475. *The Solubility of Plutonium Trifluoride, Plutonium Tetrafluoride, and Plutonium*(IV) *Oxalate in Nitric Acid Mixtures.*

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The solubility of plutonium trifluoride has been measured in mixtures of nitric and hydrofluoric acids of various molarities and that of the tetrafluoride in nitric acid. The effect of fluoride ion on the solubility is discussed and an attempt made to estimate the solubility product of each compound. This is difficult because information about the activity coefficients of the species concerned is lacking. However, on the basis of the available data the solubility products appear to be trifluoride $2{\cdot}5 \times 10^{-16}$ and tetrafluoride 6×10^{-20}.

The solubility of plutonium(IV) oxalate has been determined in mixtures of nitric acid up to 3·52M and oxalic acid up to 0·6M. The minimum solubility occurs in 1M-nitric acid–0·01M-oxalic acid, but there is evidence that after 2—3 weeks' equilibration in this mixture an abnormal effect leads to anomalous solubilities.

SOLUTIONS of plutonium(IV) nitrate in nitric acid are commonly used as stock solutions of plutonium. For analytical or preparative purposes it is often convenient to precipitate from such a solution either the tri- or the tetra-fluoride or plutonium(IV) oxalate. In order to carry out such precipitations as completely as possible, it is essential to know the solubility of the required species at different concentrations of nitric acid and of hydrofluoric and oxalic acids, respectively. Such solubilities have been measured, and a number of points of interest have arisen in the course of this work.

Plutonium Trifluoride.—The effect of hydrofluoric acid upon the solubility of plutonium trifluoride in nitric acid was determined in two ways: (i) By adding hydrofluoric acid to solutions of the trifluoride in nitric acid of known molarities, determining the total hydrogen-ion concentration, agitating the precipitate and supernatant liquid, determining the concentration of plutonium in the latter, and calculating the concentration of fluoride ion. (ii) By agitating excess of solid trifluoride with mixtures of nitric and hydrofluoric acids of predetermined molarities, and determining the concentration of plutonium in the supernatant liquid.

The solubility of *plutonium trifluoride* in nitric acid is so drastically lowered by the addition of fluoride ion, and the amount of trifluoride precipitated is so large, that the difference between the two titration values does not represent the true molarity of hydrogen fluoride after precipitation. The true molarity was calculated to give the values shown in Table 1*a*.

In principle the concentration of nitric acid must be increased by an equivalent amount, but even where the correction to the concentration of hydrofluoric acid is appreciable the equivalent correction to the concentration of nitric acid is not significant.

From the solubilities of plutonium trifluoride in nitric acid free from hydrofluoric acid the solubility product of the trifluoride, $[\mathrm{Pu}][\mathrm{F}]^3 = C_{\mathrm{PuF}_3}$, can be obtained. The concentration of fluoride ion in the presence of excess of nitric acid must itself be calculated because the concentration of free fluoride ion in the presence of hydrogen ion is so small. Sidgwick[1] quotes $K_1 = [\mathrm{H}][\mathrm{F}]/[\mathrm{HF}] = 7{\cdot}2 \times 10^{-4}$ (which involves, for example, only 1% of free fluoride ion in concentrated hydrofluoric acid), and records the second equilibrium constant $K_2 = [\mathrm{F_2H}]/[\mathrm{F}][\mathrm{HF}] = 5{\cdot}5$.

In the evaluation of K_1, the concentration of hydrogen ion must be known. The best values for the dissociation of nitric acid appear[2] to be 98% in M and 92% in 2M solution, and [H] has been calculated on this basis.

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[1] Sidgwick, " Chemical Elements and their Compounds," Oxford, 1959, p. 1105 *et seq.*

[2] McKay, private communication.

TABLE 1. *Solubility of plutonium trifluoride in nitric acid–hydrofluoric acid* (*g./l. of* Pu *at* 25°). [(*a*) Corrected concentration of hydrofluoric acid (M); (*b*) solubility of plutonium(III) ion (g./l.).]

