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DENSITIES OF AMMONIUM FLUORIDE - AMMONIUM
NITRATE - AMMONIUM HEXAFLUOZIRCONATE SOLUTIONS

J. L. Teague
D. P. Pearson

October 28, 1960

PHILLIPS
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ATOMIC ENERGY DIVISION

NATIONAL REACTOR TESTING STATION
US ATOMIC ENERGY COMMISSION

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Chemical Development Branch

DENSITIES OF AMMONIUM FLUORIDE-AMMONIUM NITRATE-AMMONIUM
HEXAFLUOROZIRCONATE SOLUTIONS

J. L. Teague
D. P. Pearson

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HEXAFLUOROZIRCONATE SOLUTIONS

by

J. L. Teague
D. P. Pearson

A B S T R A C T

The densities of various Zirflex-type solutions at 25°C can be expressed by the equation:

$$\rho_{\text{calc}} = (0.99710 + 0.03157 \cdot m) + (0.02046 - 0.002659 \cdot m) \cdot c \\ - (0.003346 - 0.000703 \cdot m) \cdot c^{3/2} + 0.14349x + 0.49z$$

where m = moles liter⁻¹ NH_4NO_3

c = moles liter⁻¹ NH_4F

x = moles liter⁻¹ $(\text{NH}_4)_2\text{ZrF}_6$

z = moles liter⁻¹ $\text{UO}_2(\text{NO}_3)_2$

This equation fits the data with a sigma value of 0.00018 g/ml for NH_4F - NH_4NO_3 solutions, 0.00024 g/ml for NH_4F - $(\text{NH}_4)_2\text{ZrF}_6$ solutions, and 0.0002 g/ml for solutions containing $\text{UO}_2(\text{NO}_3)_2$ and/or NH_4F - NH_4NO_3 , over the range of 0.0M to 6.0M NH_4F , 0.0M to 1.6M NH_4NO_3 , 0.0M to 0.5M $(\text{NH}_4)_2\text{ZrF}_6$, and 0.0M to 0.0025M $\text{UO}_2(\text{NO}_3)_2$.

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DENSITIES OF AMMONIUM FLUORIDE-AMMONIUM NITRATE-AMMONIUM HEXAFLUOZIRCONATE SOLUTIONS

J. L. Teague
D. P. Pearson

I. SUMMARY

The present work was undertaken because of current interest in the Zirflex (ammonium fluoride) process for dissolving zirconium clad nuclear fuel. Studies were made of the density of various solutions of ammonium fluoride, with added amounts of ammonium nitrate and/or ammonium hexafluozirconate or uranyl nitrate.

The experimental method involved the use of the "Weld's precision" model of weighing bottle and conventional methods of determining the density of a known volume of solution. All determinations were carried out at a temperature of $25.00 \pm 0.03^\circ\text{C}$.

Application of least-squares analysis to the data yielded the equation

$$\rho_{\text{calc}} = (0.99710 + 0.03157 m) + (0.02046 - 0.002659 m)c - (0.003346 - 0.000703 m)c^{3/2} + 0.14349x + 0.49z$$

where m = moles liter⁻¹ NH_4NO_3

c = moles liter⁻¹ NH_4F

x = moles liter⁻¹ $(\text{NH}_4)_2\text{ZrF}_6$

z = moles liter⁻¹ $\text{UO}_2(\text{NO}_3)_2$

This equation fits the data with a sigma value of 0.00018 g/ml for $\text{NH}_4\text{F}-\text{NH}_4\text{NO}_3$ solutions, 0.00024 g/ml for $\text{NH}_4\text{F}-(\text{NH}_4)_2\text{ZrF}_6$ solutions, and 0.0002 g/ml for solutions containing $\text{UO}_2(\text{NO}_3)_2$ and/or $\text{NH}_4\text{F}-\text{NH}_4\text{NO}_3$, over the range of 0.0M to 6.0M NH_4F , 0.0M to 1.6M NH_4NO_3 , 0.0M to 0.5M $(\text{NH}_4)_2\text{ZrF}_6$, and 0.0M to 0.0025M $\text{UO}_2(\text{NO}_3)_2$.

II. INTRODUCTION

The Zirflex process for dissolution of zirconium and Zircaloy-clad fuel elements has received considerable attention⁽¹⁾⁽²⁾⁽³⁾ in recent years as a possible alternate to the STR process now in use.

One proposed modification⁽¹⁾⁽²⁾ of the original ammonium fluoride process consists of addition of ammonium nitrate to suppress hydrogen evolution during dissolution, according to the equation:

The solutions treated in this report are of the type to be expected in a system involving the above modification of the original ammonium fluoride process. The density determinations covered a range of solution concentrations that were 0.0M to 6.0M in ammonium fluoride and 0.0M to 1.6M in ammonium nitrate. In addition, a few measurements were made with 0.1M to 0.5M ammonium hexafluorozirconate solutions plus ammonium fluoride additions up to the solubility limits of the ammonium hexafluorozirconate. In two experiments, densities of saturated uranium (VI)-ammonium fluoride-ammonium nitrate solutions were determined.

