

Densities and Molar Volumes of Isotopically Altered Liquid Uranium Hexafluoride

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The liquid density data of Wertz and Hedge for isotopically altered uranium hexafluoride have been mathematically extrapolated over the range of 64.05° to 230.20° C. Equations for the densities and molar volumes of isotopically altered uranium hexafluoride are presented.

WERTZ AND HEDGE (3) determined the density of liquid isotopically unaltered uranium hexafluoride at 65°, 70°, 80°, and 90° C. They used bivalved, 125-ml. nickel pycnometers, each equipped with a thermowell to accommodate a calibrated platinum resistance thermometer, and with a fluorothene reservoir attached to each valve to provide expansion volumes for the uranium hexafluoride. The volume of each pycnometer was calibrated with triple-distilled water. An excess of uranium hexafluoride was condensed at 0° C. in the pycnometers. The pycnometers were then placed in a water bath controlled to $\pm 0.1^\circ$ C. of the desired temperature of the density measurements. As the uranium hexafluoride melted, the melting point curve was followed with the resistance thermometer, and the excess material required to fill the pycnometer was expanded into the fluorothene reservoirs. When the desired temperature was attained, and remained constant for one hour, the valves on the pycnometer were closed and the bath temperature was lowered. As the uranium hexafluoride froze, the triple point was determined. The data obtained from this procedure were fitted to a least-squares equation to obtain the expression:

$$\rho = 3.668 - 1.553 \times 10^{-2} \Delta t + 7.356 \times 10^{-4} \Delta t^2 - 1.576 \times 10^{-5} \Delta t^3 \quad (1)$$

where ρ is the density in grams per cubic centimeter, and Δt is the temperature in degrees Centigrade minus 64.052° C.

Since Equation 1 is applicable to liquid uranium hexafluoride density values at 90° C. or lower, Wertz and Hedge (3) pooled their data with Hoge and Wechsler (1) and Llewellyn (2) to obtain the following expression for the density of isotopically unaltered liquid uranium hexafluoride:

$$\rho = 2.0843 - 0.0031t + 0.3710(230.2 - t)^{0.3045} \quad (2)$$

where ρ is the density in grams per cubic centimeter, and t is the temperature in degrees Centigrade.

Equations 1 and 2 are complementary. Table I compares density values obtained from Equations 1 and 2 to the observed data obtained by Wertz and Hedge (3). The calculated values obtained from Equation 1 are not significantly different from the observed data at the 95% confidence limits, whereas the values calculated from Equation 2 are significantly different from the observed data below 80° C., but not at or above 80° C. Thus Equation 1 is used for calculation of the densities and molar volumes of liquid isotopically altered uranium hexafluoride at or below 90° C., and Equation 2 used for those above 90° C.

Wertz and Hedge (3) also determined the ratio of the densities of isotopically unaltered uranium hexafluoride to that of isotopically altered uranium hexafluoride. These measurements were made using 8-ml. nickel pycnometers adapted with small (about 0.15 cc.), closed, fluorothene sight capillaries. The pycnometers were liquid filled with uranium hexafluoride and placed in an air bath maintained at $70^\circ \pm 0.1^\circ$ C. The ratio of densities was determined

using the fluorothene sight capillaries as weight burets, and weighing the quantities of the uranium hexafluoride species for equivalent volumes (Table II). From these data the observers concluded that "the ratio of these densities varies directly as that of the molecular weight of uranium hexafluoride. . ."

CALCULATIONS

Utilizing the concept of molar volumes, the density data of Wertz and Hedge (3) are extrapolated to include all species of uranium hexafluoride throughout the liquid range of 64.05° to 230.20° C. The molar volume is defined as the volume occupied by the molecular weight of the liquid in grams, which is numerically equal to the molecular weight divided by the density of the liquid as expressed in Equation 3,

$$\bar{V}_t = \frac{M}{\rho_t} \quad (3)$$

where \bar{V}_t is the molar volume at temperature t , M is the molecular weight, and ρ_t is the density of the liquid at temperature t .

