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THE MOLYBDENUM HEXAFLUORIDE-HYDROGEN FLUORIDE TRIPLE POINT CURVE AND ITS APPLICATION TO A METHOD OF ANALYSIS

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Report Number: K-1698   Subject Category: CHEMISTRY

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         HYDROGEN FLUORIDE TRIPLE POINT
         CURVE AND ITS APPLICATION TO A
         METHOD OF ANALYSIS

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ABSTRACT

The triple point curve for the binary system molybdenum hexafluoride-hydrogen fluoride has been determined over the range of 0.0 to 5.0 mole percent hydrogen fluoride. This system is represented by the following general equation:

$$\Delta t = A(N_2) + B(N_2)^2 + C(N_2)^3$$

where Δt is the depression of the triple point of pure molybdenum hexafluoride in degrees centigrade, N_2 is the mole fraction of hydrogen fluoride, and A, B, and C are constants with

$$A = 159.86 - 129.19(R) + 36.44(R)^2$$

$$B = -3624.5 + 2965.0(R) - 407.5(R)^2$$

$$C = 26239.0 - 17875.0(R) - 1796.2(R)^2$$

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 as represented by the above general equation. A method is also presented to estimate the liquid, gross, and vapor compositions.

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THE MOLYBDENUM HEXAFLUORIDE-HYDROGEN FLUORIDE TRIPLE POINT CURVE AND ITS APPLICATION TO A METHOD OF ANALYSIS

A nondestructive analytical method was needed to measure the purity of molybdenum hexafluoride. Since hydrogen fluoride was the major impurity encountered in this laboratory, cryoscopic analyses appeared to be the most promising. Preliminary calculations from the heat of fusion of molybdenum hexafluoride (1) indicate that the molal freezing (triple) point constant is $38.3^{\circ}C$ per mole of hydrogen fluoride per 1000 grams of molybdenum hexafluoride, assuming an ideal solution. The purpose of this study is to provide a nondestructive method of analysis for molybdenum hexafluoride.

SUMMARY

The triple point curve for the binary system molybdenum hexafluoride-hydrogen fluoride has been determined over the range of 0.0 to 5.0 mole percent hydrogen fluoride. This system is represented by the following equation:

$$\Delta t = 67.11(N_2) - 1067.0(N_2)^2 + 6567.8(N_2)^3 \qquad \text{(Equation 1)}$$

where Δt is the triple point depression of pure molybdenum hexafluoride in degrees centigrade, and N_2 is the mole fraction of hydrogen fluoride.

A method is presented for correcting the deviations resulting from non-ideality of the binary system. Extensions of the observed triple point depressions of different ratios of liquid volume to total volume are represented by the following equation:

$$\Delta t = A(N_2) + B(N_2)^2 + C(N_2)^3 \qquad \text{(Equation 2)}$$

where $A = 159.86 - 129.19(R) + 36.44(R)^2$

$B = -3624.5 + 2965.0(R) - 407.5(R)^2$

$C = 26239.0 - 17875.0(R) - 1796.2(R)^2$, and

Δt is the triple point depression of molybdenum hexafluoride

and N_2 is the mole fraction of hydrogen fluoride

R is the ratio of liquid volume to total volume.

EQUIPMENT

APPARATUS

A 50 ml triple point cell (figure 1) was used to contain the solution. It was a 4-1/2-inch Monel cylinder, 1-5/16-inch-diameter, with a small

DWG. NO. G-67-149

1/2 O.D.

5/16 I.D.