III. EXPERIMENTAL

A. Materials

The ammonium fluoride used was Bakers Analyzed Reagent. Master solutions (approximately 6M) were prepared directly from the salt, filtered, and stored in polyethylene bottles.

The ammonium nitrate used was Baker & Adamson Reagent ACS. A master solution (approximately 10M) of this salt was also prepared and stored in a polyethylene container.

Both the ammonium fluoride and ammonium nitrate solutions were analyzed by the Chemical Processing Plant Analytical Section. The density of the stock solution of ammonium fluoride was checked against literature values.⁽⁴⁾

The ammonium hexafluorozirconate was obtained from Bios Laboratories Inc., 17 W. 60th St., New York, New York. Analysis showed this salt contained 37.72% Zr (37.80% Zr calculated for ammonium hexafluorozirconate) and had a fluoride to zirconium mole ratio of 6.07:1. The solutions were prepared by accurately weighing out, in an anhydrous atmosphere, the correct amount of the dry salt, then dissolving the salt in a volumetric flask along with a pipetted aliquot of ammonium fluoride solution. After preparation, these solutions were also stored in polyethylene containers.

Baker's Analyzed Reagent uranyl nitrate hexahydrate was used. Initially, weighed amounts of the salt (based upon reference (3)) were added to ammonium nitrate and/or ammonium fluoride solutions of known composition. However, precipitation of ammonium uranyl pentafluoride⁽⁵⁾ necessitated filtration of the solutions and analysis for uranium. This low solubility of uranyl nitrate is consistent with the information found later in reference (6).

B. Apparatus

Densities were determined using a set of 25 ml Pyrex "Weld's Precision" model weighing bottles. A thermostatted water bath provided a temperature of $25.00 \pm 0.03^\circ\text{C}$.

C. Procedure

The experimental solutions were prepared by pipetting an amount of stock ammonium fluoride and/or nitrate, containing the desired weight of salt, into a volumetric flask and diluting. The solutions were then

immediately transferred to polyethylene storage bottles, to eliminate any contamination from the glass.

For each density determination, the weighing bottles were washed, rinsed with distilled water, and then rinsed and dried with acetone before weighing. The experimental solution was then put into the weighing bottles, the stoppers put into place and excess solution wiped off the outside. The weighing bottles were placed in the water bath and equilibrated for approximately thirty minutes. Since initial solution temperatures were about 20°C, expansion and consequent overflow occurred during the equilibrating process. This excess solution (and any dried salt) was carefully removed with a cotton swab. After initial expansion, any evaporation losses due to an extended time in the bath were made up with distilled water (usually a microliter or two). After equilibration, the protective caps were replaced and the weighing bottles removed from the bath. The bottles were then wiped dry and weighed. After weighing, the bottles were emptied, washed, rinsed with distilled water and acetone, dried and reweighed. They were then refilled with boiled distilled water, equilibrated in the constant temperature bath, removed and reweighed, exactly as the experimental sample had been. This procedure gave a reference volume, and minimized any error due to weight loss or volume gain caused by etching of the glass weighing bottles by the more concentrated ammonium fluoride solutions. All experimental solutions were run in duplicate determinations, and all weighings were made to 0.1 mg with calibrated weights.

The density of the experimental solutions was then calculated by means of the following formula:

$$\frac{(0.99707)W_s - W_{e1}}{W_{H_2O} - W_{e2}} = \rho_{\text{exp}}$$

where W_s = weight bottle + sample

W_{e1} = weight bottle initially (empty)

W_{H_2O} = weight bottle + H₂O

W_{e2} = weight bottle after sample run (empty)

0.99707 = density of H₂O at 25.0°C

The density values determined from the above formula were calculated to five places and then the duplicate determinations were averaged and rounded to four places. All duplicate determinations gave an internal agreement of ± 0.00025 g/ml from the mean. Data are presented in Tables I, II and III, and depicted graphically in Figures 1 and 2 of the Appendix.

IV. RESULTS

After the density determinations of the series of $\text{NH}_4\text{F}-\text{NH}_4\text{NO}_3$ solutions (ranging from 0.0M to 6.0M in NH_4F and 0.0M to 1.6M NH_4NO_3) were made, the data were subjected to a least-squares analysis for the density as a function of the concentrations. Since it was found that the density of ammonium fluoride solution is not a linear function of concentration, several types of curves had to be tried before one was found which fit the data satisfactorily.

