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CRITICALITY CALCULATIONS FOR PLUTONIUM
NITRATE SOLUTIONS

Deanne Dickinson

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CRITICALITY CALCULATIONS FOR PLUTONIUM NITRATE SOLUTIONS

Deanne Dickinson

Abstract. Number density formulas for plutonium nitrate solution are derived with the use of an empirical formula for the water content of such solutions. The number densities given by these formulas are compared with those for actual solutions, and the effect of differences in number densities on critical dimensions is examined. Finally, the critical radii for bare spheres of plutonium solution are calculated.

INTRODUCTION

In the study of plutonium solution systems, one frequently needs to calculate number densities for a solution of a certain concentration and normality. However, the concentration and normality together are not sufficient to determine the nuclide number densities for the solution. The additional information needed is either the density of water in the solution or the total density of the solution. Formulas for the total solution density as a function of concentration and normality have been reported by Bouly *et al.* (2) and Carter *et al.* (4).¹ A formula for the density of water in plutonium nitrate solution had been given by Richey (8), and was later corrected by Richey (9). In this report, the corrected formula for the water density (9) has been used to derive number densities for hydrogen and oxygen in plutonium nitrate solutions.

NUMBER DENSITIES FOR PLUTONIUM NITRATE SOLUTIONS

The solution is assumed to be composed of plutonium nitrate [as $\text{Pu}(\text{NO}_3)_4$], nitric acid (HNO_3), and water (H_2O). The amount of water in the solution is determined from the formula given by Richey (8) (9). Using a formula for water

density rather than one for total solution density [such as those given by Bouly and Carter (2, 4)] results in simpler number density formulas. Also, the formula by Bouly (2) applies only to a limited range of concentrations and normalities.

The following symbols are used:

- c = total plutonium concentration
in grams per cubic
centimeter (g/cm^3)
- (theta) θ = weight fraction of
plutonium 240 (^{240}Pu)
- H^+ = nitric acid normality ($N \text{HNO}_3$)
- [] = number density (nuclei or molecules
per barn-cm) of quantity
in brackets

From the corrected formula for water density (9), adjusted to a density of 0.9982 for pure water, one finds:

$$[\text{H}_2\text{O}] = (0.033444)(0.9982) \\ (1.0 - 0.3619c - 0.0331\text{H}^+)$$

From the definition of normality (N) one has:

$$[\text{HNO}_3] = 0.0006025 \text{H}^+$$

The number densities for the plutonium isotopes are:

$$[^{239}\text{Pu}] = \frac{(1 - \theta)c(0.6025)}{239.0522}$$

$$[^{240}\text{Pu}] = \frac{\theta c(0.6025)}{240.0540}$$

The remaining component of the solution is the nitrate ions associated with the plutonium. Since all the plutonium is assumed to be in the tetravalent state, one has:

$$[\text{NO}_3^-] = 4[^{239}\text{Pu}] + 4[^{240}\text{Pu}]$$

¹ Numerals in parentheses relate to references at end of text.

The hydrogen, nitrogen, and oxygen number densities are:

$$\begin{aligned}[\text{H}] &= 2[\text{H}_2\text{O}] + [\text{HNO}_3] \\[\text{N}] &= [\text{HNO}_3] + [\text{NO}_3^-] \\[\text{O}] &= [\text{H}_2\text{O}] + 3[\text{HNO}_3] + 3[\text{NO}_3^-]\end{aligned}$$

The number density formulas, expressed in terms of c , θ , and H^+ , are summarized in Table I.

COMPARISON OF MEASURED AND CALCULATED NUMBER DENSITIES

The hydrogen and oxygen number densities calculated from the formulas of Table I are compared with those for actual solutions in Table II. The water content of the actual solution was calculated from the formula:

$$[\text{H}_2\text{O}] = 0.033444 \times \left\{ d - \left(c + \frac{62.0049 [\text{NO}_3^-]}{0.6025} + 0.063013 \text{H}^+ \right) \right\}$$

Where, d = total solution density in grams per cubic centimeter.

The solutions in Table II have concentrations ranging from 412 grams per liter (g/l) down to 23.4 g/l and normalities from 3.5 to 1.3. The concentration range includes most solutions used in critical experiments or in plutonium processing, but the range of normalities is too low to cover all of the solutions found in plant processes.