MONEL

FEMALE MONEL
HOKE COUPLING

1-7/8

3/4

3/16

HOKE VALVE #1479

3/8

1-5/16

1" SCH. 40 MONEL PIPE

5/16

3/8 O.D. TYPE "K" HARD
DRAWN COPPER TUBING

4-1/2

2

3/8 O.D. STREAMLINE NO. WG
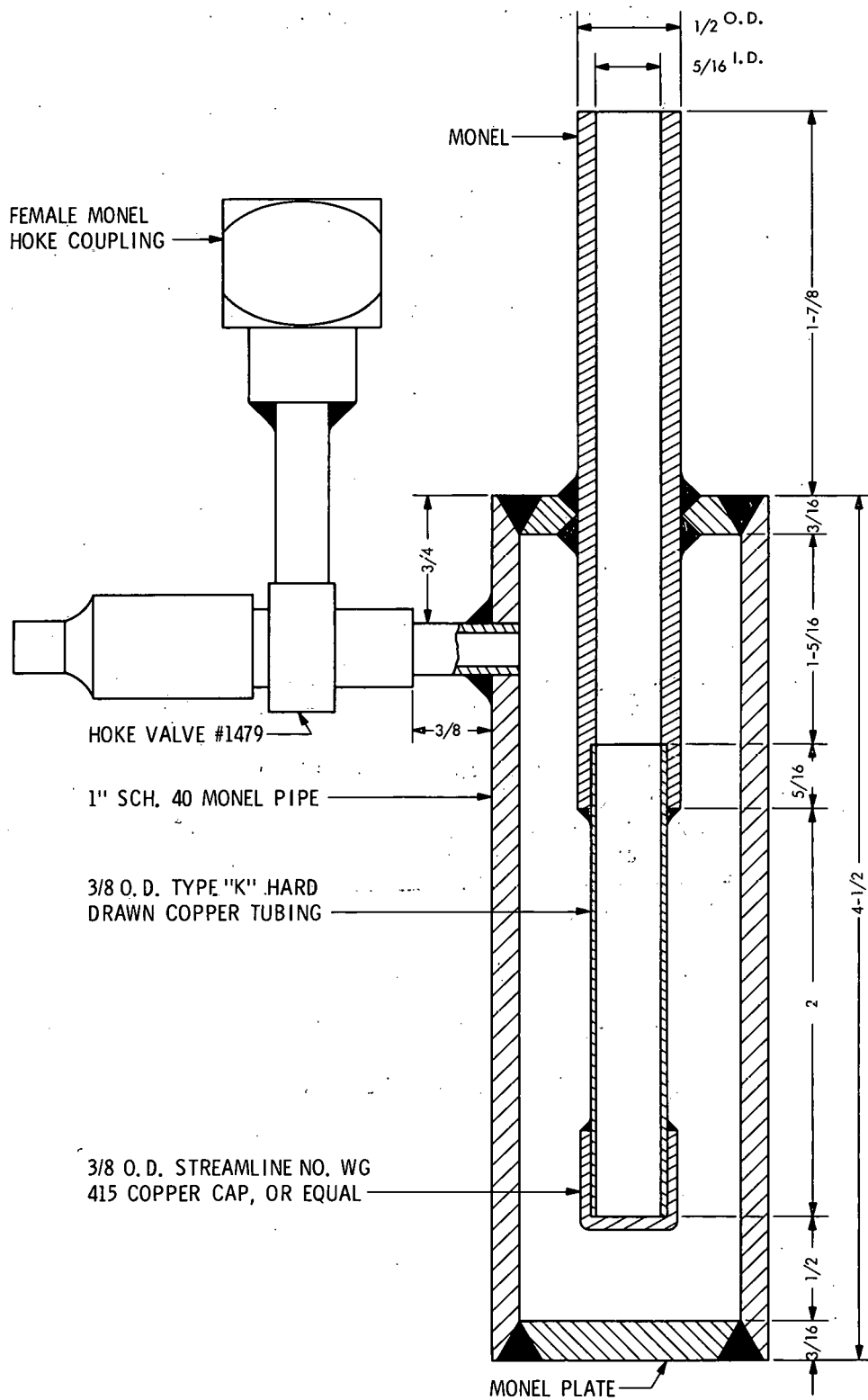415 COPPER CAP, OR EQUAL

1/2

MONEL PLATE

3/16

Figure 1
TRIPLE POINT CELL

Hoke valve silver-soldered near the top. A 3/8-inch-diameter thermowell extended through the top of the cylinder to within 1/2 inch of the bottom. The top half of the thermowell was made of Monel and the bottom half was made of copper tubing. The thermowell was closed inside the cell with a 3/8-inch copper cap.

A calibrated gas pipette (figure 2) was used to dilute the molybdenum hexafluoride with milligram quantities of hydrogen fluoride. The pipette had a volume of about one liter, and was made of Monel with copper tubing as transfer lines. 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. An insulated box was maintained at $104^\circ C$, and enclosed the volume chamber, valves, transmitter, hydrogen fluoride container, and all transfer lines (except the output line). The pipetted hydrogen fluoride was condensed into the 50 ml triple point cells at liquid nitrogen condensation temperatures (about $-190^\circ C$).

