URANIUM DENSITY OF SYSTEMS
INVOLVING MUTUALLY INSOLUBLE MATERIALS

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URANIUM DENSITY OF SYSTEMS INVOLVING MUTUALLY INSOLUBLE MATERIALS

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ABSTRACT

Critical masses, as they apply to the establishment of safe geometries, are altered by the involvement of hydrogen as a moderator. Theoretically, uranium compounds and hydrogen compounds which exhibit mutual insolubility should make proportional contributions to the composite uranium density of any system wherein they are combined. The uranium densities of four such systems were determined experimentally and the results obtained support the validity of the theory. Certain fundamental considerations are examined which are potential sources of error in the application of these physical principles.
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Critical mass criteria, by which safe geometries are established for various forms of uranium, are altered considerably when environments of chemically bound hydrogen become involved. Due to the magnitude of this effect and the relatively small contribution hydrogen normally makes toward the composite densities of such systems, the question of possible irregularities existing in uranium densities as a function of the hydrogen to uranium (H/U) ratio continues to arise at intervals. This investigation was undertaken to show that reliable maximum uranium densities of systems involving mutually insoluble materials may be derived from the properties of the individual components.

SUMMARY

Composite uranium-hydrogen systems in which the uranium compound and the hydrogen compound exhibit mutual insolubility should behave as mixtures of independent species, each making a proportionate contribution to the uranium density of the composite. Four typical systems have been examined experimentally for any evidence that the measured uranium density of the composite exhibits a positive deviation from the density calculated on the basis of this premise. Over the range of H/U ratios of interest, the experimental densities and the calculated values were in agreement. In fact, if interaction between the components of a system is conceivable, and the resultant products remain mutually insoluble, safe geometries based upon the theoretical composition yielding the higher calculated uranium density at a given H/U ratio may be conservative.

EXPERIMENTAL

Method

Applying appropriate variations of the liquid displacement principle, composite or average gross densities were measured for four combinations, each of which involved a compound of uranium which was virtually insoluble in the hydrogen-bearing compound combined with it. The following systems chosen for investigation were considered typical examples:

- Uranium tetrafluoride - - water,
- Uranium tetrafluoride - - 48 percent aqueous hydrofluoric acid,
- Uranium tetrafluoride - - hydrocarbon,
- Uranyl fluoride - - hydrocarbon.

Within each of these systems predetermined compositions were made up to correspond with various H/U atomic ratios in the range from 14 to 25. The measured composite densities were converted to average uranium densities by use of the appropriate factor for the particular uranium compound.
Apparatus

All of the density measurements were made in pycnometers similar in design to Hubbard type specific gravity bottles. The volume of each bottle was determined precisely from the total masses observed before and after filling with triply distilled mercury at the specified temperature. Glass specific gravity bottles were used for all measurements except those which involved the 48 percent hydrofluoric acid. For obvious reasons it was necessary to make these measurements in a bottle fabricated from some corrosion resistant material such as Fluorothene.*

Materials

The uranium tetrafluoride used in these measurements was prepared by the reduction of uranium hexafluoride with hydrogen in a flame reactor followed by sintering to produce densification. The uranyl fluoride used was prepared by the reaction at room temperature between a water slurry of uranium trioxide and a slight stoichiometric excess of 48 percent aqueous hydrofluoric acid. The reaction mixture was sealed for 24 hours in a Fluorothene bottle after which the entire contents of the bottle was transferred to five volumes of water. After the small amount of unreacted oxide was removed by filtration, the solution was evaporated to dryness and dried to a constant weight in an oven at 105°C. An analysis of the crystalline product for total uranium and fluoride indicated it was anhydrous uranyl fluoride free of residual hydrogen fluoride.

The 48 percent hydrofluoric acid was prepared by introducing anhydrous hydrogen fluoride vapor into a weighed quantity of distilled water in a closed polyethylene container. The final composition which was initially established by the weight gained was confirmed by titration of a weighed sample with standard alkali.

The hydrocarbon used for the measurements was a commercial paraffin wax melting at 53° to 56°C. Its measured density just above the melting point was 0.76 g./cc. Comparing these values with those given for various hydrocarbons (3), this particular wax is a reasonably pure normal paraffin with an average composition of C_{28-29}H_{54}. In practice, suspensions of uranium-bearing solids in hydrocarbon oils are more commonly encountered; but since all displacement liquids having the required solubility behavior toward the hydrocarbon systems were more dense than the hydrocarbons yet less dense than the uranium salts, a solid suspension of the salts in the paraffin wax was employed to prevent separation of the system components by the displacement liquid. In view of the experimental objective, i.e., proof of a theoretical concept, the use of paraffin as a typical hydrocarbon is permissible. Furthermore, since the densities of all liquid and solid paraffinic hydrocarbons lie within a relatively narrow range, variation of the particular hydrocarbon used would have a somewhat minor effect upon the resulting density of the composite.

