Table 3. Worldwide deposition of strontium-90 computed from New York City rainfall analyses.

| Date | Cumulative N.Y.C. (mc/mi$^2$) | Worldwide deposition (Mc) | | |
|---|---|---|---|---|
| | | Cumul. N.Y.C. × 0.055 | Av. from Table 2 | Difference (%) |
| Dec. 1954 | 8 | 0.44 | 0.35 | 23 |
| Jun. 1955 | 14.4 | 0.79 | 0.70 | 12 |
| Dec. 1955 | 16.9 | 0.93 | 0.95 | 2 |
| Jun. 1956 | 24.9 | 1.37 | 1.07 | 25 |
| Dec. 1956 | 27.9 | 1.54 | 1.50 | 3 |
| Jun. 1957 | 35.9 | 1.97 | 1.75 | 12 |
| Dec. 1957 | 38.6 | 2.12 | 2.00 | 6 |
| Apr. 1958 | 43.2 | 2.38 | 2.30 | 3 |
| Jun. 1958 | 47.4 | 2.61 | 2.45 | 6 |
| Dec. 1958 | 53.4 | 2.94 | 2.85 | 3 |
| Jun. 1959 | 72.7 | 4.00 | 3.97 | 1 |
| Dec. 1959 | 74.3 | 4.08 | 4.10 | 1 |
| Jun. 1960 | 76.5 | 4.20 | 4.45 | 0 |
| Dec. 1960 | 76.5 | 4.20 | 4.45 | 6 |
| Jun. 1961 | 78.7 | 4.33 | 4.25 | 2 |
| Dec. 1961 | 80.8 | 4.45 | 4.85 | 9 |
| Apr. 1962 | 87.9 | 4.83 | 4.90 | 1 |
| Dec. 1962 | 100.8 | 5.54 | 5.90 | 6 |
| Dec. 1963 | 163.8 | 9.00 | 8.26* | 9 |
| | | | Average | 6.8 |

* Computed from previous data plus that from (*10*) and (*11*).

worldwide fallout averages of Table 2 is only 20 percent, Fig. 1 was plotted to illustrate the agreement.

To attempt a prediction of the worldwide deposition of Sr$^{90}$ for the entire year of 1964, the fallout of the nuclide in the New York City area must first be estimated. At this time, data for only the first 3 months of 1964 from New York City are available. It has been observed that over the last 9 years, the first quarter of the year has had, on the average, 29 percent of the annual Sr$^{90}$ deposition. Thus, by computation, the total New York City fallout for the first quarter of 1964 is 13 mc/mi$^2$, and the anticipated 1964 New York City fallout is 45 mc/mi$^2$.

If this value is adjusted to worldwide deposition by use of the DRWN of 0.055, the predicted global fallout for 1964 would be 2.48 Mc.

The results of this study suggest that deposition of nuclear debris on the earth's surface has been relatively systematic when considered on an annual basis.

Regardless of the actual mechanism of transfer of the particles within the stratosphere and through the tropopause, and in spite of the geographical and spatial heterogeneity of the testing programs from year to year, the relationship of deposited Sr$^{90}$ in the New York City area to that on the entire earth's surface has remained constant. This observation leads to the conclusion that the distribution of debris in the stratosphere does not appreciably affect the ultimate distribution of that material on the ground. Recognizing the well-documented rapid deposition rate of particles in the troposphere, it seems clear that the controlling factor in the final distribution on the earth's surface must be the latitude and longitude at which debris crosses the tropopause. This must be relatively constant to produce the observed results.

Any single fallout collection site could serve as well as New York City as an indicator of worldwide fallout. New York City was chosen for this report because it is the site with the longest continuous documentation of fallout and therefore promises the most accurate average ratio. As an indication of the magnitude of the deposition ratio at other remote locales, Iwo Jima and Adelaide, Australia, were considered. For Iwo Jima a deposition ratio, based upon four years of data (1960–1963), of 0.141 Mc per mc/mi$^2$ was calculated. Measurements at Adelaide, Australia, (1959–1963) gave a deposition ratio of 0.438.