The freezing point bath was a stainless steel container enclosed in about an inch of Styrofoam with a split Styrofoam cover. The bath solution was a 1:1 mixture of isopropyl alcohol and water, and was maintained at about $0.3^\circ C$ below the expected triple points. A thyratron control panel was used to control a variable speed circulating pump. The thyratron tube was activated by temperature changes of $\pm 0.05^\circ C$ sensed with a thermistor inserted in the bath. A verneir was used to set the desired bath temperature. A motor-driven propeller, manually controlled by a transformer, circulated the solution in the bath (figure 3).

Temperature measurements were obtained using a ten-junction, copper-constantan thermocouple that was calibrated against a certified platinum resistance thermometer. Melting distilled water ice was used as the reference junction for the thermocouple. The emf produced was measured on a Leeds and Northrup potentiometer using an Electronik null point indicator. A standard calomel cell was used as a reference for the bridge circuit of the potentiometer.

MATERIALS

To separate the molybdenum hexafluoride from nonvolatile material, the molybdenum hexafluoride was distilled into a receiving trap maintained at $0^\circ C$. Continuous vacuum pumping on the trap removed noncondensable matter. The condensed molybdenum hexafluoride was sampled and a triple point of $17.4 \pm 0.09^\circ C$ was obtained, indicating no significant difference from the $17.4^\circ C$ triple point of pure molybdenum hexafluoride (2). Infra-red and mass spectrometer scans of the purified material revealed no detectable impurities. A molal freezing (triple) point constant of $19.3^\circ C$ per mole of molybdenum hexafluoride per 1000 grams of uranium hexafluoride, compared to the established constant of $19.2 \pm 0.7^\circ C$ (3), was obtained, which indicated pure molybdenum hexafluoride.