Thus, since Equations 1 and 2 describe the density of liquid isotopically unaltered uranium hexafluoride through-

Table I. Observed and Calculated Densities of Isotopically Unaltered Uranium Hexafluoride^a

Temp., ° C.	Density, G./Cc. (Equation 1)	Equation 1 Minus Observed Data	Equation 2 Minus Observed Data
65	3.654	-0.002 \pm 0.014	-0.016 \pm 0.014
70	3.599	+0.002 \pm 0.007	+0.011 \pm 0.007
80	3.543	-0.001 \pm 0.009	-0.001 \pm 0.009
90	3.485	+0.002 \pm 0.009	-0.006 \pm 0.009

^a 95% confidence limits of mean deviation of values calculated from Equation 1 and observed data of Wertz and Hedge (3).

Table II. Ratio of Densities of Isotopically Unaltered Uranium Hexafluoride to That of Isotopically Altered Uranium Hexafluoride

Uranium Hexafluoride, M.W.	Ratio of Densities \pm Standard Deviation
352.02	1.0000 ^a
351.56	1.0011 \pm 0.0003
350.91	1.0033 \pm 0.0003
350.20	1.0056 \pm 0.0004
349.62	1.0066 \pm 0.0006
349.21	1.0082 \pm 0.0004

^a Value for isotopically unaltered uranium hexafluoride given for reference.

out the liquid range of 64.05° to 230.2° C., the molar volumes of liquid isotopically unaltered uranium hexafluoride throughout the liquid density temperature range may be determined by combining Equations 1 and 3 and Equations 2 and 3.

$$\bar{V}_i = \frac{M}{3.668 - 1.553 \times 10^{-2} \Delta t + 7.356 \times 10^{-4} \Delta t^2 - 1.576 \times 10^{-5} \Delta t^3} \quad (4)$$

$$\bar{V}_i = \frac{M}{2.0843 - 0.0031 t + 0.3710(230.2 - t)^{0.3045}} \quad (5)$$

Since the molecular weight, M , of isotopically unaltered uranium hexafluoride is 352.02, Equation 4 becomes

$$\bar{V}_i = [10.42 \times 10^{-3} - 44.12 \times 10^{-6} \Delta t + 20.90 \times 10^{-7} \Delta t^2 - 44.77 \times 10^{-10} \Delta t^3]^{-1} \quad (6)$$

and Equation 5 becomes

$$\bar{V}_i = [59.21 \times 10^{-4} - 8.81 \times 10^{-6} (t) + 105.39 \times 10^{-5} (230.2 - t)^{0.3045}]^{-1} \quad (7)$$

Table III lists the densities of isotopically unaltered uranium hexafluoride at various temperatures as calculated from Equations 1 and 2, and the molar volumes as calculated from Equations 6 and 7.

The relationship of the densities of isotopically altered uranium hexafluoride as obtained from a least-squares fit of the data in Table II is

$$\rho_M(70^\circ \text{C.}) = 0.0102238 (M) \quad (8)$$

Thus the molar volume of isotopically altered uranium hexafluoride at 70° C. is obtained by combining Equations 1 and 8, or

$$\bar{V}_M(70^\circ \text{C.}) = \frac{M}{\rho_M(70^\circ \text{C.})} = \frac{M}{0.0102238 (M)} = \frac{1}{0.0102238} = 97.81 \text{ cc.} \quad (9)$$

Table IV compares the densities calculated from Equation 1 and the ratios from Table II with the calculated densities

Table III. Density and Molar Volumes of Isotopically Unaltered Uranium Hexafluoride

Temp., ° C.	Density, G./Cc.		Molar Volume	
	Equation 1	Equation 2	Equation 6	Equation 7
64.052	3.668		95.97	
65	3.654		96.34	
70	3.599		97.81	
80	3.543		99.36	
90	3.485		101.01	
		Equation 2		Equation 7
100		3.409		103.26
120		3.269		107.68
140		3.115		113.01
160		2.946		119.49
180		2.754		127.82
200		2.542		138.48
210		2.364		148.91
220		2.159		163.05
230.2		1.375		256.01

Table IV. Densities and Molar Volumes of Uranium Hexafluoride at 70° C.

