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THE TRIPLE POINT DEPRESSION CURVES FOR THE BINARY SYSTEMS TUNGSTEN HEXAFLUORIDE IN URANIUM HEXAFLUORIDE AND MOLYBDENUM HEXAFLUORIDE IN URANIUM HEXAFLUORIDE: THEIR APPLICATION TO METHODS OF ANALYSES

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Title: THE TRIPLE POINT DEPRESSION CURVES FOR THE BINARY SYSTEMS WF_6-UF_6 AND MoF_6-UF_6

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ABSTRACT

The triple point depression curves for the binary systems tungsten hexafluoride - uranium hexafluoride and molybdenum hexafluoride - uranium hexafluoride have been determined over the range of 100.0 to 98.5 mole percent uranium hexafluoride. The observed data are represented by the following general equations obtained by the least squares method:

$$WF_6\text{-}UF_6: \quad N_2 = (\Delta t)\exp[-4.2114 + 0.2001(R)]$$

$$MoF_6\text{-}UF_6: \quad N_2 = (\Delta t)\exp[-4.0357 + 0.0252(R)]$$

Where N_2 is the mole fraction of solute, (Δt) is the triple point depression in $^{\circ}C$, and R is the ratio of liquid volume to total volume.

The deviations resulting from non-ideality are discussed. Corrections for these deviations are applied by extrapolation of observed triple point depressions and ratios of liquid volume to total volume. A method is presented to estimate the liquid, gross, and vapor compositions.

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Triple point depression measurements offer a precise method for the determination of solutes in uranium hexafluoride. Several binary systems with uranium hexafluoride as the solvent have been previously studied (1, 2) to (a) provide a method for analyzing dilute solutions of solutes in uranium hexafluoride, and (b) to estimate the non-ideality of such solutions. This study provides this data for the binary systems tungsten hexafluoride in uranium hexafluoride and molybdenum hexafluoride in uranium hexafluoride.

SUMMARY

The triple point depressions, obtained by introducing progressive quantities of tungsten hexafluoride and molybdenum hexafluoride into individual containers of uranium hexafluoride, were used to provide data for a method of cryoscopic determination of the solutes in the binary systems. Dilute solutions in the solute range of 0.0 to 1.5 mole percent are described by the following general equation:

$$N_2 = (\Delta t)e^{-(a + bR)} \qquad \text{(Equation 1)}$$

Where N_2 is the mole fractions of solute

Δt is the triple point depression

R is the ratio of liquid volume to total volume.

For WF_6 as solute: a = 4.2114 and b = -0.2001.

For MoF_6 as solute: a = 4.0357 and b = -0.0252.

A method is presented to estimate the gross, liquid, and vapor compositions of the uranium hexafluoride binary systems.

EQUIPMENT

APPARATUS

Monel cylinders, 7.75 in. long by 1.61 in. inside diameter, equipped with small Hoke valves and thermistor wells (figure 1), were used as triple point cells.

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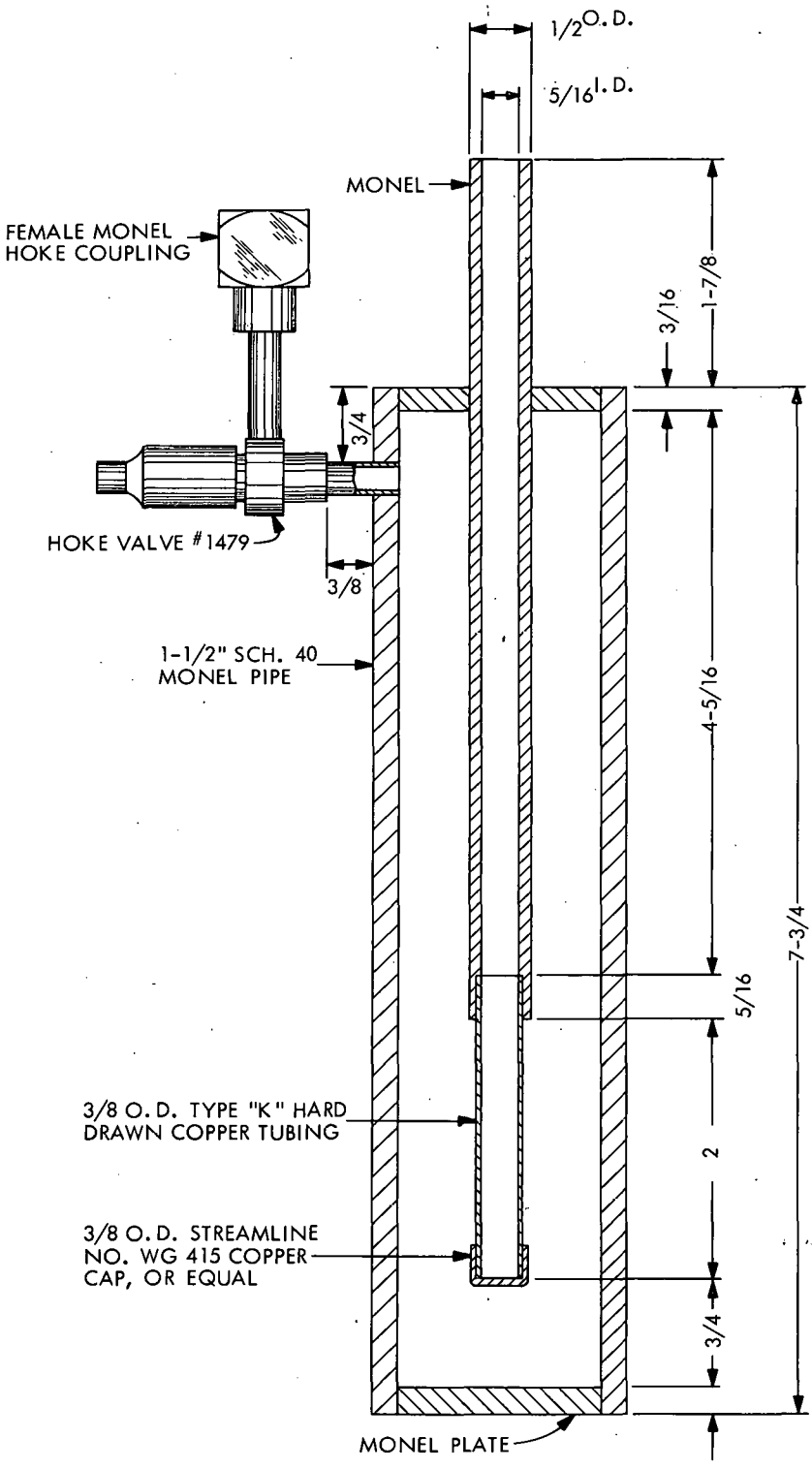