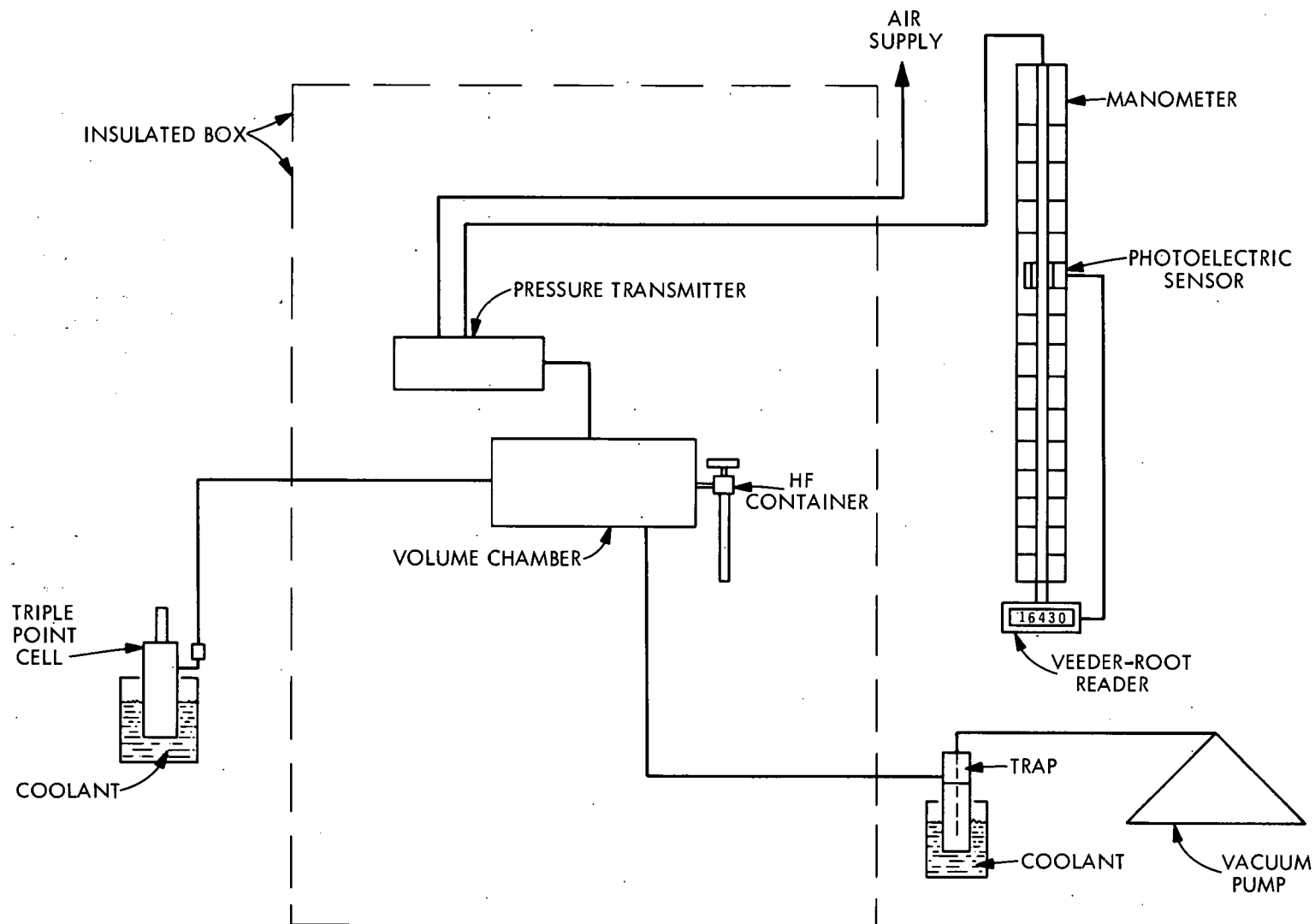Anhydrous hydrogen fluoride was prepared by selective sorption on sodium fluoride pellets.
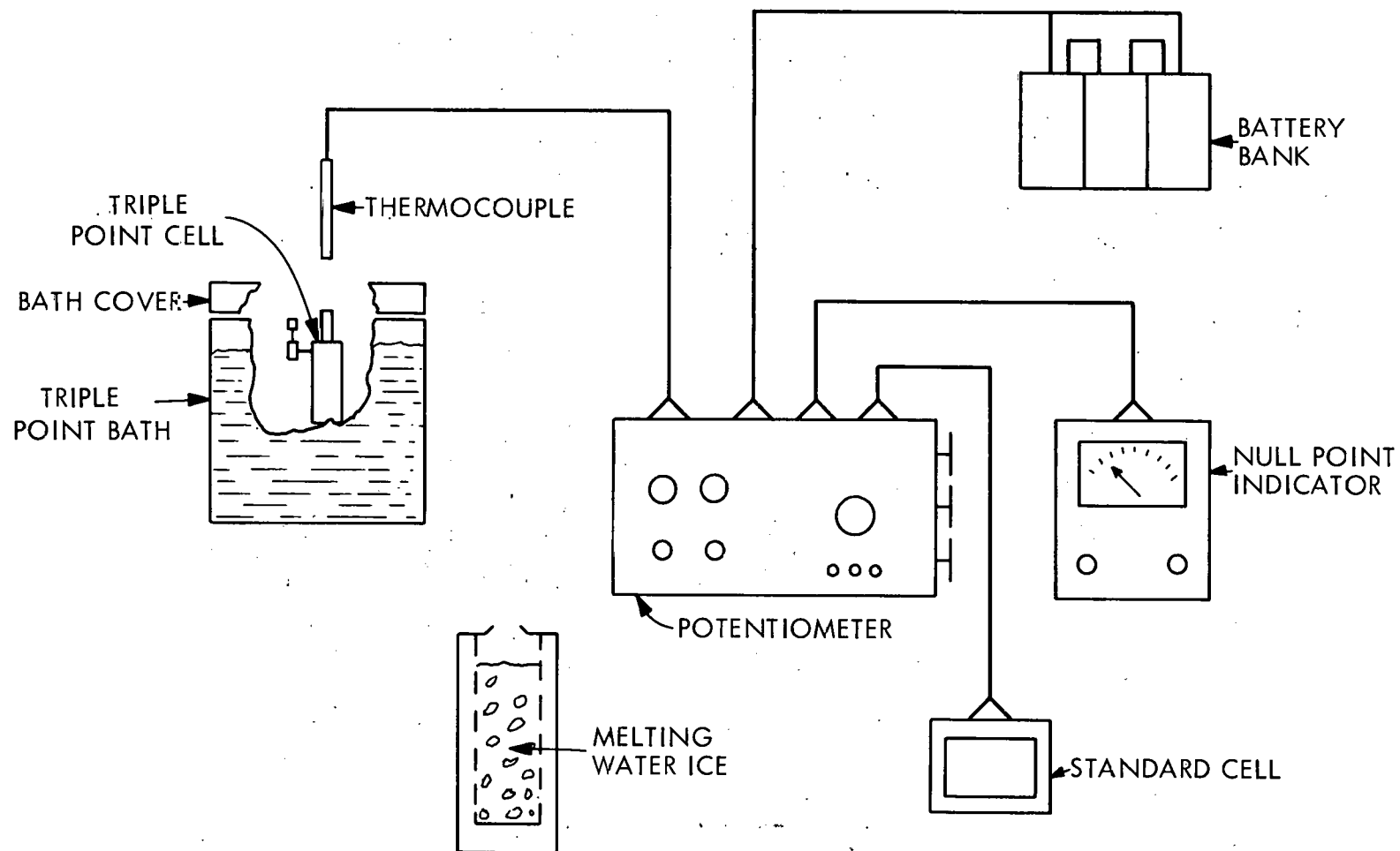
Figure 2
AUTOMATIC GAS PIPETTE

