^{+4+3y-2w}$ and $\text{UAl}_y(\text{PO}_4)_w^{+4+3y-3w}$ can be used to explain the precipitation boundary in chloride solutions. The main part of the double complexes is probably of the type $\text{UAl}_y(\text{HPO}_4)_w^{+4+3y-2w}$ since the actual pH range is 0.1–2.5. The precipitate yields obtained indicate indirectly a maximum number of phosphate around each

Fig. 15. Calculated precipitation boundaries under assumption of soluble complexes of the type $\text{UAl}_y(\text{HPO}_4)_8^{+3y-12}$. I) $\text{UAl}_{12}(\text{HPO}_4)_8^{24+}$; II) $\text{UAl}_{10}(\text{HPO}_4)_8^{18+}$; III) $\text{UAl}_8(\text{HPO}_4)_8^{12+}$; IV) $\text{UAl}_6(\text{HPO}_4)_8^{6+}$; V) $\text{UAl}_4(\text{HPO}_4)_8$.

uranium atom. The distance U—O in uranium dioxide⁵ is 2.34 Å and distance P—O in phosphate⁶ 1.56—1.69 Å. This shows that around each uranium(IV), there is sufficient space for a maximum of 8 phosphate groups. This would correspond to complexes of the type $\text{UAl}_y(\text{HPO}_4)_8^{+3y-12}$. Fig. 15 shows a few precipitation boundaries calculated using complexes of this type. The figure shows that the formulas $\text{UAl}_6(\text{HPO}_4)_8^{6+}$ and $\text{UAl}_8(\text{HPO}_4)_8^{12+}$ give the best fit with the experimentally found precipitation boundary.

The distances between the aluminium ions and the phosphate groups in the above mentioned complexes are too great for a stable complex to be formed. According to tests with models on the other hand, a stable complex with the formula $\text{UAl}_8(\text{HPO}_4)_8(\text{H}_2\text{O})_{12}^{12+}$ is possible, where each aluminium is surrounded octahedrally by 2 water units and 4 oxygens from 2 phosphate groups.

In a solution with 0.0025 M uranium(IV)sulfate, 0.8 M sodium sulfate and sulfuric acid to pH 0.4, no precipitate was obtained with a concentration of 0.0105 M phosphoric acid, with 0.046 M 86 % yield and with 0.084 M phosphoric acid 96 %. If the complexity constant for $[\text{USO}_4^{2+}] / [\text{U}^{4+}] \cdot [\text{SO}_4^{2-}] = 1740$ l/mole (Betts and Leigh²) and the dissociation constant for $\text{HSO}_4^- = 10^{-2}$ l/mole and the dissociation constant for $\text{H}_3\text{PO}_4 = 7.5 \times 10^{-3}$ l/mole and that for $\text{H}_2\text{PO}_4^- = 6.2 \times 10^{-8}$, then the solubility product may be estimated from the above mentioned precipitation yields:

$$L = [\text{U}^{4+}] \cdot [\text{HPO}_4^{2-}]^2 \approx 10^{-25} \text{ (mole/l)}^3$$

If the complex $\text{UAl}_8(\text{HPO}_4)_8^{12+}$ represents all the forms of double complexes that may give an explanation of the precipitation boundary obtained in chloride solutions, then the complexity constant for this complex may be estimated to be:

$$K_{1,8,8} = \frac{[\text{UAl}_8(\text{HPO}_4)_8^{12+}]}{[\text{U}^{4+}] \cdot [\text{Al}^{3+}]^8 \cdot [\text{HPO}_4^{2-}]^8} \approx 10^{82} \text{ (l/mole)}^{16}$$

CONCLUSIONS

In acid *chloride* solutions containing 0.0017 M uranium(IV) chloride and 0.042 M orthophosphoric acid but different concentrations of aluminium chloride and different pH values, it was found that uranium phosphate precipitates only within an area marked with + in Fig. 1. Within the greater part of this area, the precipitate yield is over 90 %. The precipitates are amorphous with a somewhat variable composition, corresponding approximately to the formula $\text{U}(\text{HPO}_4)_2$. According to certain extinction measurements, the uranium phosphate is prevented from precipitating by some soluble uranium(IV) phosphate complexes. A plausible explanation of the precipitation boundary in Fig. 1 is that these complexes are double complexes of uranium, aluminium and phosphate. Calculations show that the following types of complexes give a precipitation boundary corresponding well with the experimental one, considering the conditions under which this boundary was obtained:

- a) $\text{UAl}_y(\text{HPO}_4)_w^{+4+3y-2w}$ where $\frac{2-w}{y} = -0.9 \pm 0.3$
 b) $\text{UAl}_y(\text{PO}_4)_w^{+4+3y-3w}$ where $w/y = -1 \pm 0.3$

Complexes of the type $\text{UAl}_y(\text{H}_2\text{PO}_4)_w^{+4+3y-w}$ cannot give a precipitation boundary similar to the experimental one.

Since the actual pH range is 0.1—2.5 the double complexes are probably mainly of the type $\text{UAl}_y(\text{HPO}_4)_w^{+4+3y-2w}$. The more aluminium ions there are in the complex, the smaller is that region in the neighbourhood of the precipitation boundary where the precipitation yield falls from over 90 % to zero. Thus, in order to correspond to the precipitation yields obtained, the number of aluminium ions in the complex and hence also the number of phosphate groups must be considered to be as large as possible. Since 8 phosphate groups is the maximum number which can be accommodated around each uranium(IV) ion, this indicates that complexes of the type $\text{UAl}_y(\text{HPO}_4)_8^{+3y-12}$. Of these complexes, $\text{UAl}_6(\text{HPO}_4)_8^{6+}$ and $\text{UAl}_8(\text{HPO}_4)_8^{12+}$ fit in best with the experimentally determined precipitation boundary in acid chloride solutions.

From *sulfate* solutions containing 0.0017 M uranium(IV) sulfate and 0.042 M orthophosphoric acid but different concentrations of aluminium sulfate and different pH values, it was found that there exists a boundary (*cf.* Fig. 2) for the precipitation of uranium phosphate which has a pronounced peak at pH 0.7—1.2. Corresponding precipitation boundaries were found on adding sodium, magnesium or iron(II) sulfate as ionic medium.

A plausible explanation of the precipitation boundary in Figs. 2—5 is that, at pH values to the *right* of the peak, the uranium is prevented from precipitating because of the same soluble double complexes between uranium(IV), aluminium and phosphate as those in the chloride solutions. The shape of the curve, the precipitate yields and the extinction measurements are all in favour of this. A calculation on this part of the boundary may however be more complicated than for chloride solutions since, besides allowing for the presence of uranium and aluminium sulfate complexes, it must also be considered that the uranium does not precipitate as pure phosphate but as phosphate-sulfate: $\text{U}(\text{HPO}_4, \text{SO}_4)_2$.

At pH values to the *left* of the peak, the uranium is prevented from precipitating by uranium(IV) complexes with sulfate. With decreasing pH, the HPO_4^{2-} content decreases faster than the SO_4^{2-} content, for which reason the possibility of reaching the solubility product of the uranium(IV) phosphate decreases quicker than that for forming soluble uranium sulfate complexes. From Figs. 2—5, it is clear that, even in this part of the pH range other factors must play a part, *inter alia* the double complexes mentioned above.

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