The final equation (based on 46 points) was found to be:

$$\rho_{\text{calc}} (25^\circ\text{C}) = (0.99710 + 0.03157 m) + (0.02046 - 0.002659 m)c - (0.003346 - 0.000703 m)c^{3/2}$$

where $m = \text{moles liter}^{-1} \text{NH}_4\text{NO}_3$

$c = \text{moles liter}^{-1} \text{NH}_4\text{F}$

From Table I, this equation fits the experimental points with a sigma value of 0.00018 g/ml, which compares well with the ± 0.00025 g/ml value found for the internal agreement of duplicate experimental determinations. Thus, it can be seen that the equation will characterize the data to within experimental error.

The data for the $\text{NH}_4\text{F}-(\text{NH}_4)_2\text{ZrF}_6$ system are not quite so straightforward. Some of the solutions with high ammonium fluoride concentrations were metastable, and precipitation occurred. This introduced the necessity of having an analysis performed for the zirconium and fluoride left in the solutions. The composition of all other solutions could be established from the amount of salts initially introduced. The $\pm 3\%$ uncertainty specified for fluoride analysis detracts from the accuracy of these data points.

It was found that the ammonium fluozirconate in the stable solutions contributes an additional and linear function of concentration to the density calculated for ammonium fluoride. The average value of this factor is $0.14349x$, where $x = \text{moles liter}^{-1} (\text{NH}_4)_2\text{ZrF}_6$. From Table II, this equation fits the experimental points for the stable solutions with a sigma value of 0.00024 g/ml. However, for the metastable solutions the computed values give a fit that is only within 0.0030 g/ml of the experimental points. It can be shown though, that a $\pm 3\%$ error in the fluoride concentration would readily change the computed density value by this much.

Two experiments were also done with uranyl nitrate added to ammonium fluoride or $\text{NH}_4\text{F}-\text{NH}_4\text{NO}_3$ systems. The coefficient thus calculated for the density contribution of uranium is not very precise, due to a magnification of experimental error caused by the very low concentrations of uranyl fluoride soluble in fluoride systems.⁽⁶⁾ The average value of the factor is $0.49z$, where $z = \text{moles liter}^{-1} \text{UO}_2(\text{NO}_3)_2$. From Table III, however, the fit gives a sigma value of 0.0002 g/ml. The small amounts of uranium to be expected in Zirflex solutions therefore make this coefficient relatively unimportant.

It was also decided to ignore any effects upon the density of Zirflex solutions caused by tin, since its concentration would be low (on the order of 0.007M),⁽³⁾ and its contribution per mole could be expected to be less than that of uranium.⁽⁷⁾

The final equation can then be expressed by:

$$\rho_{\text{calc}} (25^\circ\text{C}) = (0.99710 + 0.03157 m) + (0.02046 - 0.002659 m) c \\ - (0.003346 - 0.000703 m) + 0.14349x + 0.49z$$

where m = moles liter⁻¹ NH_4NO_3

c = moles liter⁻¹ NH_4F

x = moles liter⁻¹ $(\text{NH}_4)_2\text{ZrF}_6$

z = moles liter⁻¹ $\text{UO}_2(\text{NO}_3)_2$

It is applicable over the ranges 0.0M to 6.0M NH_4F , 0.0M to 2.0M NH_4NO_3 , 0.0M to 0.5M $(\text{NH}_4)_2\text{ZrF}_6$ and 0.0M to 0.0025M $\text{UO}_2(\text{NO}_3)_2$.

This equation can be extended to somewhat higher NH_4NO_3 concentration by substituting for the linear first term $[(0.99710 + 0.03157 m)]$ in the above equation, the more precise function:

$$\rho = 0.997077 + 0.032628 m - 9.63 \times 10^{-4} m^{3/2} - 4.73 \times 10^{-5} m^2$$

which was derived by Gucker⁽⁸⁾ for the density of solutions of pure NH_4NO_3 at 25°C. For NH_4NO_3 , this equation is reported to be good from 0.0M to saturation (approximately 11.0M at 25°C).

V. CONCLUSIONS

1. The density of NH_4NO_3 solutions is approximately linear with respect to concentration over the range 0.0M to 2.0M (see Figure 1).

2. The density of NH_4F solutions is non-linear with respect to concentration (see Figure 2), and is best fitted over the range 0.0M to 6.0M by an equation of the form:

$$\rho = a + bc + dc^{3/2}$$

3. The density of $(\text{NH}_4)_2\text{ZrF}_6$ solutions is approximately linear in NH_4F solutions with respect to concentration over the range 0.0M to 0.5M $(\text{NH}_4)_2\text{ZrF}_6$.