Figure 3

TRIPLE POINT MEASUREMENT ASSEMBLY

EXPERIMENTAL AND PROCEDURE

Preparing the Solutions

The triple point of the molybdenum hexafluoride in each of the triple point cells was measured to confirm the purity of the solvent. The individual triple point cells contained the following quantities of molybdenum hexafluoride: FP-39 contained 36.5 grams; FP-47, 66.5 grams; FP-5, 95.3 grams. Each cell was individually attached to the fitting on the outlet line of the gas pipette. Liquid nitrogen was placed around the cell, and the cell permitted to cool to about -190°C. The pipette chamber and transfer lines were evacuated to less than 50×10^{-3} torr. Hydrogen fluoride was then introduced to the isolated volume chamber of the pipette to a desired pressure, and subsequently condensed into the triple point cell. The quantity of condensed hydrogen fluoride was calculated from the pressure change and known volume of the pipette. The procedure was followed for each data point.

Measuring the Triple Points

Two ml of bath solution were placed in the thermowell of the freezing point cell to act as the heat transfer agent between the thermowell and the thermocouple. The triple point cell was placed in the constant temperature cooling bath previously adjusted to a temperature slightly (about 0.3°C) below the expected triple point. The cooling curve was followed as the temperature decreased. When the molybdenum hexafluoride solution supercooled, the cell was tapped to start crystallization. Figure 4 is a representative triple point curve obtained in this manner.

Data

Table I contains the following data per point for FP-39, FP-47, and FP-5: the cumulative grams of hydrogen fluoride added to the triple point cells, the cumulative weight percent and mole fraction of hydrogen fluoride in the triple point cells, the triple point depression (Δt), the confidence limit of the temperature measurement, and the number of determinations per point. The data were fitted to a general parabolic least squares equation on an IBM 7090 computer. The equations in table II were so obtained.