* Thermoplastic polymer of chlorotrifluoroethylene made by Union Carbide Corporation for the U.S. Atomic Energy Commission.
The pertinent densities used in calculating the theoretical composite densities of the systems which were investigated are given in table I. Data given in reference 2 are plotted in figure 1. The value given in the table for 48 percent hydrofluoric acid is an interpolation taken from the curve for 0°C.

Table I

<table>
<thead>
<tr>
<th>Material</th>
<th>Density, g./cc.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF₄</td>
<td>6.70ᵃ</td>
<td>4</td>
</tr>
<tr>
<td>2UF₄ · 5H₂O</td>
<td>4.74ᵃ</td>
<td>4</td>
</tr>
<tr>
<td>UO₂F₂</td>
<td>6.38ᵃ</td>
<td>5</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.997ᵇ</td>
<td>1</td>
</tr>
<tr>
<td>48% HF</td>
<td>1.190ᶜ</td>
<td>2</td>
</tr>
<tr>
<td>Hydrocarbon Wax</td>
<td>0.903ᵈ</td>
<td>This investigation</td>
</tr>
</tbody>
</table>

ᵃ, X-ray Crystal Density; ᵇ, 25°C.; ᶜ, 0°C.; ᵈ, 26°C.

Displacement Liquids

In the measurement of densities by the liquid displacement method it is necessary that all components of the system be insoluble in the displacement liquid. It is also desirable, though not essential, that the displacement liquid be less dense than any component of the system. Consequently, xylene with a measured density of 0.857 g./cc. was chosen for both combinations of uranium tetrafluoride with an aqueous medium. Water was used as the displacement liquid for the uranium tetrafluoride-hydrocarbon system and decafluorobis(trifluoromethyl)cyclohexane, C₈F₁₆, with a measured density of 1.828 g./cc., was used with the uranyl fluoride-hydrocarbon system.

PROCEDURE AND RESULTS

Uranium Tetrafluoride--Water System

Predetermined quantities of uranium tetrafluoride and water corresponding to an H/U atomic ratio of 17 were weighed into the pycnometer. Sufficient xylene was added so that no air space remained and xylene filled the capillary when the top was set in place. Excess xylene was blotted away just before the filled pycnometer was weighed. From these data the
Figure 1
DENSITY OF AQUEOUS HYDROGEN FLUORIDE
AS A FUNCTION OF COMPOSITION
average gross density, \( \overline{\rho}_G \), for the composite was calculated according to the expression,

\[
\overline{\rho}_G = \frac{\text{combined mass of UF}_4 \text{ and water}}{\text{pycnometer volume} - \left( \frac{\text{mass of xylene}}{\rho \text{ of xylene}} \right)}
\]  

These operations were repeated for other mixtures in the system corresponding to H/U ratios of 19, 21, and 23, respectively. Finally an average uranium density, \( \overline{\rho}_U \), was calculated for each composition by substituting a mass equivalent to the uranium involved for the numerator in equation 1.

The experimental uranium densities so obtained are compared numerically in table II and graphically in figure 2 with the calculated values derived from the theory of independent proportional contribution by the separate components to both the mass and volume of the mixture.

<table>
<thead>
<tr>
<th>H/U Ratio</th>
<th>Calculated Gross Density, g./cc.</th>
<th>Calculated Uranium Density, g.U/cc.</th>
<th>Experimental Uranium Density, g.U/cc*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis: ( \text{UF}_4 ) 2( \text{UF}_4 \cdot 5\text{H}_2\text{O} ) ( \text{UF}_4 ) 2( \text{UF}_4 \cdot 5\text{H}_2\text{O} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>2.34</td>
<td>2.54</td>
<td>1.19</td>
</tr>
<tr>
<td>19</td>
<td>2.23</td>
<td>2.40</td>
<td>1.09</td>
</tr>
<tr>
<td>21</td>
<td>2.13</td>
<td>2.29</td>
<td>1.01</td>
</tr>
<tr>
<td>23</td>
<td>2.05</td>
<td>2.19</td>
<td>0.94</td>
</tr>
</tbody>
</table>

* Determined at 25°C.

