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DENSITIES AND BOILING POINTS OF URANYL

NITRATE--NITRIC ACID SOLUTIONS

By

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DENSITIES AND BOILING POINTS
OF
URANYL NITRATE-NITRIC ACID SOLUTIONS

I. INTRODUCTION

The intercycle evaporators in the Chemical Processing Plant are controlled by density-measuring instruments. Because of difficulties in controlling these evaporators in a satisfactory manner, a series of investigations was begun to measure the boiling points at the elevation of the CPP, and densities near boiling temperatures of a number of solutions in the uranyl nitrate-nitric acid-water system. From these data it was hoped to evaluate temperature sensitive devices as controllers for the evaporators.

II. SUMMARY AND CONCLUSIONS

The boiling points at 635 mm mercury pressure and the densities at 91° C. were determined for a series of solutions containing 0.75, 1.5 and 2.0 molar uranyl nitrate and 0, 2 and 5% nitric acid. The results are summarized in attached graphs.

The densities of these solutions change by about 0.030 g./ml for a 0.1 molar change in uranyl nitrate concentration at the boiling point, while the boiling temperature changes 0.2 to 0.5° C. for the same change in uranium concentration. Since variations in barometric

pressure may cause the boiling points to change by as much as 1.6° C., it appears that a temperature measuring device offers disadvantages as a primary controller for the intercycle evaporators, but could operate an upper limit cut off for the prevention of over concentration.

III. DISCUSSION

The boiling point of synthetic solutions 0.75, 1.5, and 2.0 M in uranyl nitrate and containing 0, 2 and 5% nitric acid were measured by means of a Cottrell-type ebulliometer with an iron-constantan thermocouple. Tests indicated that, with this apparatus, boiling temperatures could be measured accurately to 0.1° C. The results of these measurements are summarized in Table I.

TABLE I

Boiling Point of UNH—HNO₃—H₂O system
Corrected Barometric Pressure — 635.81 mm of Hg
Boiling Point of Water — 95.08° C.

<u>Molarity UNH</u>	<u>%HNO₃</u>	<u>Potentiometer Reading</u>	<u>Boiling Point ° C.</u>	<u>Boiling Point Elevation, ° C.</u>
0.75	0	5.090	96.57	1.49
0.75	2	5.122	97.17	2.09
0.75	5	5.166	98.00	2.92
1.5	0	5.196	98.49	3.41
1.5	2	5.237	99.27	4.19
1.5	5	5.298	100.34	5.26
2.0	0	5.293	100.24	5.16

TABLE I (cont'd)

Corrected Barometric Pressure = 632.05 mm of Hg

Boiling Point of Water = 94.92° C.

<u>Molarity UNH</u>	<u>% HNO₃</u>	<u>Potentiometer Reading</u>	<u>Boiling Point ° C.</u>	<u>Boiling Point Elevation, ° C.</u>
2.0	2	5.332	101.04	6.12
2.0	5	5.403	102.23	7.31

Figure 1 is a plot of the boiling point elevation at different concentrations of uranyl nitrate for 0, 2, and 5% HNO₃. The elevation in boiling for a given change in uranium concentration is considerably greater at higher concentrations of uranium than in more dilute solutions. From the boiling point data of Table I and information in the literature (1) for these solutions at 760 mm pressure, Duhring lines were plotted in Figure 2 over the range 610 - 760 mm pressure, using water as the reference liquid. The barometric pressure at the CPP varies between the extremes of 615 and 650 mm pressure. Thus a variation in barometric pressure can cause up to 1.6° C. change in the boiling temperature of a solution.

The densities of a number of the solutions were determined at 91 ± 0.1° C. by means of a 25 ml. pycnometer immersed in a constant temperature bath. These densities are recorded in Table II.