Figure 5 is a plot of the mole fractions of hydrogen fluoride in molybdenum hexafluoride (N_2) versus the triple point depression (Δt) as calculated from the equations in table II.
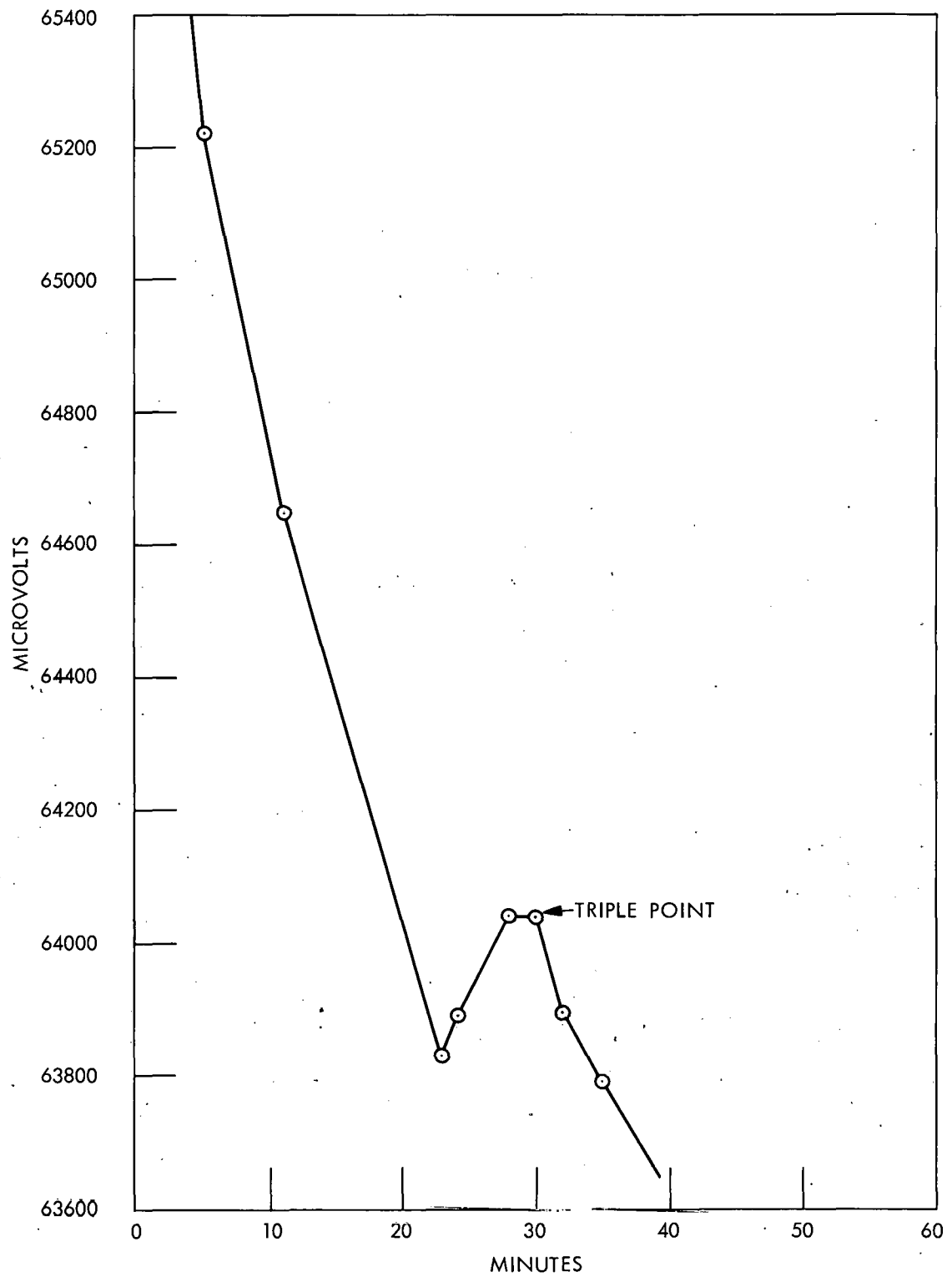
Figure 4

TYPICAL TRIPLE POINT CURVE

TABLE I

THE LOWERING OF THE MOLYBDENUM HEXAFLUORIDE TRIPLE POINT WITH HYDROGEN FLUORIDE

Cylinder Number	Net Weight MoF$_6$, g	Cumulative Grams of HF Added	Cumulative Weight Percent HF	Cumulative Mole Fraction HF	Δt (°C)	95% C.L.	Number of Triple Point Determinations
FP-39	36.5	0.0000	0.000	0.00000	0.000	± 0.019	7
		0 0208	0.057	0.00595	0.590	± 0.077	6
	R = 0.286*	0.0426	0.117	0.01211	1.019	± 0.035	7
		0.0469	0.128	0.01331	1.331	± 0.047	7
		0.0693	0.190	0.01955	1.662	± 0.051	7
		0.0937	0.256	0.02598	1.739	± 0.039	8
		0.1302	0.355	0.03610	1.744	± 0.023	8
		0.1726	0.471	0.04731	1.975	± 0.038	9
		0.2163	0.589	0.05858	1.930	± 0.029	6
		0.3020	0.821	0.07994	1.829	± 0.016	6
FP-47	66.5	0.0000	0.000	0.00000	0.000	± 0.006	7
		0.0372	0.056	0.00584	0.552	± 0.042	7
	R = 0.521*	0.0760	0.114	0.01186	0.833	± 0.017	6
		0.1047	0.157	0.01627	1.244	± 0.025	7
		0.1860	0.279	0.02854	1.514	± 0.032	7
		0.2555	0.383	0.03878	1.631	± 0.037	8
		0.3504	0.524	0.05244	1.722	± 0.009	9
		0.5183	0.773	0.07566	1.756	± 0.024	7
		0.7699	1.144	0.10841	1.807	± 0.033	7
		1.0222	1.514	0.13900	1.711	± 0.022	6
FP-5	95.3	0.0000	0.000	0.00000	0.000	± 0.016	7
		0.0776	0.081	0.00848	0.635	± 0.041	6
	R = 0.746*	0.1517	0.159	0.01644	0.966	± 0.034	7
		0.2685	0.281	0.02873	1.321	± 0.023	7
		0.3842	0.402	0.04060	1.514	± 0.021	6
		0.5133	0.536	0.05352	1.607	± 0.040	8
		0.6500	0.677	0.06681	1.583	± 0.021	9
		0.8828	0.918	0.08862	1.546	± 0.020	7
		1.2166	1.260	0.11817	1.568	± 0.026	7
		1.5470	1.597	0.14559	1.601	± 0.030	6