In the theoretical consideration of this system, two assumptions are possible: the uranium tetrafluoride may exist (1) as the anhydrous salt, \( \text{UF}_4 \), or (2) as the hydrated salt, \( 2\text{UF}_4 \cdot 5\text{H}_2\text{O} \). Results of calculations based on both assumptions are given. Since the experimental densities agree with the calculated values assuming the anhydrous salt, hydration did not occur during these measurements. For a conservative estimate of critical masses, however, calculated densities for the hydrated salt system should be observed because the higher values would prevail should the salt become hydrated.
Figure 2

URANIUM DENSITIES OF COMPOSITES IN THE SYSTEM, URANIUM TETRAFLUORIDE–WATER

LEGEND:
- EXPERIMENTAL POINTS AT 25° C.
- CALCULATED CURVES AT 25° C.
Uranium Tetrafluoride--48 Percent Aqueous Hydrofluoric Acid System

The experimental procedure for this system was a repetition of that already described except that the 48 percent hydrofluoric acid previously prepared was substituted for distilled water in making up the various compositions. Average uranium densities were determined for compositions which corresponded to H/U ratios of 17, 19, 21, and 23, respectively. The results are given in table III and figure 3.

Table III
DENSITIES OF COMPOSITES IN THE SYSTEM,
URANIUM TETRAFLUORIDE--48% AQUEOUS HYDROFLUORIC ACID

<table>
<thead>
<tr>
<th>H/U Ratio</th>
<th>Calculated Gross Density, g./cc.*</th>
<th>Calculated Uranium Density, g.U/cc.*</th>
<th>Experimental Uranium Density, g.U/cc.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis: UF₄₂UF₄·5H₂O</td>
<td>UF₄₂UF₄·5H₂O</td>
<td>UF₄·2UF₄·5H₂O</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>2.36</td>
<td>2.52</td>
<td>1.07</td>
</tr>
<tr>
<td>19</td>
<td>2.26</td>
<td>2.40</td>
<td>0.98</td>
</tr>
<tr>
<td>21</td>
<td>2.18</td>
<td>2.30</td>
<td>0.90</td>
</tr>
<tr>
<td>23</td>
<td>2.10</td>
<td>2.22</td>
<td>0.84</td>
</tr>
</tbody>
</table>

* Calculated densities based on densities of aqueous hydrofluoric acid at 0°C. Experimental densities determined at 25°C.

Comparison of the experimental densities with the corresponding theoretical values given shows that the calculated values are slightly higher. This is to be expected since the higher, more conservative density of 1.19 g./cc. for the hydrofluoric acid at 0°C. was used in making the calculations. If a density of 1.14 g./cc. at 25°C., extrapolated from the two temperature plots in figure 1 is employed, the experimental values and those calculated assuming no hydration are identical. Therefore, it is obvious that hydration of the uranium tetrafluoride did not occur during these measurements. However, as in the previous system, this possibility should be considered when deriving conservative estimates of critical masses since the uranium densities would be somewhat higher were hydration to occur. The inflection in the upper curve shown in figure 3 is the result of a maximum degree of hydration being possible in the compositional range where the density of the residual hydrofluoric acid composition also approaches its maximum value.
Figure 3

URANIUM DENSITIES OF COMPOSITES IN THE SYSTEM, URANIUM TETRAFLUORIDE-48% HYDROFLUORIC ACID
In preparation for performing the experiments in this system, the density of the paraffin wax itself was determined at the prevailing experimental temperature. A weighed quantity of the paraffin, 10.5154 g., was melted in the calibrated glass pycnometer. When the wax was cool, the volume it occupied was determined by filling the pycnometer with water and reweighing. The volume occupied was 11.64 cc., corresponding to a density at 26°C. of 0.903 g./cc.

For each experimental composition of this system, a weighed quantity of uranium tetrafluoride was distributed throughout the required weight of paraffin wax while the wax was maintained slightly above its melting point in the calibrated pycnometer. Stirring was discontinued whereupon the trapped air bubbles escaped from the mixture. As soon as possible the mixture was allowed to cool so that the paraffin solidified with the uranium tetrafluoride suspended. Using water as the displacement liquid, the volume of the mixed sample was determined. The average uranium densities, \( \tilde{\rho}_U \), were thus measured for H/U ratios of 17, 19, 21, 23, and 25. These data are given in table IV and figure 4. Incomplete removal of trapped air from the viscous medium before solidification occurred probably accounts for the experimental densities being slightly lower than theoretical.