Figure 1

TRIPLE POINT CELL

The temperature measuring probes were thermistors attached by suitable electronics to a digital read-out tape (3). The thermistors were calibrated against a NBS certified platinum resistance thermometer.

A gas pipette was used to transfer milligram quantities of the solutes to the freezing point cells. The volume chamber of the pipette was fabricated of Monel, with copper tubing as transfer lines. The chamber had a volume of about one liter as calibrated with known quantities of tungsten hexafluoride and molybdenum hexafluoride. Pneumatic valves with neoprene gaskets were used in the transfer lines. The pressure was read from an automatic manometer with a digital Veeder-Root reader in conjunction with a 50 millimeter pressure transmitter. The pipette was enclosed in an insulated box maintained at 40°C (figure 2).

MATERIALS

Isotopically unaltered uranium hexafluoride was purified by vacuum transferring at ambient temperature to the triple point cells with a condensation temperature of 0°C. The triple point of the purified material was well within experimental error of 64.05°C, the triple point of pure UF_6 (4). Mass scan analysis of the purified material did not indicate any detectable impurities.

To separate the tungsten hexafluoride from nonvolatile material, the tungsten hexafluoride was successively distilled into receiving traps at -25°C. Continuous vacuum pumping on the traps removed noncondensable matter. The condensed tungsten hexafluoride was sampled and a triple point of 1.96 ± 0.05° was obtained, indicating no significant difference from the 2°C triple point of pure tungsten hexafluoride (5). Infrared and mass spectrometer scans of the purified material revealed no detectable impurities.

Molybdenum hexafluoride was purified by the above procedure used for tungsten hexafluoride, except that the receiving traps were maintained at 0°C. A triple point of 17.4 ± 0.09°C was obtained, and may be compared to the 17.4°C triple point of pure molybdenum hexafluoride (5). No detectable impurities were revealed by infrared and mass spectrometer scanning.

EXPERIMENTAL AND PROCEDURE

PREPARING THE SOLUTION

The triple point of the uranium hexafluoride in each triple point cell was measured to confirm the purity of the solvent. Each cell was individually attached to the outlet line of the gas pipette and cooled to about -190°C with liquid nitrogen. The pipette chamber and transfer lines were evacuated to less than 50×10^{-3} torr. The solute was introduced to the isolated pipette chamber to the desired pressure, and subsequently condensed into the triple point cell. The quantity of solute condensed was calculated from the pressure change and known volume of