* R is the ratio of liquid volume to total volume.
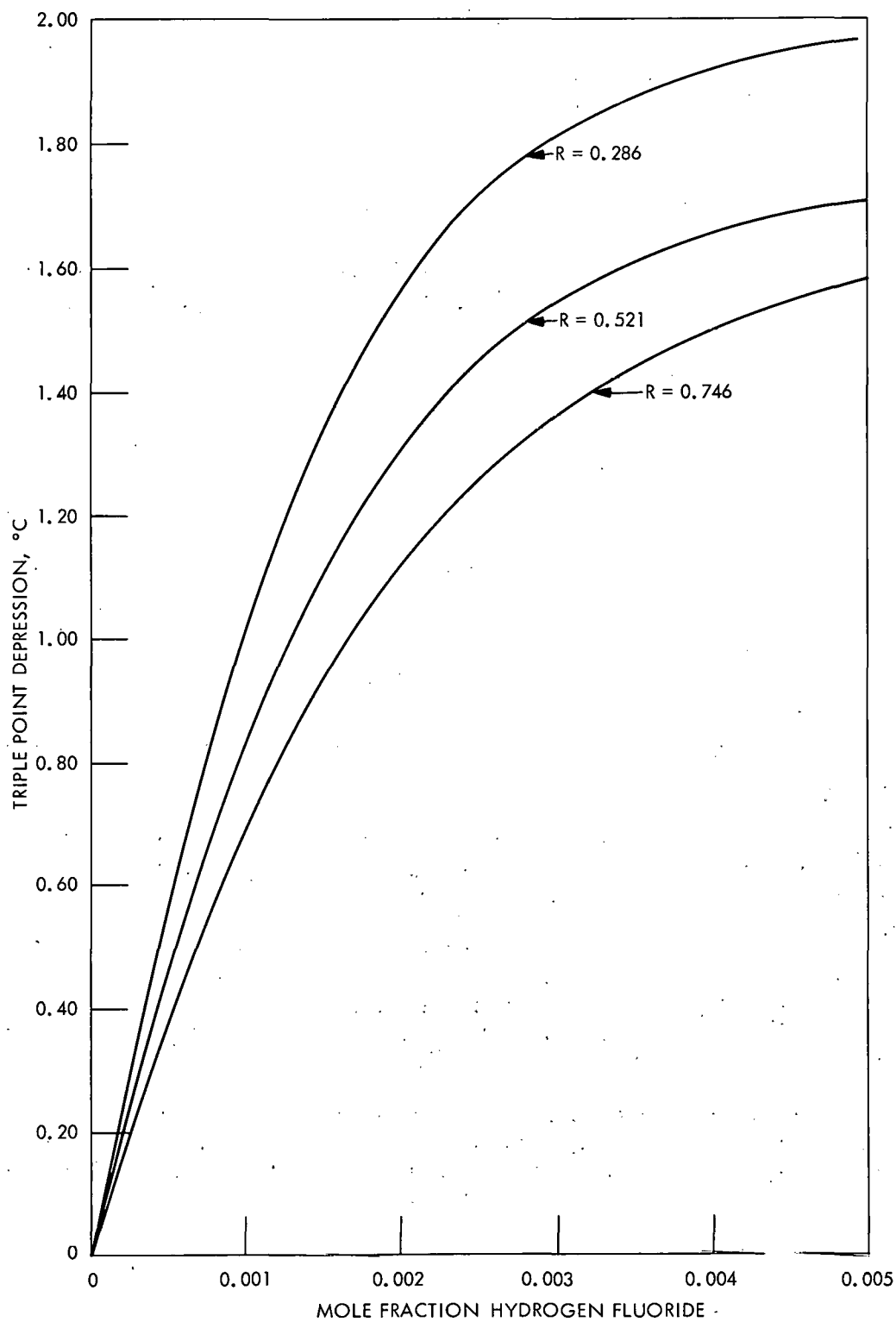
Figure 5