Molecular Weight	Calcd. Densities		Molar Volumes	
	From ratios in Table II	From Eq. 8	From Eq. 3	From Eq. 9
352.02	3.599	3.599	97.81	97.81
351.56	3.595	3.594	97.79	97.81
350.91	3.587	3.588	97.83	97.81
350.20	3.579	3.580	97.85	97.81
349.62	3.575	3.574	97.80	97.81
349.21	3.570	3.570	97.82	97.81

Table V. Density, Molar Volume, and Molecular Weight of Selected Uranium Hexafluoride Isotopic Species at Various Temperatures

T, ° C.	Molar Volume	Isotopic Species, M.W.			
		U ²³⁸ F ₆ , 352	U ²³⁶ F ₆ , 350	U ²³⁵ F ₆ , 349	U ²³⁴ F ₆ , 348
		Density, G./Cc.			
65	96.34	3.654	3.633	3.623	3.612
70	97.81	3.599	3.578	3.568	3.558
80	99.36	3.543	3.523	3.512	3.502
90	101.0	3.485	3.465	3.455	3.445
100	103.2	3.409	3.389	3.380	3.370
120	107.7	3.269	3.250	3.241	3.232
140	113.0	3.115	3.097	3.088	3.079
160	119.5	2.946	2.929	2.921	2.912
180	127.8	2.754	2.738	2.730	2.723
200	138.5	2.542	2.527	2.520	2.513
220	163.0	2.159	2.147	2.140	2.134
230.2	256.0	1.375	1.367	1.363	1.359

from Equation 8; and the molar volumes calculated from Equation 3 using the densities derived from Equation 1 and the ratios in Table II with the molar volume obtained from Equation 9. The calculated densities have 95% confidence limits of ± 0.008 gram per cubic centimeter and the resulting calculated molar volumes have 95% confidence limits of ± 0.18 cc. There are no significant differences at the 95% confidence level between the respective densities and molar volumes in Table IV.

Thus as predicted by theory and calculated from Equation 9, the molar volume of uranium hexafluoride is constant at 70° C. and is independent of the isotopic species. Consequently, the molar volumes of isotopically altered uranium hexafluoride are identical to that of isotopically unaltered uranium hexafluoride, and may be calculated directly by using Equations 6 and 7. The densities of isotopically altered uranium hexafluoride within the liquid range of 64.05° and 230.20° C. may be calculated by combining Equations 3 and 6, and Equations 3 and 7, in the following manner:

$$\bar{V}_i = \frac{M}{\rho_i}$$

by rearranging

$$\rho_i = \frac{M}{\bar{V}_i}$$

and by substituting the equivalent of \bar{V}_i from Equation 6,

$$\rho_{M(t)} = M[10.42 \times 10^{-3} - 44.12 \times 10^{-6} \Delta t + 20.90 \times 10^{-7} \Delta t^2 - 44.77 \times 10^{-10} \Delta t^3] \quad (10)$$

and by substituting the equivalent of \bar{V}_i from Equation 7,

$$\rho_{M,t} = M[59.21 \times 10^{-4} - 8.81 \times 10^{-6} (t) + 105.39 \times 10^{-5} (230.2 - t)^{0.3045}] \quad (11)$$

Table V is a tabulation of the densities and molar volumes of uranium hexafluoride of selected molecular weights at various temperatures. The molecular weights selected correspond closely to pure $U^{238}F_6$, $U^{236}F_6$, $U^{235}F_6$, and $U^{234}F_6$. The liquid densities are calculated from Equations 10 and 11 and the molar volumes from Equations 6 and 7, below and above $90^\circ C.$, respectively.