Since all but a negligible portion of the debris injected into the stratosphere originated in the Northern Hemisphere, these conclusions are valid only for such conditions. Unquestionably, a test series carried out in the Southern Hemisphere would result in a surface distribution of debris different from that of past years.

However, from a practical point of view, and barring any Southern Hemisphere injections, this method should prove useful for making predictions for the next several years, whether or not there is further testing.

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15 June 1964

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## Raoult's Law Study of Vanadium Pentafluoride in Uranium Hexafluoride

Abstract. *Binary systems of liquid vanadium pentafluoride dissolved in liquid uranium hexafluoride are nonideal, with negative deviations from Raoult's law in the temperature range 75° to 92°C.*

In order to investigate intermolecular forces between $UF_6$ and other fluorides, we have studied the solubility of $VF_5$ in $UF_6$; hitherto there has been only a limited solubility study of this system by Mears *et al.* (*1*). We measured the total pressures of six binary solutions (through the whole range of mole fractions) of $VF_5$ dissolved in $UF_6$ at 75.4°, 82.0°, and 92.7°C. A comparison of these pressures with ideal total pressures calculated from Raoult's law is given in Table 1 and Figs. 1–4; measurements were made by analysis of equilibrium liquid and vapor samples. Comparison shows that

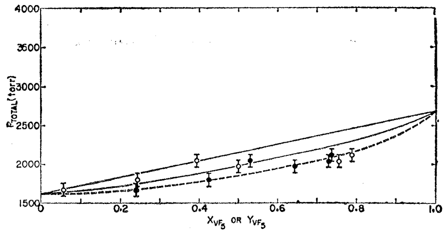

Fig. 1. Raoult's law graph for binary solutions of $UF_6$ and $VF_5$ at 75.4°C. $X_{VF_5}$ indicated by open circles and solid line; $Y_{VF_5}$, by closed circles and dotted line.

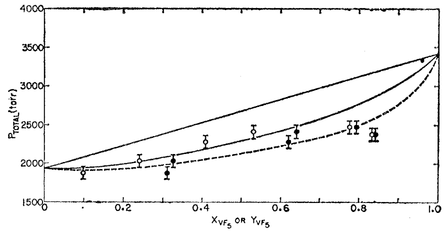

Fig. 2. Raoult's law graph for binary solutions of $UF_6$ and $VF_5$ at 82.0°C. As in Fig. 1.

$VF_5$ and $UF_6$ formed a binary system, with negative deviations in the temperature range studied; no minimum was observed.

We prepared $VF_5$ at 700°C by the method of Clark and Emeleus (*2*), collected the product at 0°C, and purified it to better than 98 percent; $VOF_3$ was the only remaining contaminant. Six special sample units were placed in an 80-liter metal can which in turn was placed in a 120-liter can insulated with fiber glass. The sampling temperature was measured with a copper-constantan thermocouple connected to a Leeds and Northrup model G Speedomax recorder. We measured the vapor pressures of the solutions with a calibrated pressure gauge placed on the outlet of a transmitter calibrated to record absolute pressure. Where necessary, all apparatus and materials were rendered inert by treatment with fluorine. After rinsing with $VF_5$, the containers were charged with liquid $UF_6$, immersed in a mixture of Freon 113 and dry ice, disconnected from the $UF_6$ transfer system, and allowed to warm to room temperature for weighing; the $UF_6$ was frozen again in order to add slightly warmed $VF_5$. We analyzed the initial withdrawals for both vanadium (*3*) and uranium (*4*); since the agreement was excellent, we obtained all other uranium values by difference. We analyzed the vapor samples with a Perkin Elmer model 21 infrared spectrophotometer and a Beckman GC-2 gas chromatograph to within 1.5 percent accuracy. We began measurements at 66.0°C and allowed 6 to 8 days for the samples to equilibrate. Duplicate measurements were made at 66.2° and 92.1°C; as a check, random samplings were made at the other temperatures. In each case 20 days separated duplicate or check measurements.