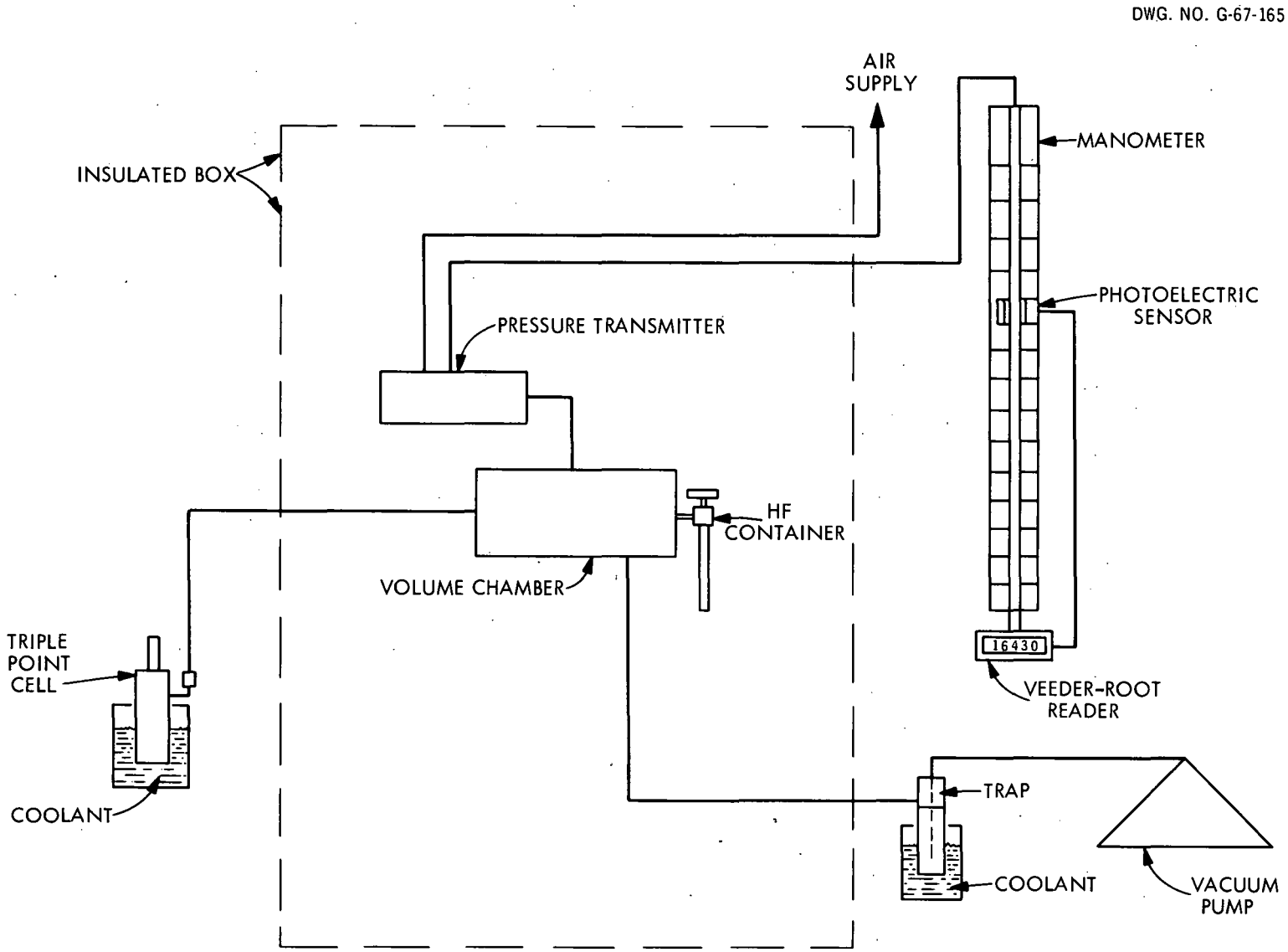

Figure 2
AUTOMATIC GAS PIPETTE

the pipette. The procedure was followed for each data point.

MEASURING THE TRIPLE POINTS

Two ml of mineral oil were placed in the thermowell of the triple point cell to act as the heat transfer agent between the thermowell and the thermistor. The triple point cell was placed in a constant temperature bath previously adjusted to a temperature about 0.3°C below the expected triple point. The cooling curve was followed as the temperature decreased. When the uranium hexafluoride solution supercooled, the cell was tapped to start crystallization. The temperature readings were recorded every minute by the digital printer.

RESULTS

Table I lists the accumulated grams of tungsten hexafluoride introduced into the uranium hexafluoride, the triple points of the various solutions with corresponding 95% confidence limits, and the cumulative mole fraction, weight percent, and triple point depressions for each of the three cells containing 360 g, 535 g, and 693 g of uranium hexafluoride, respectively, with tungsten hexafluoride as the solute. Figure 3 is a plot of the mole fractions of tungsten hexafluoride versus the triple point depression. The three curves in figure 3 are described by the following equations:

360 g: $\Delta t = N_2 e^{4.124}$ (Equation 2)

535 g: $\Delta t = N_2 e^{4.082}$ (Equation 3)

693 g: $\Delta t = N_2 e^{4.044}$ (Equation 4)

Where Δt is the triple point depression, and

N_2 is the corresponding mole fractions of tungsten hexafluoride.

Table II lists the aforementioned information for the three cells containing 325 g, 465 g, and 636 g of uranium hexafluoride, respectively, with molybdenum hexafluoride as the solute. Figure 4 is a plot of the mole fraction of molybdenum hexafluoride versus the triple point depression. The three curves in figure 4 are described by the following equations:

325 g: $\Delta t = N_2 e^{4.026}$ (Equation 5)

465 g: $\Delta t = N_2 e^{4.022}$ (Equation 6)

636 g: $\Delta t = N_2 e^{4.016}$ (Equation 7)

TABLE I

TRIPLE POINT DEPRESSION OF URANIUM HEXAFLUORIDE WITH TUNGSTEN HEXAFLUORIDE

Cylinder	New Weight UF_6, g	Ratio of Liquid Volume to Total Volume	Cumulative Grams of WF_6 Added	Cumulative Weight Percent WF_6	Cumulative Mole Fraction WF_6	Δt (°C)	95% C.L.	Number of Triple Point Determinations
225-6	360	0.436	0.0000	0.000	0.00000	0.000	± 0.009	4
			0.2756	0.076	0.00090	0.062	± 0.009	4
			0.9614	0.266	0.00315	0.190	± 0.017	4
			1.4671	0.406	0.00479	0.300	± 0.022	4
			2.2042	0.609	0.00718	0.431	± 0.009	4
			3.0546	0.841	0.00993	0.583	± 0.044	5
			3.7202	1.023	0.01206	0.733	± 0.027	8
225-17	535	0.648	0.0000	0.000	0.00000	0.000	± 0.009	4
			0.6988	0.130	0.00204	0.117	± 0.017	4
			1.8751	0.349	0.00462	0.270	± 0.035	4
			3.0856	0.573	0.00727	0.434	± 0.035	4
			3.7998	0.705	0.00882	0.539	± 0.037	4
			4.9717	0.921	0.01136	0.652	± 0.033	5
			6.0307	1.115	0.01365	0.825	± 0.041	7
225-1	693	0.839	0.0000	0.000	0.00000	0.000	± 0.001	4
			1.1030	0.159	0.00188	0.108	± 0.013	4
			2.4222	0.348	0.00411	0.236	± 0.013	4
			3.8492	0.552	0.00652	0.375	± 0.022	4
			5.5406	0.793	0.00936	0.527	± 0.034	4
			7.0562	1.008	0.01189	0.700	± 0.022	5
			8.2989	1.183	0.01395	0.771	± 0.012	7