For 20 of the 26 solutions compared in Table II, the magnitude of the error in the hydrogen number density is less than 1%. The large errors for 4 of the solutions described by Lloyd *et al.* (7) may be due to the use of the normality rather than the total nitrate to find the measured hydrogen number density. The normality computed from the measured total nitrate and other solution properties differs from the measured normality. Use of the calculated value of the normality reduced the differences between measured and calculated values of $[\text{H}]$ for all of the solutions given by Lloyd (7); in particular, the error in $[\text{H}]$ for the 412 g/l solution decreased from 8.2 to 5.4 percent.

All of the errors in $[\text{H}]$ in Table II of magnitude greater than 1 percent are positive, leading to a conservative error in the critical size. The largest negative error in $[\text{H}]$ is -0.9 percent, and the average error is +1.0 percent. The critical radius of a bare sphere was calculated for some of the solutions described in Table II in order to determine the effect on the critical size of the difference in hydrogen and oxygen number densities. These results are given in Table III. For these cases, the error in the critical radius is of opposite sign to the error in $[\text{H}]$, and the magnitude of the error on the critical radius is less than or equal to the magnitude of the error in the hydrogen number density.

CRITICAL RADII FOR SPHERES OF PLUTONIUM NITRATE SOLUTION

Richey (8) reported critical dimensions for spheres, cylinders, and slabs of plutonium nitrate solution. Because of the error in the formula for water content, the dimensions reported for systems with excess nitric acid were in error (the error is conservative, however). In this section, the formulas of Table I are used to calculate number densities for solutions with 0 or 6 percent ^{240}Pu , 0 or 2 normal nitric acid, and concentrations ranging from 10 to 1000 g/l of plutonium. The DTF-IV transport code (6) with Hansen-Roach sixteen-group cross sections (5) was used to calculate the critical radii for these solutions. The results are presented in Table IV.

A quantity of interest in nuclear safety is the minimum critical volume for a particular type of solution. From the data of Table IV, one observes that the critical radius as a function of concentration for solutions with 0 percent ^{240}Pu is nearly constant (a change of less than 0.3 cm) over the range 150 to 1000 g/l. The minimum critical radius, derived from a parabolic fit to the last three data points, occurs at about 562 g/l for solutions with 0 percent ^{240}Pu and 0-normal (N) acid, and at about 545 g/l for 0 percent ^{240}Pu and 2- N acid. For solutions containing 6 percent ^{240}Pu , the minimum critical radius occurs at a much lower concentration (193 g/l for 0- N acid and 187 g/l for 2- N acid), and the minimum is much more pronounced than for solutions with 0 percent ^{240}Pu .

TABLE I. Number Density Formulas for Plutonium Nitrate Solution.

Nuclide	Formula for Number Density in Nuclei per Barn-Centimeter
Hydrogen (H)	$0.06676704 - 0.02415980 c - 0.00160478 H^+$
Nitrogen (N)	$[0.01008148 (1 - \theta) + 0.01003940 \theta] c + 0.0006025 H^+$
Oxygen (O)	$0.03338352 + [0.03024444 (1 - \theta) + 0.03011820 \theta - 0.0120799] c + 0.00070386 H^+$
Plutonium 239 (^{239}Pu)	$0.00252037 (1 - \theta) c$
Plutonium 240 (^{240}Pu)	$0.00250985 \theta c$

Legend

c = plutonium concentration in grams per cubic centimeter
 θ = weight fraction of plutonium 240
 H^+ = nitric acid normality

TABLE II. Comparison of Calculated and Measured Number Densities for Plutonium Nitrate Solutions.