(*a*) *First method.*

HNO_3 (M)									
0·05	(*a*)	0·00	0·054	0·96	1·65	2·5	3·9	6·07	7·45
	(*b*)	0·157	0·080	0·067	0·049	0·038	0·039	0·041	0·044
0·16	(*a*)	0·00	0·52	1·00	1·68	3·34	4·94	6·84	7·94
	(*b*)	0·202	0·137	0·082	0·064	0·057	0·046	0·037	0·024
0·30	(*a*)	0·00	0·59	1·33	2·09				
	(*b*)	0·955	0·068	0·049	0·050				
0·61	(*a*)	0·00	0·57	1·074	2·01	3·07			
	(*b*)	1·710	0·233	0·074	0·058	0·070			
1·20	(*a*)	0·00	0·57	1·17	1·73	2·37	3·97	6·87	
	(*b*)	2·691	0·319	0·102	0·088	0·065	0·053	0·048	
2·40	(*a*)	0·00	0·35	0·65		2·31			
	(*b*)	4·589	0·141	0·097		0·064			

(*b*) *Second method*

HNO_3 (M)							
1·13	(*a*)	0·3	0·8	1·25	1·65		
	(*b*)	0·084	0·047	0·040	0·014(?)		
2·25	(*a*)	0·03	0·7	1·15	1·55	3·00	4·35
	(*b*)	0·073	0·053	0·038	0·019	0·055	0·059

The solubility product of plutonium trifluoride is then given by the expression

$$C_{PuF_3} = \left[\frac{K_1\,[HF]}{f\,[HNO_3]}\right]^3 [Pu]$$

where $K_1 = 7{\cdot}2 \times 10^{-4}$ and f is a factor based on the dissociation of nitric acid.

TABLE 2. *Solubility product of plutonium trifluoride.*

$[HNO_3]$ (M) ...	0·054	0·16	0·30	0·61	1·20	2·40
C_{PuF_3}	$1{\cdot}18 \times 10^{-17}$	$1{\cdot}15 \times 10^{-18}$	$1{\cdot}08 \times 10^{-16}$	$1{\cdot}45 \times 10^{-16}$	$5{\cdot}95 \times 10^{-16}$	$4{\cdot}45 \times 10^{-16}$

At first sight this might be taken to show a slight upward trend in solubility product with increasing concentration of nitric acid. However, the acid concentration is derived by microtitration, and since calculation of the solubility product involves a third power of the concentration of hydrogen ion too much reliance should not be placed on the values at the lowest acidity. On the other hand, the calculation omits any consideration of the activity coefficients of the species involved, and the correction which they would introduce might increase the values of C_{PuF_3} much more (possibly by a power of ten) at lower acidities than at higher. Information for the precise application of this correction is not available but the evidence suggests that it would make the values of C_{PuF_3} more constant. The assumption has also been tacitly made that the concentration of free fluoride ion is negligible by comparison with that of hydrofluoric acid, and thus that the latter can be set equal to the concentration of dissolved fluoride. This cannot be true at acidities below about 0·1M, particularly as the total fluoride molarity is also low at this acidity. The best mean value of the solubility product can be taken as $C_{PuF_3} = 2{\cdot}5 \times 10^{-16}$.

The abrupt flattening of the solubility curves with increasing concentration of hydrofluoric acid does not necessarily indicate complexing of plutonium(III), being rather the behaviour to be expected from the small dissociation of the hydrofluoric acid itself. At concentrations of hydrofluoric acid above 2M, the addition of more acid does not appreciably affect the concentration of fluoride ion. The agreement between the results in Table 1*a* and Table 1*b* is as good as can be expected from the short time allowed for equilibration. The solubility of plutonium trifluoride in hydrofluoric acid–nitric acid mixtures, where the hydrofluoric acid molarity is greater than 2M, can be confidently stated to lie between 0·035 and 0·065 g. of Pu/l.

Plutonium Tetrafluoride.—The solubility of plutonium tetrafluoride was measured in nitric acid solutions only.

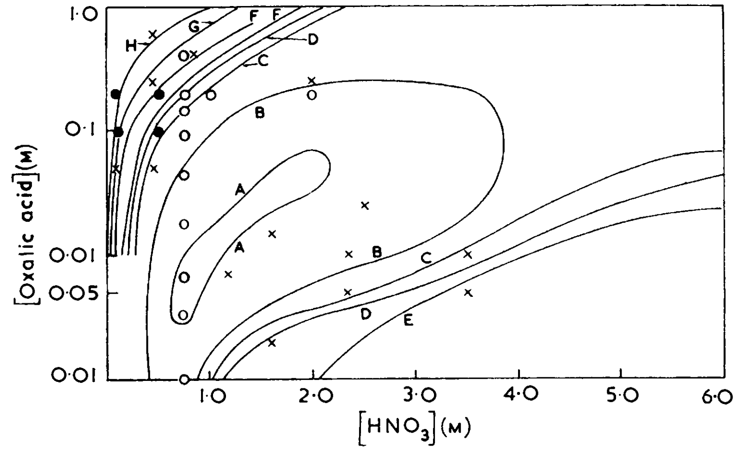
TABLE 3. *Solubility of plutonium tetrafluoride (g. of* Pu/*l.).*

