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ATOMIC ENERGY

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THE SOLUBILITY OF Pu (IV) OXALATE IN NITRIC ACID/OXALIC ACID MIXTURES

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AN A. E. R. E. REPORT

BY

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MINISTRY OF SUPPLY
HARWELL, BERKS.
1953

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ABSTRACT

The solubility of Pu (IV) oxalate has been determined in nitric acid/oxalic acid mixtures (0 - 3.5 M HNO_3, 0 - 0.6 M $(COOH)_2$) and a region of minimum solubility found around 1.5 M HNO_3/0.025 M $(COOH)_2$.

CONTENTS

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1. EXPERIMENTAL

Plutonium (IV) oxalate was precipitated by the addition of a small excess of oxalic acid crystals to a solution of Pu (IV) nitrate in 6M nitric acid. The precipitate was well washed to remove nitric and oxalic acids.

Portions of the oxalate prepared in this way were continuously agitated with nitric acid/oxalic acid mixtures of known strengths in a thermostat at 300°K. Equilibrium was achieved after agitation for two to three weeks. The solubility of the plutonium was then determined by counting aliquots. Each operation was carried out in duplicate and the values were not accepted unless the consequent four determinations agreed to within a few units per cent.

2. RESULTS

The values obtained are shown in Table I.

TABLE I

$[HNO_3]$	$[(COOH)_2]$	Solubility (as Pu) mg/litre
0.0M	0.0M	45.9
"	0.05	334
"	0.25	242
0.1	0.0	26.6
"	0.5	132
0.5	0.0	69.0
"	0.05	26.6
"	0.25	97.1
"	0.60	361
0.78	0.40	144
1.00	0.0	122
"	0.05	13.3
"	0.25	36.9
"	0.60	133
1.18	0.0071	16.3
1.61	0.002	65.8
"	0.015	15
2.00	0.0	128
"	0.05	9.7
"	0.25	15.1
2.34	0.01	15.3
"	0.005	24.9
2.52	0.025	16.7
3.52	0.005	92.1
"	0.01	45.8
"	0.05	18
"	0.1	18.2
"	0.5	21.4

In order to express these results on a two dimensional graph, the expedient of plotting solubility contours has been adopted. In Figure 1 the concentration of nitric acid is plotted 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.

3. DISCUSSION

Good agreement has been found between the figures in Table I and the available American data (1,2) and also with some values determined by Kemp and Welch (3).

Kemp and Welch had difficulty in obtaining equilibrium in some cases; they found that after prolonged equilibration, the solubility values ceased to tend towards constancy, and abruptly become much higher. They tentatively attributed this to the oxidation of the oxalic acid by the nitric acid. The present authors found a similar effect on three occasions, but have not investigated it further. In each case, the whole set of observations at that concentration was discarded.

It may be that oxidation is progressing at a finite rate throughout the equilibration, but since such good agreement is found between four independent sets of results, in which presumably the equilibration times differed, it seems unlikely that the acid concentrations could have been appreciably altered from their nominal values by such an oxidation. If such a mechanism is the explanation of the occasional anomalies, it therefore seems likely that there is an induction period of 2-3 weeks at least before it is effective; unfortunately the solutions used by the present authors were discarded before their attention was drawn to this possibility, and they were, therefore, unable to investigate it further. It seems safe to say that the solubility values in Figure 1 and Table I are reliable over the range of concentrations investigated, where the operation for which the solubility conditions are important is completed in less than 10-14 days.

REFERENCES

1. Reas "The Transuranium Elements" (NNES, Vol. XIV b) paper 4.9 (p.423)

2. O'Connor, C.N. 1702

3. E.T. Kemp and G.A. Welch Private Communication

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+ Standard Circulation

NOTE ADDED IN PROOF

WSL/R-42, "Some studies in the precipitation of pure plutonium IV oxalate" by G.A. Welch et al has now become available. This summarises the results obtained in measuring the solubility of the oxalate by precipitating the plutonic ion with oxalic acid, and determining the plutonium content in the supernatant. They find that on standing, the concentration in the solubility tends to decrease for the first 100-500 hours, and then to increase, in some cases fairly rapidly. This they attribute to decomposition of the oxalate by the nitric acid. However, the values near the consequent minimum of solubility (100-500 hours standing - 4-20 days) are in good agreement with the values reported in this paper (14-21 days equilibration) in all cases where the acid concentrations are comparable.