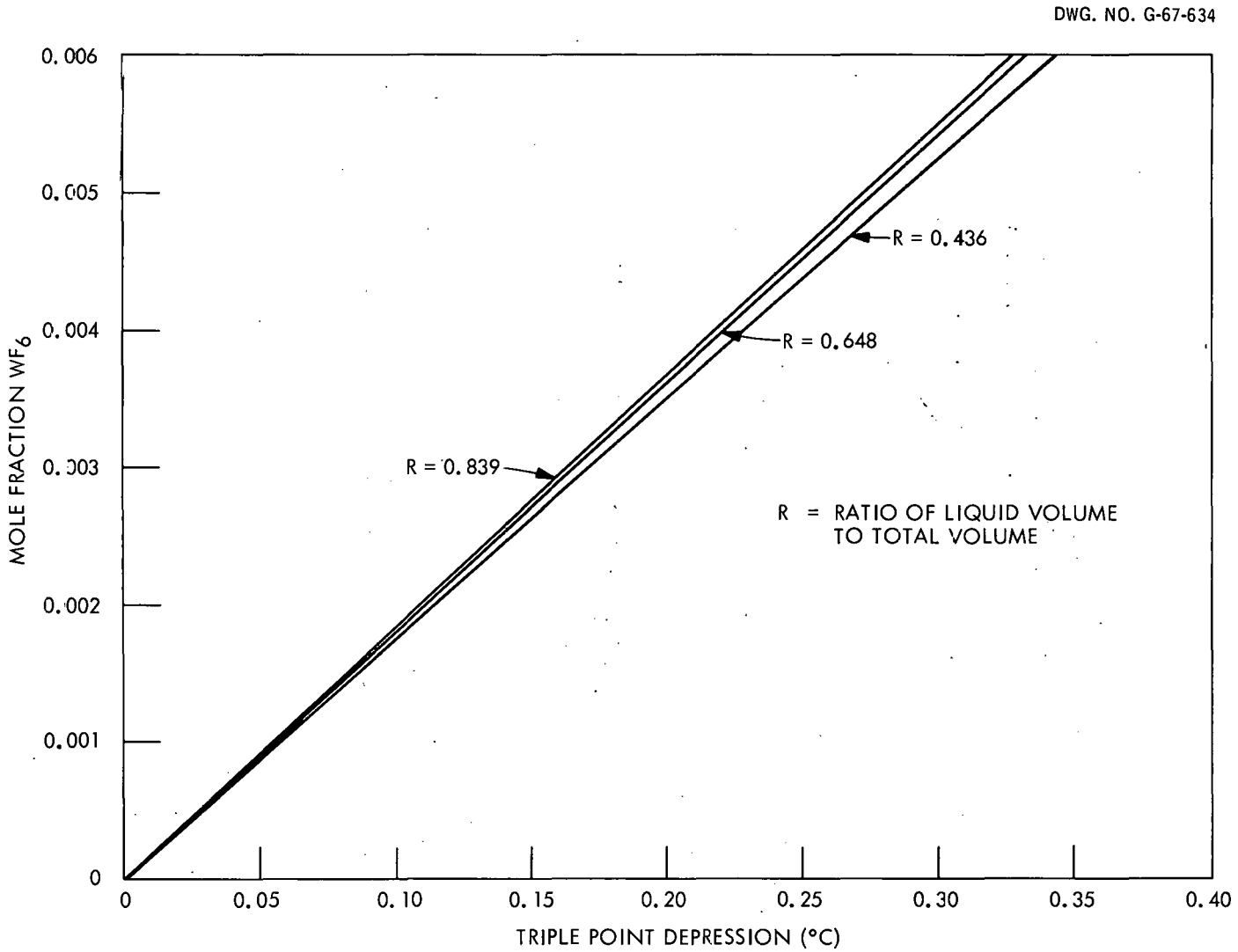

Figure 3

TRIPLE POINT CURVES FOR THE BINARY SYSTEM UF_6-WF_6

TABLE II

TRIPLE POINT DEPRESSION OF URANIUM HEXAFLUORIDE WITH MOLYBDENUM HEXAFLUORIDE

Cylinder	Net Weight UF_6, g	Ratio of Liquid Volume to Total Volume	Cumulative Grams of MoF_6 Added	Cumulative Weight Percent MoF_6	Cumulative Mole Fraction MoF_6	Δt (°C)	95% C.L.	Number of Triple Point Determinations
225-13	325	0.393	0.0000	0.000	0.00000	0.000	± 0.022	4
			0.4446	0.137	0.00229	0.125	± 0.009	5
			0.6357	0.195	0.00327	0.180	± 0.009	5
			0.8332	0.256	0.00428	0.251	± 0.012	4
			1.1072	0.340	0.00567	0.327	± 0.014	5
			1.3518	0.414	0.00692	0.390	± 0.012	5
225-15	465	0.564	0.0000	0.000	0.00000	0.000	± 0.012	4
			0.3492	0.075	0.00185	0.102	± 0.012	5
			0.7380	0.158	0.00324	0.184	± 0.012	5
			1.0915	0.234	0.00451	0.248	± 0.009	4
			1.4385	0.308	0.00575	0.311	± 0.016	5
			1.7927	0.384	0.00701	0.380	± 0.015	5
225-14	636	0.771	0.0000	0.000	0.00000	0.000	± 0.013	4
			0.5146	0.081	0.00135	0.078	± 0.006	5
			1.2602	0.198	0.00331	0.187	± 0.009	5
			1.8068	0.283	0.00474	0.259	± 0.009	4
			2.3393	0.366	0.00613	0.338	± 0.015	5
			3.1038	0.486	0.00812	0.448	± 0.006	5