### Table IV

**Densities of Composites in the System, Uranium Tetrafluoride--Hydrocarbon**

<table>
<thead>
<tr>
<th>H/U Ratio</th>
<th>Calculated Gross Density, g./cc.</th>
<th>Calculated Uranium Density, g.U/cc.</th>
<th>Experimental Uranium Density, g.U/cc.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>2.46</td>
<td>1.36</td>
<td>1.33</td>
</tr>
<tr>
<td>19</td>
<td>2.34</td>
<td>1.26</td>
<td>1.23</td>
</tr>
<tr>
<td>21</td>
<td>2.23</td>
<td>1.16</td>
<td>1.14</td>
</tr>
<tr>
<td>23</td>
<td>2.14</td>
<td>1.08</td>
<td>1.05</td>
</tr>
<tr>
<td>25</td>
<td>2.06</td>
<td>1.01</td>
<td>0.98</td>
</tr>
</tbody>
</table>

* Determined at 25°C.
Figure 4
URANIUM DENSITIES OF COMPOSITES IN THE SYSTEM, URANIUM TETRAFLUORIDE–HYDROCARBON

LEGEND:
- EXPERIMENTAL POINTS AT 25° C.
- CALCULATED CURVE AT 25° C.
Uranyl Fluoride--Hydrocarbon System

Weighed portions of the anhydrous uranyl fluoride, prepared as described earlier, were stirred into samples of molten paraffin wax which resulted in combinations equivalent to H/U ratios of 14, 17, 20, 23, and 25. The cooling and density measurement procedures used for the uranium tetrafluoride-hydrocarbon system were repeated except that use of a different displacement liquid was necessitated by the solubility of uranyl fluoride in water. A completely fluorinated liquid, decafluorobis(trifluoromethyl)cyclohexane ($C_{8}F_{16}$), in which both components of the system were insoluble, proved to be a satisfactory displacement liquid. The solidified paraffin which contained the dense uranyl fluoride was covered by the fluorocarbon even though the density of the latter is 1.828 g./cc. at 26°C. The measured uranium densities given in table V and figure 5 agree within the limits of experimental error with the corresponding theoretical values.

Table V

<table>
<thead>
<tr>
<th>H/U Ratio</th>
<th>Calculated Gross Density, g./cc.</th>
<th>Calculated Uranium Density, g./cc.</th>
<th>Experimental Uranium Density, g./cc.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>2.62</td>
<td>1.55</td>
<td>1.55</td>
</tr>
<tr>
<td>17</td>
<td>2.40</td>
<td>1.35</td>
<td>1.35</td>
</tr>
<tr>
<td>20</td>
<td>2.23</td>
<td>1.20</td>
<td>1.17</td>
</tr>
<tr>
<td>23</td>
<td>2.10</td>
<td>1.08</td>
<td>1.07</td>
</tr>
<tr>
<td>25</td>
<td>2.02</td>
<td>1.01</td>
<td>1.01</td>
</tr>
</tbody>
</table>

* Determined at 25°C.

DISCUSSION

In each of the systems of mutually insoluble components considered in this study, the calculated uranium densities of the various compositions have been in complete agreement with the experimentally determined values. This is ample evidence that the following relationship is valid for any system of this nature:

$$V_C = V_1 + V_2$$
Figure 5
URANIUM DENSITIES OF COMPOSITES IN THE SYSTEM, URANYL FLUORIDE–HYDROCARBON
where $V_C$ is the volume occupied by the composite,

$V_1$ is the volume occupied independently by one component,

and $V_2$ is the volume occupied independently by the other component.

Therefore, since the average gross density, $\bar{\rho}_G$, of the composite is equal to $W_C/V_C$, and the total mass of the composite, $W_C$, equals the sum of the masses of the individual components, $W_1 + W_2$, it follows that

$$\bar{\rho}_G = \frac{W_1 + W_2}{V_1 + V_2}$$

is also valid for these systems.

By analogy, the expression for the average uranium density would be

$$\bar{\rho}_U = \frac{W_U}{V_C} = \frac{W_1 + W_2}{V_1 + V_2}$$

where $W_U$ represents the mass of uranium present in the composite and $W_1$ and $W_2$ represent the uranium contained in the respective components. In the systems considered here, one of the components contained no uranium, consequently $W_U$ was identical with the mass of uranium in the other component.

It should be remembered that certain restrictions apply if valid safe geometries for composite systems such as these are to be established upon the basis of theoretical uranium densities. It is essential that the components exhibit mutual insolubility and preferably no interaction. In the event that interaction is a possibility, e.g., hydrate formation in the uranium tetrafluoride-water system, the calculations must be made assuming those chemical species, the individual densities of which result in the highest calculated uranium density for the composite. Furthermore, since the density of any of the individual components is subject to conditional variation, e.g., the variation in the density of 48 percent hydrofluoric acid produced by changes in temperature, the anticipated conditions which would result in the maximum density must be assumed. True crystal densities, calculated from X-ray measurement of the unit cell dimensions, are available for many uranium compounds. Whenever possible, these values should be used in the calculation of theoretical composite densities since gross crystal imperfections and undetermined void fraction always result in apparent densities which are too low.
BIBLIOGRAPHY


NOTEBOOK REFERENCE

Karl E. Rapp  Notebook No. 1826

Experimental Work was completed September 7, 1954