4. Uranium contribution to Zirflex solution density is minor.

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A P P E N D I X

TABLE I

Density of Ammonium Fluoride and/or Ammonium Nitrate
Solutions at $25.00 \pm 0.03^\circ\text{C}$

NH_4F (M) ^{1/2}	NH_4NO_3 M	Density (Exp.) g/ml	Density (Calc.) g/ml	$\Delta\rho$ g/ml $\times 10^4$
0.3153	0.0928	1.0018	1.0019	+1
0.4894	"	1.0045	1.0045	0
0.6921	"	1.0086	1.0086	0
1.0090	"	1.0174	1.0172	-2
1.4346	"	1.0319	1.0319	0
1.7224	0.0220	1.0432	1.0432	0
1.9550	0.0928	1.0527	1.0527	0
2.3214	"	1.0681	1.0679	-2
0.3153	0.2413	1.0064	1.0066	+2
0.4894	"	1.0091	1.0091	0
0.6921	"	1.0132	1.0132	0
1.0090	"	1.0217	1.0216	-1
1.4139	"	1.0353	1.0354	+1
1.7303	"	1.0476	1.0476	0
1.9550	"	1.0565	1.0567	+2
2.3214	"	1.0720	1.0718	-2
0.3153	0.4640	1.0136	1.0136	0
0.4894	"	1.0160	1.0160	0
0.6921	"	1.0201	1.0200	-1
1.0090	"	1.0285	1.0282	-3
1.4139	"	1.0416	1.0417	+1
1.7303	"	1.0536	1.0537	+1
1.9550	"	1.0624	1.0627	+3
2.3214	0.4640	1.0775	1.0776	+1
0.3162	0.9820	1.0278	1.0281	+3
0.4894	"	1.0303	1.0304	+1
0.6921	"	1.0341	1.0341	0
1.0090	"	1.0420	1.0420	0
1.4139	"	1.0548	1.0548	0
1.7303	"	1.0664	1.0663	-1
1.9550	"	1.0748	1.0751	+3
2.2314	"	1.0898	1.0897	-1
0.3208	0.0000	0.9985	0.9991	+6
0.5000	"	1.0018	1.0018	0
0.7070	"	1.0063	1.0062	-1
1.0144	"	1.0145	1.0147	+2
1.4346	"	1.0292	1.0294	+2
1.7147	"	1.0403	1.0404	+1
1.9922	"	1.0519	1.0518	-1
2.4249	"	1.0699	1.0696	-3
2.4470	"	1.0708	1.0705	-3
0.0000	0.0928	1.0001	1.0000	-1
"	0.2320	1.0046	1.0044	-2
"	0.4640	1.0120	1.0118	-2
"	0.9280	1.0264	1.0264	0
Pure H ₂ O @ 25°C	----	0.99707	0.9971	0
0.3208	1.3920	1.0423	1.0427	+4
1.7147	1.3920	1.0748	1.0483	-1
2.1000	1.6240	1.0989	1.0091	+2

TABLE II

Density of Ammonium Fluoride and Ammonium Hexafluorozirconate
Solutions at $25.00 \pm 0.03^\circ\text{C}$

NH_4F <u>(M)^{1/2}</u>	$(\text{NH}_4)_2\text{ZrF}_6$ <u>M</u>	Density (Exp.) <u>g/ml</u>	Density (Calc.) <u>g/ml</u>	$\Delta\rho$ <u>g/ml $\times 10^4$</u>
0.0000	0.1065	1.0128	0.0124	-4
0.3005	0.1015	1.0135	1.0134	-1
0.4490	0.1100	1.0166	1.0167	+1
0.5514	0.1010	1.0171	1.0173	+2
0.6514	0.1090	1.0205	1.0205	0
0.7318	0.1090	1.0222	1.0224	+2
1.1638	0.1000	1.0338	1.0339	+1
(1.5374)	(0.077)	1.0455	1.0443	(-12)
0.0000	0.4975	1.0688	1.0685	-3
0.7071	0.4975	1.0771	1.0775	+4
(1.0015)	(0.336)	1.0653	1.0625	(-28)

Values in parenthesis refer to Analytical Section results.

TABLE III

Density of Ammonium Fluoride, Ammonium Nitrate and
Uranyl Nitrate Solutions at $25.00 \pm 0.03^\circ\text{C}$

NH_4F <u>(M)^{1/2}</u>	NH_4NO_3 <u>M</u>	$\text{UO}_2(\text{NO}_3)_2$ <u>M</u>	Density (Exp.) <u>g/ml</u>	Density (Calc.) <u>g/ml</u>	$\Delta\rho$ <u>g/ml $\times 10^4$</u>
2.09971	1.6240	(0.00176)	1.0998	1.1000	+2
2.42432	0.0000	(0.00218)	1.0709	1.0707	-2

Values in parenthesis refer to Analytical Section results.

Figure 1. Density of NH₄F-NH₄NO₃ solutions at 25.0°C as a function of NH₄NO₃ concentration.

Figure 2. Density of NH₄F-NH₄NO₃ solutions at 25.0°C as a function of NH₄F concentration.

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