[HNO_3]	Concn. Pu	Solubility product	[HNO_3]	Concn. Pu	Solubility product
0·00	0·060	($2·55 \times 10^{-16}$)	0·74	2·90	$5·32 \times 10^{-20}$
0·015	0·088	$0·82 \times 10^{-20}$	1·00	4·19	$16·0 \times 10^{-20}$
0·15	0·460	$0·32 \times 10^{-20}$	1·59	5·8	$8·0 \times 10^{-20}$
0·30	0·820	$0·36 \times 10^{-20}$	3·19	10·4	$23·0 \times 10^{-20}$
0·59	2·24	$7·31 \times 10^{-20}$			

The solubility product was calculated in a similar manner to that already described for the trifluoride. The only other published value for the solubility is *ca.* 0·1 g./l. in water (two values in hydrofluoric–nitric acids mixtures are also reported [3]).

There is good evidence of complex-formation in plutonium(IV) solutions in nitric acid, but there is little evidence of this in the solubility product of plutonium(IV) fluoride. This shows a change comparable with that of C_{PuF_3}, which was attributed to the absence of activity coefficients and the formal assumption that [F′] = [HF], which does not hold at the lowest acidities. On the evidence, $6·0 \times 10^{-20}$ is probably the best value for the solubility product of the tetrafluoride.

Solubility of plutonium(IV) *oxalate in nitric acid–oxalic acid mixtures at* 26·5°. *Isosols join points of equal solubility (expressed in mg. of plutonium per litre).*



A, 10 mg./l. B, 20 mg./l. C, 40 mg./l. D, 60 mg./l. E, 80 mg./l. F, 100 mg./l. G, 130 mg./l. H, 200 mg./l.

×, This paper. ●, O'Conner (ref. 5). ○, Reas (ref. 4).

Plutonium(IV) *Oxalate.*—There is good agreement between our results, American data,[4,5] and those of Kemp and Welch.[6] The last measured the solubility of plutonium(IV) oxalate by precipitation with oxalic acid and determination of the plutonium content of the supernatant liquor. They found that the concentration of plutonium in this liquor decreased during the first 100—500 hr., and then increased. Sometimes the rate of increase was rather rapid. They attributed the increase in solubility to some decomposition of the oxalate by the nitric acid. However, their figures for the solubilities near the minimum (*i.e.* after 100—500 hr.) agree well with those now reported (14—21 days' equilibration) for comparable concentrations of acid. We found a similar solubility minimum on only three occasions, but unfortunately the solutions concerned were discarded after 21 days and before Kemp and Welch's results were available to us.

It may be that oxidation progresses at a finite rate throughout equilibration, but since

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[3] Meyer and Zoolner, CK. 1763.
[4] Reas, " The Transuranium Elements," NNES, Vol. XIVb, paper 4.9, p. 423.
[5] O'Connor, CN. 1702.
[6] Kemp and Welch, U.K.A.E.A., C.1, report 69.

there is such good agreement between our results and the findings of Reas, of O'Connor, and of Kemp and Welch it seems unlikely that the acid concentrations were appreciably changed from their nominal values by such an oxidation during 3 weeks. If oxidation is the explanation of the occasional anomalies which we found, there would appear to be an induction period of at least 2—3 weeks. It seems reasonable to conclude that the solubility values in the Figure and Table 4 are reliable over the range of concentrations investigated, where the precipitation is completed in less than 10—14 days.

EXPERIMENTAL

Plutonium Trifluoride.—Method (i). Plutonium trifluoride was prepared by passing sulphur dioxide through a plutonium(IV) nitrate solution (8 g. of Pu/l.) for 15 min. and then adding hydrofluoric acid in slight excess to the plutonium(III) nitrate solution thus produced. The solution was centrifuged and the precipitate well washed with distilled water to remove excess of fluoride ion.

Various concentrations were prepared of nitric acid containing 10 g./l. of hydroxylamine to prevent the oxidation of plutonium(III) by atmospheric oxygen. The acid concentration was determined by titration with standard sodium carbonate.

To each solution (in lusteroid tubes) an excess of solid plutonium trifluoride was added, and the mixtures were agitated in a thermostat at 25° for 15—18 hr. The tubes were then centrifuged, the liquid was removed, and the concentration of plutonium determined by counting the alpha activity of an aliquot portion in a Simpson chamber, the efficiency of which had been checked with a standard source counted in a Ward chamber of known geometry. The maximum counting error was probably $\pm 1\%$.