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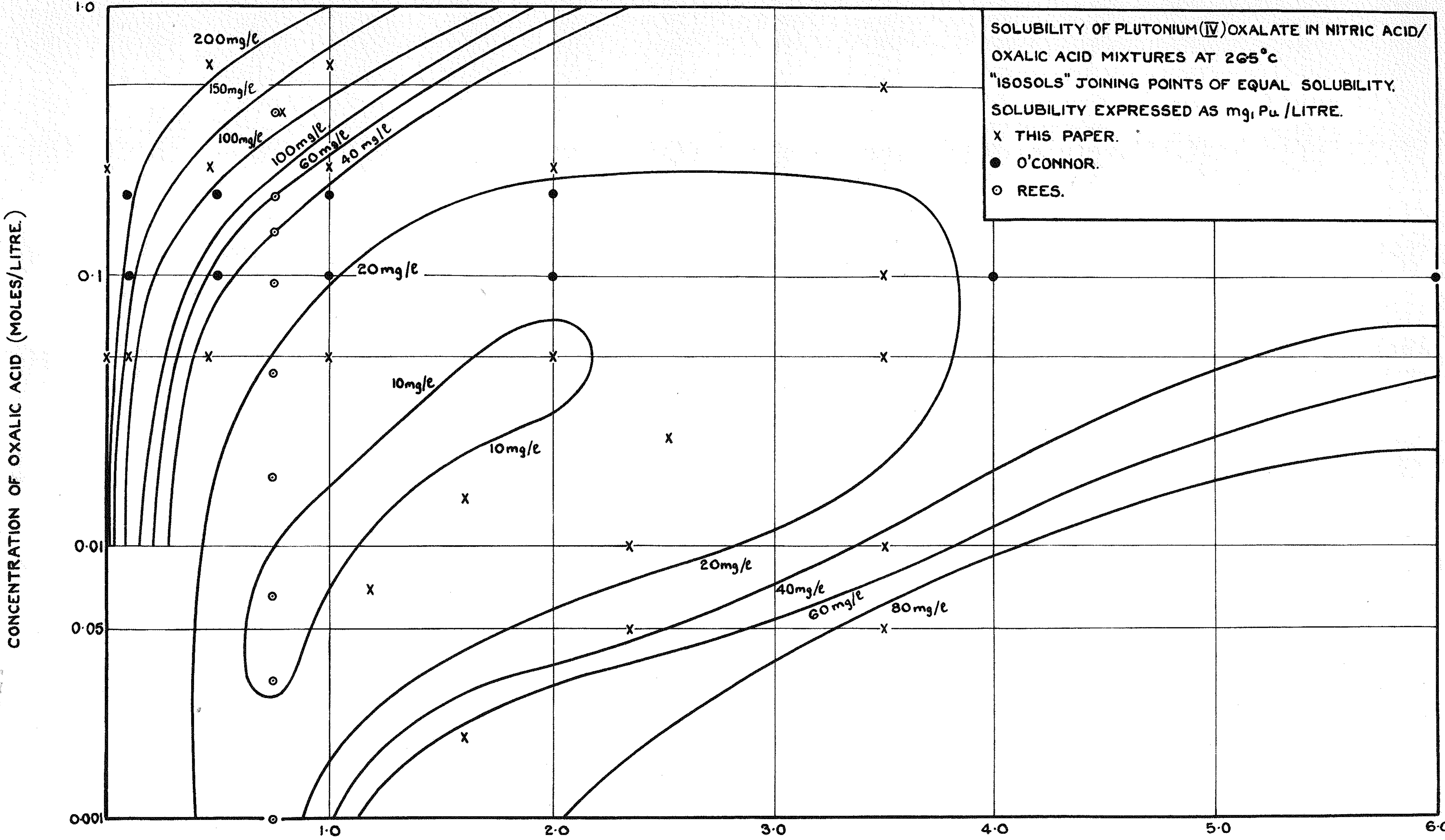

FIG. I. CONCENTRATION OF NITRIC ACID - MOLES/LITRE.