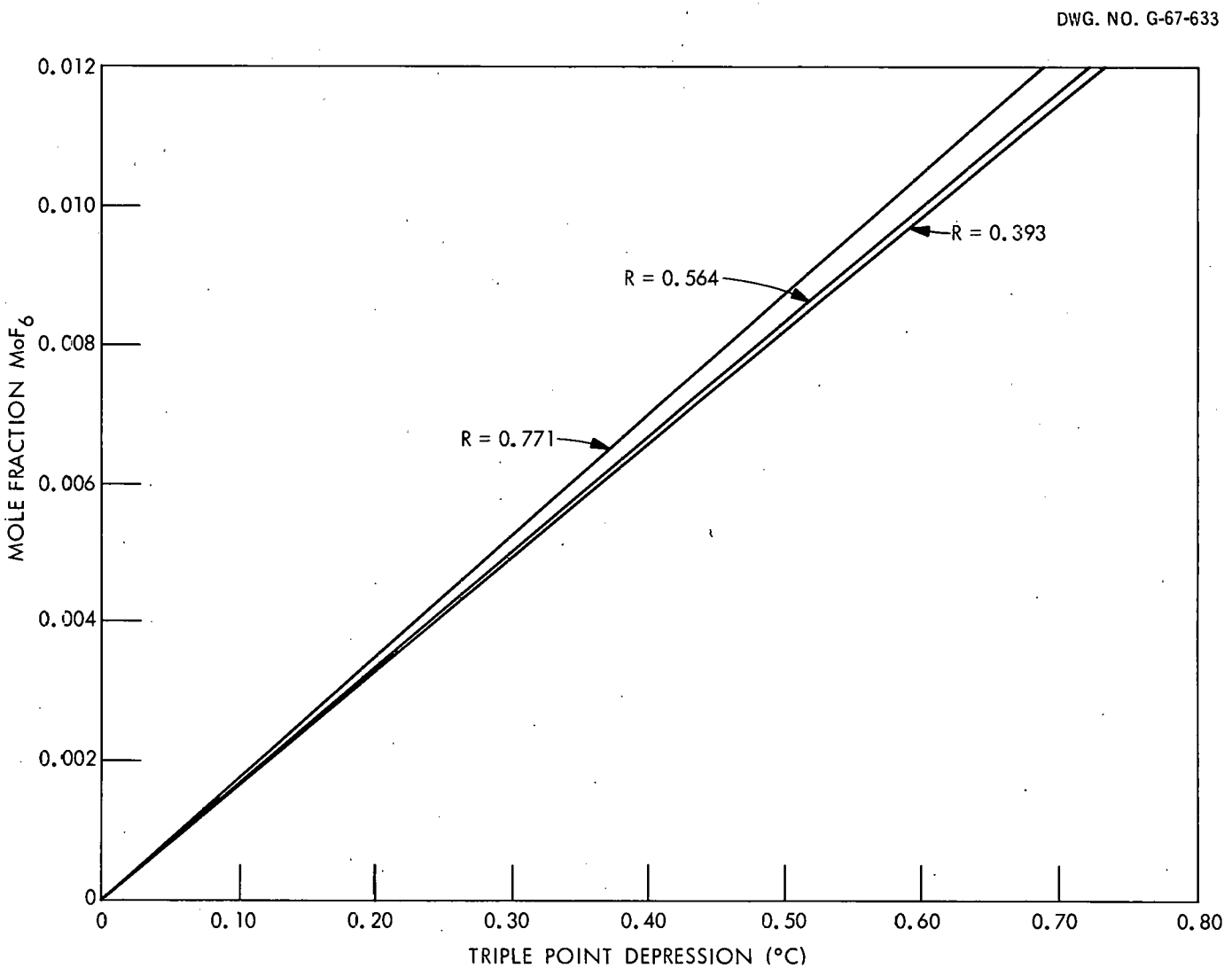

Figure 4

TRIPLE POINT CURVES FOR THE UF_6-MoF_6 BINARY SYSTEM

DISCUSSION

The three curves in each of figure 3 and figure 4 indicate that the two binary systems studied are non-ideal. If the solution were ideal in behavior, only one curve would have been obtained for each, and they would have been identical to each other and to the molal triple point depression curve of uranium hexafluoride. The differences between the curves represent the magnitude of the non-ideality. To determine the triple point constants obtained for uranium hexafluoride by each of the solutes for all ratios of liquid volume to total volume, the curves of figures 3 and 4 need be extrapolated to a ratio of liquid volume to total volume of one. This ratio would represent a cell containing all liquid with no vapor volume.

Using the ratios of liquid volume to total volume and the equations representing each of the three different cells for each solute, the mole fraction of solute was expressed as a function of the triple point depression and the ratio of liquid volume to total volume. The following equations represent this function for each of the solutes:

$$WF_6: \quad N_2 = (\Delta t)\exp[-4.2114 + 0.2001(R)] \qquad \text{(Equation 8)}$$

$$MoF_6: \quad N_2 = (\Delta t)\exp[-4.0357 + 0.0252(R)] \qquad \text{(Equation 9)}$$

Where N_2 is the mole fraction of solute

Δt is the triple point depression

R is the ratio of liquid volume to total volume.