Effects of Surfactants on Coalescence Rest Times of Drops

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Data are reported for the rest times of drops coalescing at a flat interface in the presence of a chemically pure surface active agent. Benzene-water and water-benzene systems were used with seven surface active agents. Rest time distributions were essentially Gaussian. Film drainage time followed by a rupture time showed an exponential decay pattern. Values reported included average, minimum, maximum, median, and drainage times and the rate of rupture constant.

IF TWO nearly immiscible liquids be intimately mixed by a turbulence-creating device in the absence of a surface active agent, a temporary emulsion will form. If allowed to settle in a quiescent environment, the primary break will occur in seconds or a few minutes. A secondary emulsion, consisting of micron and submicron size droplets of the dispersed phase, will usually persist in one of the bulk phases. To separate the dispersed phase from such a dispersion it is necessary to coalesce the submicroscopic droplet into large ones of settleable size. One measure of the difficulty of the coalescence operation is the rest time of large drops at a flat interface between large volumes of the two phases. Recent reviews by Hartland (5) and Lawson (8) treat the theoretical and experimental aspects of the determination of rest time and its significance. In the present instance we are concerned not only with rest time criteria but with the effect of definable surface active agents upon them.

EXPERIMENTAL

The equipment used for the determination of drop rest time was slightly modified from that of Charles and Mason (1) and was similar to that used by others (2, 3, 4). An open-top cell design was used to facilitate construction, cleaning, and assembly. One of the two coalescent cells (6) was designed for using an organic continuous phase. The aqueous drops were allowed to fall to the interface. The other cell was so constructed that a light drop of an organic liquid could be released from a submerged nozzle and rise through a continuous aqueous phase to the interface. Provision was made for renewal of the interface by periodic flushing with the aqueous phase. The temperature of the water bath surrounding the cell was controlled to $\pm 0.5^\circ C.$ An electric timer was used to determine rest time. Its 0.01-second scale divisions were so spaced as to permit estimations of 0.001 second, although the accuracy of such an estimation was somewhat questionable. Drop volumes were measured with a microburet.

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The two cells are illustrated in Figure 1. The open top, A, was covered with clean hard paper during operation to prevent contamination. The continuous phase was contained in the central portion across the top of the inner cup, B, which was used for the renewal of the organic-aqueous interface. The side arm, C, permitted waste liquid to be removed from the cell. The drop was released from

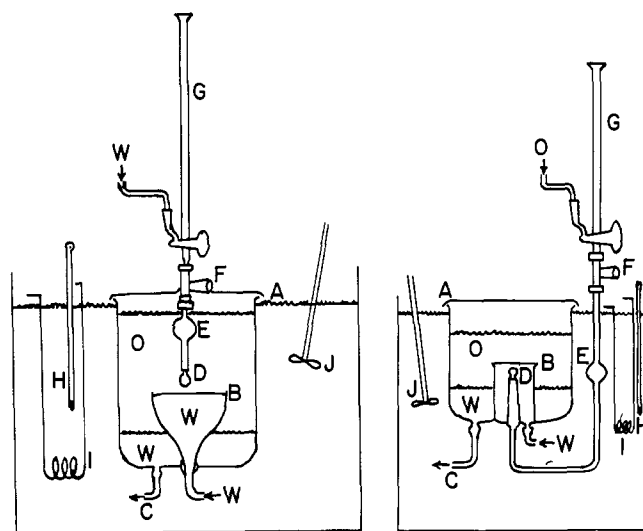


Figure 1. Diagram of coalescence cells

Left. Falling drop

Right. Rising drop

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|-----------------------------|----------------|
| A. Coalescence cell mouth | F. Micrometer |
| B. Continuous phase removal | G. Microburet |
| C. Waste liquid suction | H. Thermometer |
| D. Drop forming tip | I. Heater |
| E. Reservoir | J. Stirrer |