To the supernatant liquid from each determination was added one drop of 40% aqueous hydrofluoric acid, which caused further precipitation of fluoride; the total acidity of each solution was determined by titration, a calibrated Rehburg microburette being used. The solution and precipitate were then agitated for 15—18 hr. at 25° and the plutonium concentration in the supernatant liquid determined as before, care being taken that (*a*) there was always an excess of solid trifluoride during equilibration, and (*b*) the solid was violet and the solution blue. When, as in a few determinations, the excess of solid or the solution appeared greenish, the results were discarded since oxidation to plutonium(IV) had take place.

The procedure was repeated in each case, after more hydrofluoric acid solution had been added.

Method (ii). Two solutions (1·15M and 2·25M) of nitric acid each containing 10 g./l. of hydroxylamine hydrochloride were prepared and standardised. To portions of each, different amounts of 40% aqueous hydrofluoric acid were added, and the total acidity determined by titration. To each solution was added an excess of solid plutonium trifluoride, and the mixtures were agitated at 25° for 15—18 hr. They were then centrifuged, and the concentrations of plutonium in the supernatant liquid determined.

Plutonium Tetrafluoride.—Purest available plutonium(IV) nitrate dissolved in 3M-nitric acid was precipitated with a 40% aqueous solution of hydrofluoric acid added dropwise. The supernatant liquid was removed after centrifugation, and the precipitate was washed repeatedly to remove all traces of hydrofluoric acid. Nitric acid solutions were accurately standardised against sodium carbonate solutions. Portions of the washed plutonium tetrafluoride, together with a few ml. of the standardised nitric acid, were placed in stoppered tubes. A rotary stirrer holding such tubes was designed, and the whole immersed in a thermostat bath at 26·8°. The solubility at each molarity of nitric acid was determined in duplicate, and the concentration of plutonium was found by withdrawing an aliquot portion, diluting it accurately 100—1000 fold as necessary, and preparing from an aliquot portion a source which was counted in a Simpson chamber whose geometry was determined in each case by means of a source accurately standardised in a Ward chamber. Equilibrium was assumed to be attained when two samples withdrawn at intervals of 48 hr. had the same concentration to within 1%, and when the concentration in the two duplicate samples also agreed within 1%.

Plutonium(IV) *Oxalate.*—This was precipitated by adding a small excess of oxalic acid crystals to plutonium(IV) nitrate in 6M-nitric acid. The precipitate was well washed to remove nitric and oxalic acids.

Portions of this oxalate were continuously agitated with nitric acid–oxalic acid of known strengths in a thermostat at 27°. Equilibrium was achieved after agitation for 2—3 weeks. The solubility of the plutonium was then determined by pipetting portions of the supernatant liquid on to counting trays and measuring the alpha activity in a proportional counter. Each operation was carried out in duplicate and the values were accepted only when four determinations agreed within a few units per cent; these are shown in Table 4.

TABLE 4.

$[HNO_3]$ (M)	$[(COOH)_2]$ (M)	Solubility (g. of Pu/l.)	$[HNO_3]$ (M)	$[(COOH)_2]$ (M)	Solubility (g. of Pu/l.)	$[HNO_3]$ (M)	$[(COOH)_2]$ (M)	Solubility (g. of Pu/l.)
0·0	0·0	45·9	0·78	0·40	144	2·00	0·0	128
,,	0·05	334	1·00	0·0	122	,,	0·05	9·7
,,	0·25	242	,,	0·05	13·3	,,	0·25	15·1
0·1	0·0	26·6	,,	0·25	36·9	2·34	0·01	15·3
,,	0·5	132	,,	0·60	133	,,	0·005	24·9
0·5	0·0	69·0	1·18	0·0071	16·3	2·52	0·025	16·7
,,	0·05	26·6	1·61	0·002	65·8	3·52	0·005	92·1
,,	0·25	97·1	,,	0·015	15	,,	0·01	45·8
,,	0·60	361				,,	0·05	18
						,,	0·1	18·2
						,,	0·5	21·4

Solubility contours have been plotted in order to express these results on a two-dimensional graph. The Figure shows the concentration of nitric acid as abscissa on a linear scale, and that of oxalic acid as ordinate on a logarithmic scale. Smooth curves have been drawn to join points representing concentrations at which the solubility of plutonium is equal.

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