Thus, by substituting a value of R = 1.0 into the above equations, equations are determined for a cylinder containing all liquid and no vapor volume. These are:

$$WF_6: \quad N_2 = (\Delta t)e^{-4.0113} \qquad \text{(Equation 10)}$$

$$MoF_6: \quad N_2 = (\Delta t)e^{-4.0105} \qquad \text{(Equation 11)}$$

Application to a Method of Analysis

The relationship of the curves in figures 3 and 4 indicate that the composition of the vapor phase is relatively richer in solvent than is the composition of the liquid phase for both systems observed in this study. To obtain the gross composition of such solutions, the disparity in the vapor and liquid compositions must be considered. For example, the same triple point depression would yield a gross composition dependent upon the quantity of solution present in a given cell; and in withdrawing liquid samples from such solutions, the samples would represent only the liquid composition. The normal analytical situation usually involves the analysis for the gross compositions, and the triple point curves provide a base for estimating gross compositions.

A cell with a total volume of 225 ml, and containing 700 grams of uranium hexafluoride-molybdenum hexafluoride solution, has a triple point depression of 0.60°C. The ratio of liquid volume to total volume is

$$R = \frac{G}{dV} \qquad \text{(Equation 12)}$$

Where R is the ratio of liquid volume to total volume

G is the grams of solution

d is the density of solution

V is the total volume of the container.

Thus, R = 700/(3.67)(225) = 0.85, assuming the solute does not alter the density of the solvent. The dashed lines in figure 5A represent this solution. The dashed horizontal line from $\Delta t = 0.60°C$ represents the triple point depression of the solution. The intersection of this horizontal line with the curve R = 1.0 (calculated from equation 11) is the liquid composition: 0.0109 mole fraction molybdenum hexafluoride. The intersection with the curve R = 0.85 (calculated from equation 9) is the gross composition: 0.0108 mole fraction. The intersection with the curve R = 0.0 (calculated from equation 9 with R = 0.0) is the vapor composition: 0.0106 mole fraction.

Once a liquid sample is withdrawn from such a system as represented in figure 5A, the compositions of the different phases of the remaining material readjust to the new conditions. Thus if 400 grams of solution were withdrawn as a liquid, the new ratio of liquid volume to total volume would be

$$R = 300/(3.67)(225) = 0.36.$$

The compositions of the liquid and vapor phases, and the gross compositions may be estimated from the following procedure represented in the half-tone overlay figure 5B. From the intersection of triple point depression (0.60°C) with the curve R = 0.36, extend a line parallel to the triple point depression axis to an intersection with the curve R = 0.85. From this latter intersection, generate a line parallel to the mole fraction axis. The intersection of this latter line with the curve R = 1.0 is the new liquid composition: 0.0108 mole fraction molybdenum hexafluoride. The intersection with the curve R = 0.36 is the new gross composition: 0.0106 mole fraction, and the intersection with the curve R = 0.0 is the new vapor composition: 0.0105 mole fraction.

This graphical procedure may be mathematically obtained from the following substitutions in equation 9. Substitute the new ratio of liquid volume to total volume (R = 0.36) into the equation using the same triple point depression ($\Delta t = 0.60$) as in the gross composition as before liquid sampling, and solve for N_2, the mole fraction of molybdenum hexafluoride.

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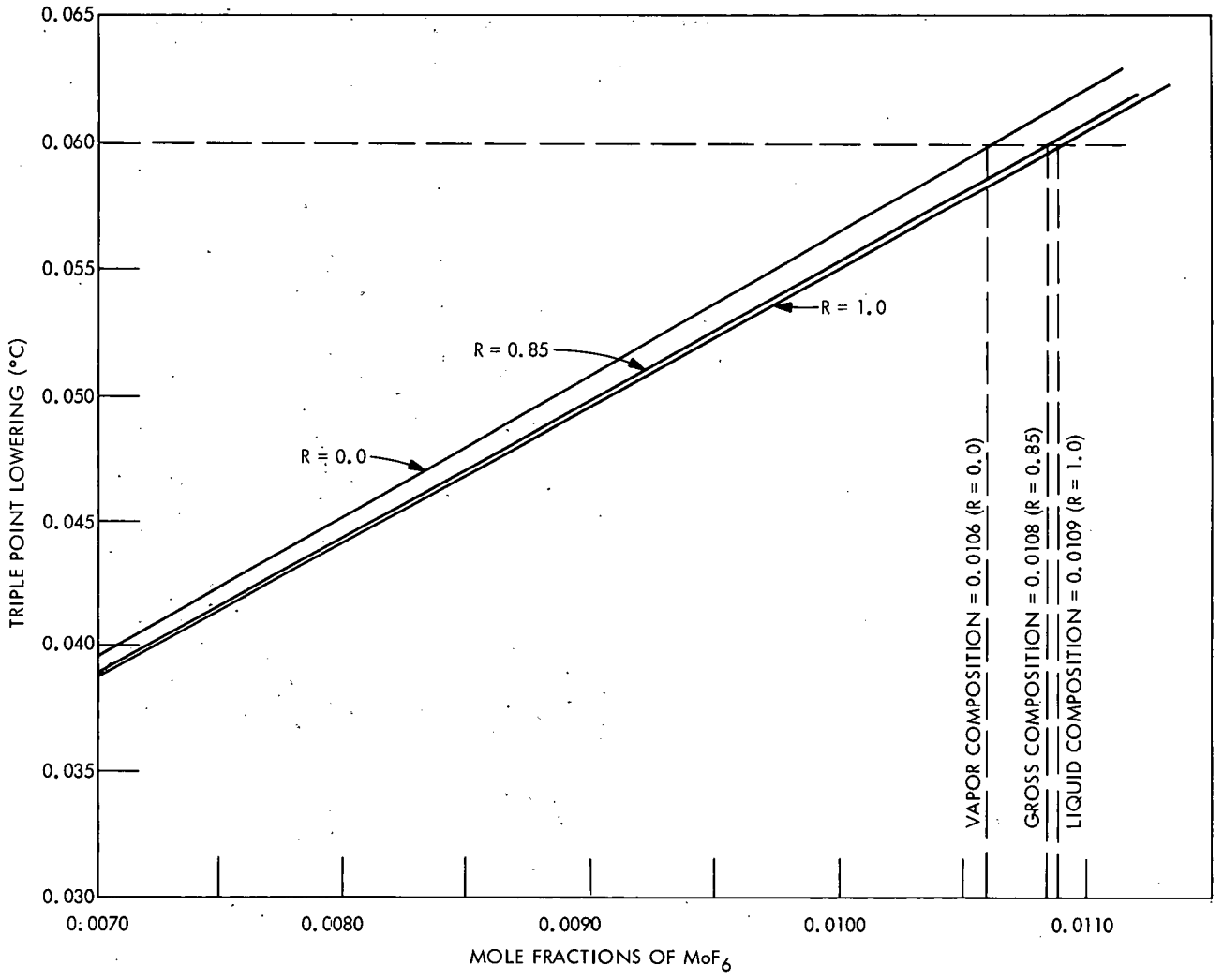