Density of Solution (grams per cubic centimeter)	Plutonium Concentration	Plutonium-240 Fraction	Nitric Acid Normality (H^+)	[H] Hydrogen Number Density			[O] Oxygen Number Density			Reference for Solution Data
				Measured	Calculated	Percent Difference	Measured	Calculated	Percent Difference	
1.649	0.355	0.0313	2.46	0.053034	0.054243	+2.3	0.040958	0.041562	+1.5	1
1.617	0.332		2.48	0.053956	0.054766	+1.5	0.040753	0.041158	+1.0	
1.566	0.300		2.42	0.055122	0.055636	+0.9	0.040278	0.040535	+0.6	
1.527	0.273		2.48	0.055976	0.056192	+0.4	0.039979	0.040087	+0.3	
1.489	0.252		2.47	0.056332	0.056715	+0.7	0.039507	0.039699	+0.5	
1.413	0.203		2.48	0.057890	0.057883	-0.01	0.038819	0.038816	-0.01	
1.331	0.1517		2.51	0.059288	0.059074	-0.4	0.038012	0.037905	-0.3	
1.288	0.1246		2.50	0.060141	0.059745	-0.7	0.037604	0.037406	-0.5	
1.246	0.099		2.51	0.060784	0.060347	-0.7	0.037167	0.036948	-0.6	
1.539	0.279	0.0423	2.56	0.055673	0.055918	+0.4	0.040129	0.040252	+0.3	
1.307	0.1409		2.14	0.060491	0.059929	-0.9	0.037730	0.037448	-0.8	
1.372	0.1786		2.29	0.059160	0.058777	-0.7	0.038430	0.038239	-0.5	
1.094	0.0234	0.0148	1.94	0.062979	0.063088	+0.2	0.035119	0.035174	+0.2	3
1.133	0.0455		2.09	0.062034	0.062314	+0.5	0.035541	0.035681	+0.4	
1.151	0.0574		2.01	0.061887	0.062147	+0.4	0.035714	0.035844	+0.4	
1.149	0.0666		1.55	0.062179	0.062671	+0.8	0.035438	0.035684	+0.7	
1.159	0.076		1.30	0.062470	0.062845	+0.6	0.035491	0.035679	+0.5	
1.702	0.391	0.08393	3.1	0.049367	0.052346	+6.0	0.041174	0.042664	+3.6	7
1.510	0.271		2.4	0.055405	0.056368	+1.7	0.039511	0.039993	+1.2	
1.388	0.197		2.2	0.058050	0.058477	+0.7	0.038295	0.038508	+0.6	
1.271	0.110		2.9	0.059550	0.059456	-0.2	0.037469	0.037422	-0.1	
1.183	0.074		2.2	0.061098	0.061449	+0.6	0.036100	0.036275	+0.5	
1.167	0.063		2.0	0.062249	0.062035	-0.3	0.036042	0.035935	-0.3	
1.265	0.121		2.1	0.060540	0.060474	-0.1	0.037091	0.037058	-0.1	
1.535	0.275		3.4	0.052920	0.054667	+3.3	0.039895	0.040769	+2.2	
1.736	0.412		3.5	0.047335	0.051196	+8.2	0.041396	0.043326	+4.7	

TABLE III. Critical Radii of Spheres of Plutonium Nitrate Solution Using the Measured or Calculated Values for the Water Content.

Plutonium Concentration (grams per cubic centimeter)	Percent Difference in [H]	Critical Radius (centimeters) for Bare Sphere		Percent Difference in Critical Radii
		[H] and [O] from Measured Data	[H] and [O] from Formula for [H ₂ O]	
0.412	+8.2	22.47	20.89	-7.0
0.355	+2.3	18.54	18.17	-2.0
0.332	+1.5	18.55	18.30	-1.4
0.063	-0.3	19.43	19.49	+0.3
0.1409	-0.9	17.98	18.13	+0.8

NOTE: The critical radii were calculated using the DTF-IV transport code (6) with Hansen-Roach sixteen-group cross sections (5).
 [H] - hydrogen number density [O] - oxygen number density [H₂O] - water number density

TABLE IV. Critical Radii for Unreflected Spheres of Plutonium Nitrate [Pu(NO₃)₄] Solution.

Concentration (grams per liter)	Critical Radius (centimeter)			
	0-Percent Plutonium 240		6-Percent Plutonium 240	
	0-Normal Nitric Acid	2-Normal Nitric Acid	0-Normal Nitric Acid	2-Normal Nitric Acid
10	38.836	43.030	46.066	52.783
15	26.298	27.846	28.662	30.554
20	22.553	23.644	24.164	25.438
35	18.865	19.598	20.010	20.636
50	17.676	18.324	18.842	19.581
150	16.224	16.768	17.813	18.476
200	16.061	16.585	17.792	18.462
450	15.965	16.489	18.542	19.251
1000	16.110	16.661	-	-

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