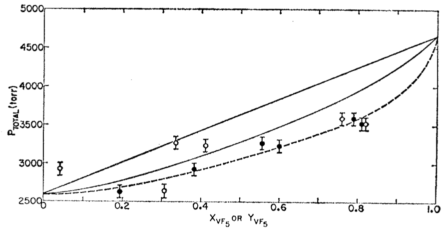

Fig. 3. Raoult's law graph for binary solutions of $UF_6$ and $VF_5$ at 92.7°C. As in Fig. 1.

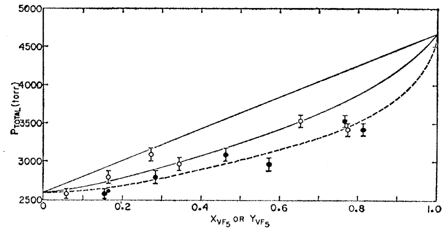

Fig. 4. Raoult's law graph for binary solutions of $UF_6$ and $VF_5$ at 92.1°C. As in Fig. 1.

A theoretical vapor pressure for $UF_6$ and $VF_5$ was calculated from the equations of Oliver *et al.* (*5*) and Trevorrow *et al.* (*6*), respectively; the data for 66°C were not included because of the large, random scatter. This scatter may have resulted from a lack of equilibrium, since the temperature was only 2 degrees above the melting point of $UF_6$ The sealed system prevented visual observation of the sample, but the presence of undissolved solid $UF_6$ was unlikely. A graph of the data in Table 1 indicates some scatter which may be related to the liquid-vapor equilibration, since it cannot be attributed to errors in analyses or pressure measurements, or both.

The greatest deviations occur in the region of 0.8 mole fraction $VF_5$ where the vapor curve approaches the liquid curve but cannot form a confluence, since no minimum is observed. These deviations cannot be attributed to nonideality of $UF_6$ vapors which Ackley (*7*) found to be nearly an ideal gas in this temperature range. The negative deviations indicate the presence of strong intermolecular forces, an analogy to the behavior of $UF_6$ with AgF and the alkali metal fluorides (other than Li) reported by Seaborg and Katz (*8*). In these latter cases the forces were strong enough to form a complex salt in the region of 0.25 mole fraction $UF_6$. We do not believe (because of the region of maximum deviation and the known ability of $UF_6$ to form complex salts) that intermolecular forces reflect any interaction between $UF_5^+$ and $VF_6^-$, although Clark and Emeleus (*2*) have shown that pure $VF_5$ is probably associated and self-ionizing.

Table 1. Total experimental and theoretical pressures of binary solutions of $VF_5$ in $UF_6$ at various temperatures.

| Mole fraction, $VF_5$ | | Total pressure | |
|---|---|---|---|
| Liquid | Vapor | Exptl. (Torr) | Calcd. (Torr) |
| | *75.4°C* | | |
| 0.787 | 0.735 | 2109 | 2459 |
| .755 | .730 | 2047 | 2424 |
| .500 | .643 | 1968 | 2150 |
| .391 | .530 | 2038 | 2032 |
| .241 | .423 | 1799 | 1871 |
| .059 | .240 | 1654 | 1675 |
| | *82.0°C* | | |
| 0.832 | 0.840 | 2386 | 3161 |
| .775 | .792 | 2468 | 3078 |
| .531 | .640 | 2419 | 2722 |
| .407 | .620 | 2278 | 2540 |
| .239 | .327 | 2042 | 2296 |
| .098 | .310 | 1881 | 2090 |
| | *92.7°C* | | |
| 0.820 | 0.810 | 3505 | 4283 |
| .760 | .790 | 3598 | 4158 |
| .411 | .600 | 3231 | 3434 |
| .335 | .558 | 3257 | 3277 |
| .041 | .381 | 2916 | 2667 |
| .309 | .193 | 2626 | 3223 |
| | *92.1°C* | | |
| 0.773 | 0.811 | 3407 | 4185 |
| .652 | .766 | 3536 | 3934 |
| .342 | .572 | 2957 | 3291 |
| .271 | .462 | 3092 | 3144 |
| .165 | .283 | 2797 | 2924 |
| .059 | .155 | 2564 | 2704 |