Figure 5A

GROSS, VAPOR, AND LIQUID COMPOSITION OF THE SYSTEM UF_6-MoF_6

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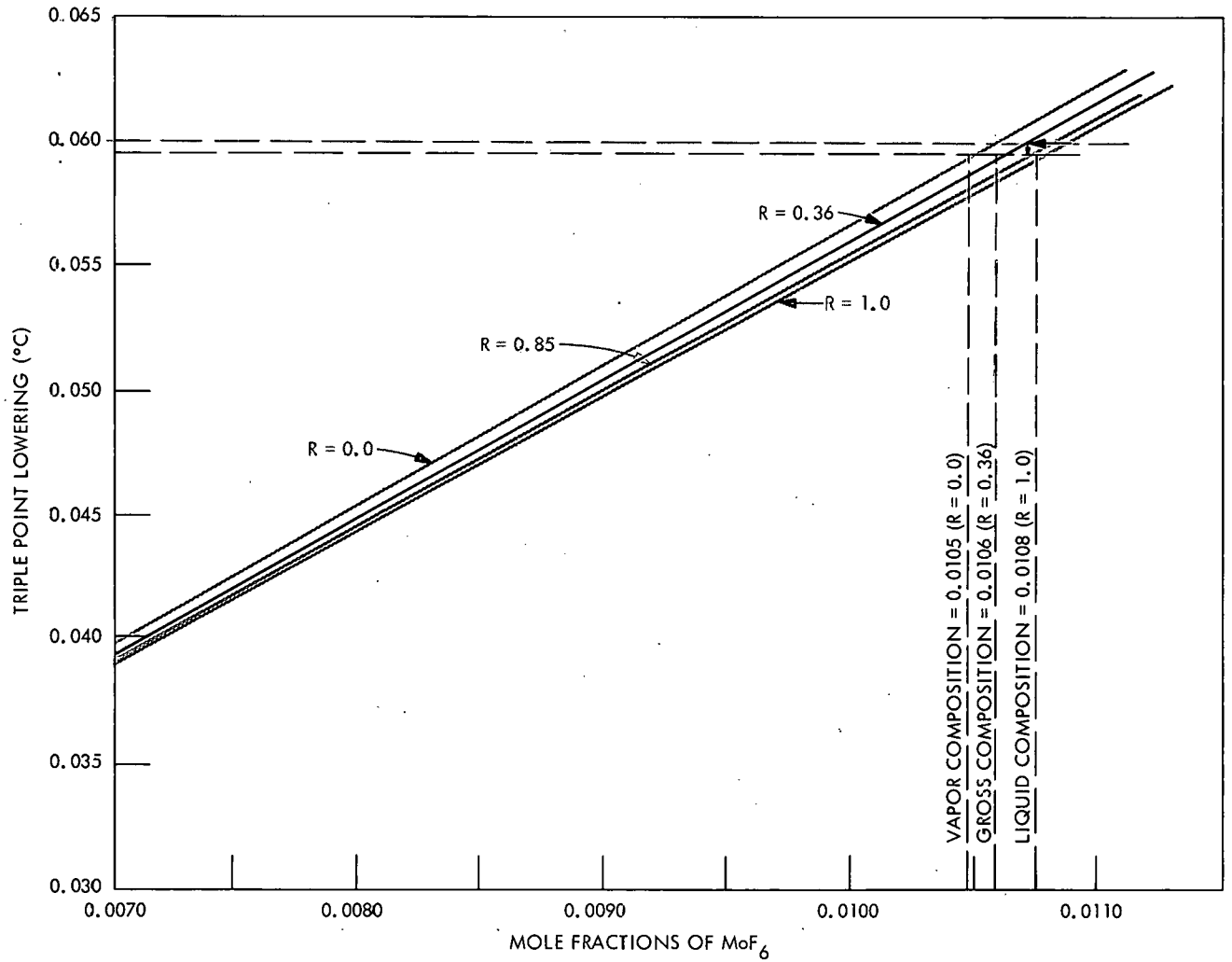