The densities of these solutions at 25° C. are available in the literature (2) as experimental values, or can be calculated by use of the formula:

$$(a) \quad \rho_{25} = 1.0012 + 0.3177 \text{ M U} + 0.03096 \text{ M HNO}_3$$

$$(b) \quad \rho_{\frac{t}{4}} = 1.0125 \rho_{\frac{25}{4}} + 0.000145 t - 0.000500 \rho_{\frac{25}{4}} - 0.0036$$

The formula (2) is used to calculate the densities of these solutions at 15 and 40° C.

TABLE II

Molarity UNH	Wt. %HNO ₃	Density			
		10° C.	25° C.	40° C.	91° C.
0	0	0.9997*	0.9971*	0.9922*	0.9657*
0.75	0	1.2243	1.2395	1.2324	1.1966
0.75	2	1.2566	1.2517	1.2445	1.2134
0.75	5	1.2750	1.2700	1.2627	1.2275
1.5	0	1.4838	1.4778*	1.4689	1.4285
1.5	2	1.4985	1.4924	1.4834	
1.5	5	1.5208	1.5146	1.5054	
2.0	0	1.6440	1.6372*	1.6271	1.5864
2.0	2	1.6587	1.6518	1.6416	
2.0	5	1.6838	1.6768	1.6664	1.6173

* Experimental values available in the literature.

The results of Table II are plotted in Figure 3. Where the density of a solution at 91° C. was not known, the temperature vs. density line was made to parallel that line for the same uranium concentration and another nitric acid concentration.

The densities of the various solutions at 100° C. were determined from Figure 3 and compared with the calculated value, using equation (b).

This comparison is shown below.

<u>Molarity UNH</u>	<u>%HNO₃</u>	<u>$\rho \frac{100}{4}$</u>	<u>from Figure 3</u>	<u>$\rho \frac{100}{4}$</u>	<u>Calculated</u>	<u>$\Delta \rho$</u>
0.75	0	1.1920		1.2040		0.012
0.75	2	1.2130		1.2153		0.0023
0.75	5	1.2290		1.2326		0.0036
1.5	0	1.4220		1.4331		0.0111
1.5	2	1.4365		1.4426		0.0061
1.5	5	1.4590		1.4567		-0.0023
2.0	0	1.5800		1.5861		0.0073
2.0	2	1.5920		1.6002		0.0088
2.0	5	1.6095		1.6232		0.0137

Since formula (b) was calculated from experimental data obtained at 15, 25, and 40° C., better agreement could not be expected at elevated temperatures.

Figure 4 was prepared by choosing an atmospheric pressure of 635 mm of mercury and plotting density of the boiling point versus concentration of uranium. With a fixed percentage of nitric acid there is a change in density of 0.030 for a 0.1 M change in uranium concentration.

A sensitive density-measuring instrument appears to be the most suitable primary controller for the intercycle evaporators. However, a temperature measuring device connected to a steam shutoff could be used as a secondary controller to prevent the uranium concentration in the evaporators from ever becoming so great that uranium would precipitate upon cooling. At the higher concentrations of uranium,

the 1.6° C. range in boiling temperature due to the barometric pressure variation corresponds to a 0.3 M change in uranium concentration. Thus a temperature-measuring controller set so the uranium concentration is below saturation at low barometric pressure would still operate effectively at high barometric pressure.

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FIGURE 2

BOILING POINT - VAPOR PRESSURE
FOR SYSTEM: $\text{UO}_2(\text{NO}_3)_2 \cdot \text{HNO}_3 - \text{H}_2\text{O}$

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FIGURE 3.
DENSITY VS. TEMPERATURE FOR THE
SYSTEM $\text{UO}_2(\text{NO}_3)_2 - \text{HNO}_3 - \text{H}_2\text{O}$

DENSITY - GRAMS/ML

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TEMPERATURE - DEGREES CENTIGRADE

FIGURE 4

DENSITY AT BOILING POINT- URANIUM
CONCENTRATION FOR SYSTEM $UO_2(NO_3)_2$
 HNO_3-H_2O AT 635 MM PRESSURE

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