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20 July 1964

## Vapor Pressure of Ice Containing $D_2O$

Abstract. *The vapor pressures of solid $D_2O$ and ice containing $D_2O$ in various amounts were measured with an oil manometer. The result gives the lowest vapor pressure for $D_2O$ ice ever obtained. The observed value for ice with different proportions of $D_2O$ and $H_2O$ agreed well with the values calculated on the assumption that the vapor pressure of HDO is the geometrical mean of those of $H_2O$ and $D_2O$ and that the equilibrium constant of isotopic exchange is 4. The fractionation factor of D between ice and vapor phases increases from 1.128 at 0°C to 1.210 at −38°C.*

Vapor pressure of ice consisting of heavy water and light water in various proportions was measured in the temperature range from 0° to −38°C. Water samples of 3 ml each were degassed and frozen at different temperatures in freezing mixtures made of water, ethyl alcohol, carbon tetrachloride, dichlorethane, and dry ice. The vapor pressure was measured with an oil manometer (oil, dioctyl sebacate). The temperature of each freezing mixture was determined with a low-temperature standard thermometer (sensitivity, 0.01°C) (*1*). The vapor pressure and density of the oil were, respectively, $5 \times 10^{-8}$ mm-Hg and 0.916 at 25°C; the density of the oil was corrected for the temperature change. The height of the meniscus of the manometer was determined with a cathetometer, which permits the reading of the pressure to 0.001 mm-Hg.

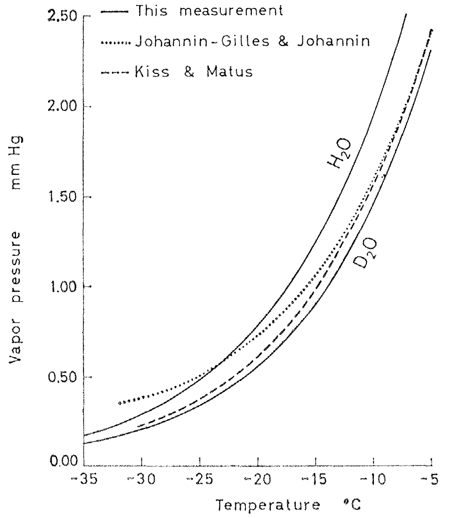

Fig. 1. Vapor pressure of $D_2O$ and $H_2O$ ice.

To check the accuracy of the measurement, the vapor pressure of the ice from ordinary water was determined. The results agreed well with previous values (*2*) within the experimental error of ± 0.01 mm-Hg.

Then the vapor pressure of ice from pure heavy water ($D_2O$) was determined. The sample of heavy water used was of the concentration of 99.65 percent (mole) (manufactured by Showa Denko Co., Tokyo). The results differ from those of Johannin-Gilles and Johannin (*3*) especially in the lower temperature range (Fig. 1 and Table 1). The results of Kiss and Matus (*4*) are close to our values though they are still a little higher than ours (2 to 9 percent). Based on the result of our measurement, the relation between the vapor pressure of $D_2O$ ice and temperature (°K) is expressed by the following empirical equation.

$$\log P = -(2783.66/T) + 10.7478$$

The vapor pressure of the ice containing other proportions of $D_2O$ was measured in the same way. Five samples which consisted, respectively, of 10, 30, 50, 70, and 90 percent of the heavy water (by volume) were prepared for this purpose (Table 2).

The vapor pressure $P$ is regarded as a sum of those of $H_2O$, HDO, and $D_2O$ in ice as follows:

$$P = M_{H_2O}P_{H_2O} + M_{D_2O}P_{D_2O} + M_{HDO}P_{HDO}$$

where $P_{H_2O}$, $P_{HDO}$, and $P_{D_2O}$ are vapor pressures of pure ice phase of $H_2O$, HDO, and $D_2O$, and $M$ denotes the molar fraction of each component. The vapor pressure $P_{HDO}$ was estimated under the assumption that it is represented by the geometric mean of $P_{D_2O}$ and $P_{H_2O}$. This assumption was proved valid (*5*) for the gas-liquid phases. The mole fraction of HDO was calculated by assuming that the equilibrium constant of isotopic exchange of $H$ and $D$ is 4.