Figure 5B

GROSS, VAPOR, AND LIQUID COMPOSITION OF THE SYSTEM UF_6-MoF_6

$$N_2 = (0.60)\exp[-4.0357 + (0.0252)(0.36)]$$

$$N_2 = 0.0107$$

Substitute this new N_2 and compute a new Δt at R = 0.85,

$$0.0107 = (\Delta t)\exp[-4.0357 + (0.0252)(0.85)]$$

$$\Delta t = 0.592$$

This is the new calculated triple point depression of the solution. Substitute this new Δt into equation 9 with applicable liquid volume to total volume ratios (R = 1.0, R = 0.36, and R = 0.0) and solve for the liquid, gross, and vapor compositions respectively. Thus the new liquid composition would now be 0.0108 mole fraction molybdenum hexafluoride, the new gross composition would be 0.0106 mole fraction, and the new vapor composition would be 0.0105 mole fraction.

Figure 6 is a graphic presentation of the expected gross, liquid, and vapor compositions of a typical uranium hexafluoride-molybdenum hexafluoride binary solution. Note that when the ratio of liquid volume to total volume equals one (all liquid), the gross and liquid compositions are equal. When the ratio of liquid volume to total volume equals zero (all vapor), the gross and vapor compositions are equal.

Identical procedures may be applied to the system uranium hexafluoride-tungsten hexafluoride using the appropriate equations (equations 8 and 10).

ACKNOWLEDGEMENTS

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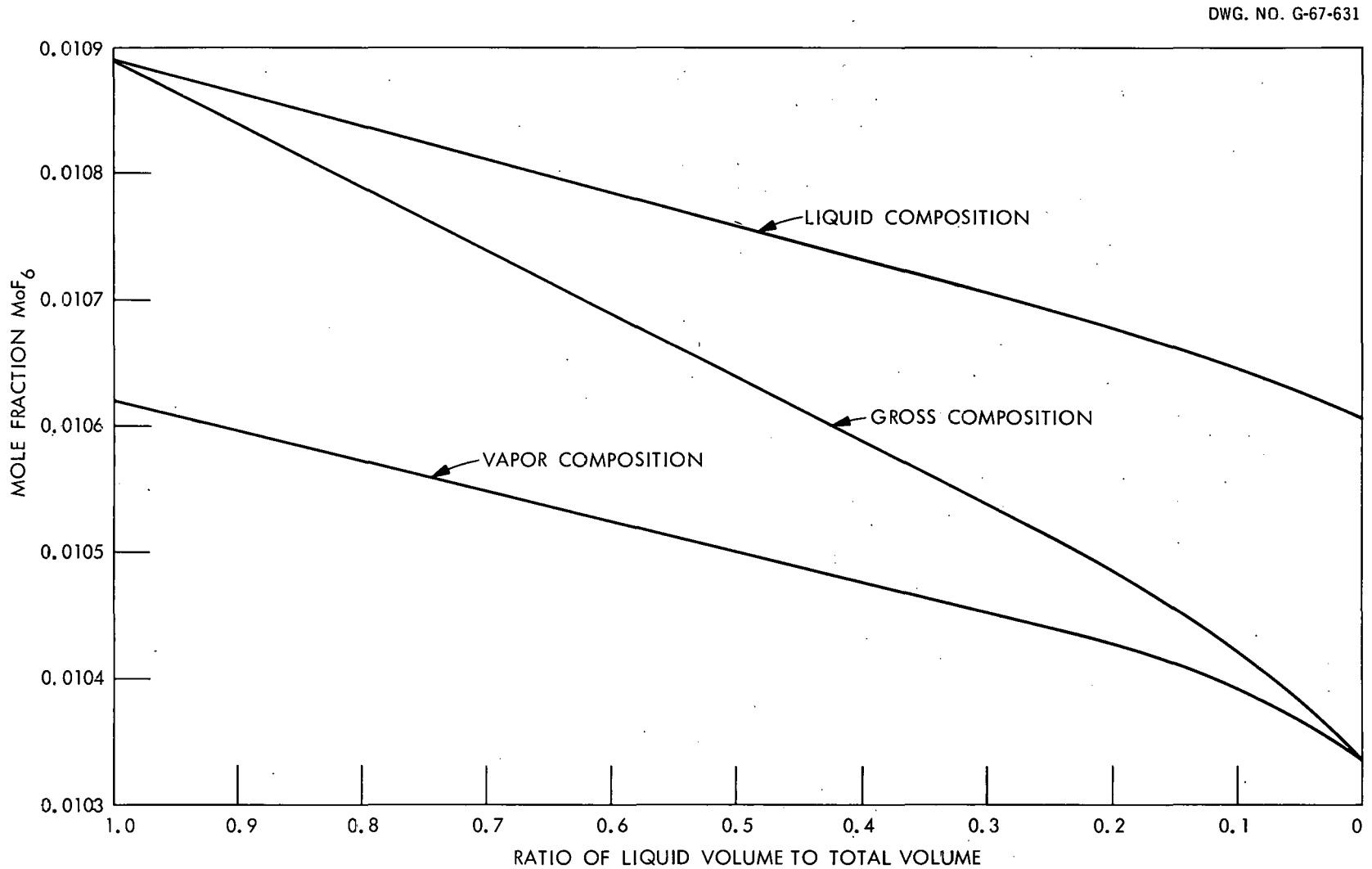

Figure 6

MOLE FRACTION MOLYBDENUM HEXAFLUORIDE DISTRIBUTION FOR THE SYSTEM UF_6-MoF_6 CONTAINING 0.0108 MOLE FRACTION MoF_6

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