The calculated values for $P$ are given in Table 2. The fairly good agreement between the calculated and observed values suggests the validity of the foregoing assumptions for ice too.

From these results the fractionation coefficient $\alpha$ of deuterium between water vapor and ice phases at different temperature was calculated by

$$\alpha = (D/H)_{sol}\,(D/H)_{vap} = P_{H_2O}/P_{HDO}$$

Table 1. Vapor pressure of $D_2O$ ice.

| T (°C) | $P_{D_2O}$ (mm-Hg) |
|---|---|
| −0.02 | 3.59 |
| −2.7 | 2.86 |
| −4.6 | 2.42 |
| −11.1 | 1.34 |
| −14.4 | 0.98 |
| −19.5 | 0.59 |
| −24.6 | 0.35 |
| −28.0 | 0.25 |
| −38.4 | 0.08 |

Table 2. Vapor pressure (P) of ice containing heavy water (mm-Hg) at varying ratios of $H_2O$ to $D_2O$.

| Temp. (°C) | $P_{obs.}$ | $P_{calc.}$ |
|---|---|---|
| | *$9H_2O$ : $1D_2O$* | |
| 0.00 | 4.49 | 4.48 |
| −4.2 | 3.16 | 3.15 |
| −12.4 | 1.55 | 1.53 |
| −14.5 | 1.25 | 1.26 |
| −20.7 | 0.69 | 0.70 |
| −24.0 | .48 | .51 |
| −28.4 | .33 | .33 |
| −37.9 | .12 | .11 |
| | *$7H_2O$ : $3D_2O$* | |
| 0.00 | 4.26 | 4.28 |
| −3.3 | 3.22 | 3.25 |
| −4.4 | 2.93 | 2.96 |
| −8.0 | 2.14 | 2.15 |
| −10.4 | 1.68 | 1.74 |
| −15.1 | 1.09 | 1.13 |
| −16.5 | 0.97 | 0.99 |
| −27.0 | .35 | .35 |
| | *$5H_2O$ : $5D_2O$* | |
| 0.01 | 4.07 | 4.07 |
| −4.2 | 2.87 | 2.86 |
| −10.9 | 1.58 | 1.57 |
| −15.6 | 1.00 | 1.02 |
| −19.9 | 0.66 | 0.67 |
| −23.3 | .47 | .48 |
| −28.5 | .28 | .28 |
| −38.0 | .10 | .10 |
| | *$3H_2O$ : $7D_2O$* | |
| 0.03 | 3.85 | 3.87 |
| −4.5 | 2.64 | 2.65 |
| −10.5 | 1.56 | 1.55 |
| −15.1 | 1.00 | 1.01 |
| −19.9 | 0.62 | 0.63 |
| −23.0 | .45 | .46 |
| −27.9 | .27 | .28 |
| −37.9 | .09 | .10 |
| | *$1H_2O$ : $9D_2O$* | |
| 0.02 | 3.68 | 3.69 |
| −4.3 | 2.57 | 2.57 |
| −10.0 | 1.53 | 1.52 |
| −15.2 | 0.93 | 0.93 |
| −19.2 | .62 | .63 |
| −23.3 | .42 | .42 |
| −27.7 | .27 | .28 |
| −37.9 | .09 | .09 |

Table 3. Fractionation factor $\alpha$ of D and H between ice and vapor.

| T °C | $\alpha$ |
|---|---|
| 0 | 1.128 |
| −5 | 1.137 |
| −10 | 1.148 |
| −15 | 1.161 |
| −20 | 1.174 |
| −25 | 1.187 |
| −28 | 1.194 |
| −38 | 1.210 |