MOLYBDENUM HEXAFLUORIDE-HYDROGEN FLUORIDE TRIPLE POINT CURVES

TABLE II

LEAST SQUARES EQUATIONS FROM THE THREE TRIPLE POINT CURVES
OF HYDROGEN FLUORIDE IN MOLYBDENUM HEXAFLUORIDE

General Equation*: $\Delta t = A(N_2) + B(N_2)^2 + C(N_2)^3$

Cylinder Number	Ratio of Liquid Volume to Total Volume	General Equation Constants
FP-39	0.286	A = 144.9 B = - 4031.0 C = 38900.4
FP-47	0.521	A = 113.1 B = - 2720.6 C = 22718.8
FP-5	0.746	A = 83.77 B = - 1639.3 C = 11904.5

*N_2 is the mole fraction hydrogen fluoride.
Δt is the triple point depression in °C.

Discussion

The molybdenum hexafluoride-hydrogen fluoride binary system does not form an ideal solution since each cell is described by a different curve (figure 5). The differences between the curves represent the magnitude of the non-ideality. To determine the molal triple point curve for molybdenum hexafluoride, the curves of figure 5, each representing a different ratio of liquid volume to total volume, need to be extrapolated to a curve representing a cell containing all liquid with no vapor volume. The extrapolated curve would be represented by a curve at the ratio of liquid volume to total volume of one (R = 1).

Using the ratios and equations of the three different cells from table II, the mole fractions of hydrogen fluoride was expressed as a function of the triple point depression and the ratio of liquid volume to total volume. Equation 2 represents this relationship.

$$\Delta t = A(N_2) + B(N_2)^2 + C(N_2)^3 \qquad \text{(Equation 2)}$$

where
A = 159.86 - 129.19(R) + 36.44(R^2)
B = -3624.5 + 2965.0(R) - 407.5(R^2)
C = 26239.0 - 17875.0(R) - 1796.2(R^2)
Δt is the triple point depression of molybdenum hexafluoride
and R is the ratio of liquid volume to total volume.

Table III are values of N_2 at various combinations of R and Δt. Figure 6 is a plot of the observed triple point depression curves with the extrapolated curves at ratios of liquid volume to total volume values of one and zero. These latter curves were determined by substituting values of Δt at R = 1 and R = 0 in equation 2.

$$R = 1 \quad \Delta t = 67.11(N_2) - 1067.0(N_2)^2 + 6567.8(N_2)^3 \qquad \text{(Equation 1)}$$

$$R = 0 \quad \Delta t = 159.9(N_2) - 3624.5(N_2)^2 + 26239.0(N_2)^3 \qquad \text{(Equation 3)}$$

Application to a Method of Analysis

From the position of the curves in figure 6, it is indicated that the composition of the vapor phase is relatively richer with solvent than is the composition of the liquid phase in the binary system molybdenum hexafluoride-hydrogen fluoride. Thus to obtain the gross composition of such a solution, the disparity in the liquid and vapor compositions must be considered. For example, in cryoscopic measurements the same triple point depression would yield a gross composition dependent upon the amount of solution present in a given cell; and in withdrawing liquid samples from such a solution, the samples would represent only the liquid composition. The normal analytical situation usually involves gross compositions, and the triple point curves form a base for estimating gross compositions.

A cell with a total volume of 225 ml, and containing 460 grams of molybdenum hexafluoride, has a triple point depression of 0.90°C. The ratio of liquid volume to total volume is

$$R = \frac{G}{d\,V} \qquad \text{(Equation 4)}$$

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 for the system described above,

$$R = 460/(2.55)(225) = 0.80$$

assuming the solute does not alter the density of the solvent.

The dashed lines in figure 7A represent this solution. The dashed horizontal line from $\Delta t = 0.90$ represents the triple point depression of the solution. The intersection of this horizontal line with the curve at R = 1.0 is the liquid composition: 0.0182 mole fraction hydrogen fluoride. The intersection with the curve R = 0.80 is the gross composition: 0.0153. The intersection with the curve R = 0.0 is the vapor composition: 0.0062.

TABLE III

MOLE FRACTION HYDROGEN FLUORIDE IN MOLYBDENUM HEXAFLUORIDE AT DIFFERENT RATIOS OF LIQUID VOLUME TO TOTAL VOLUME

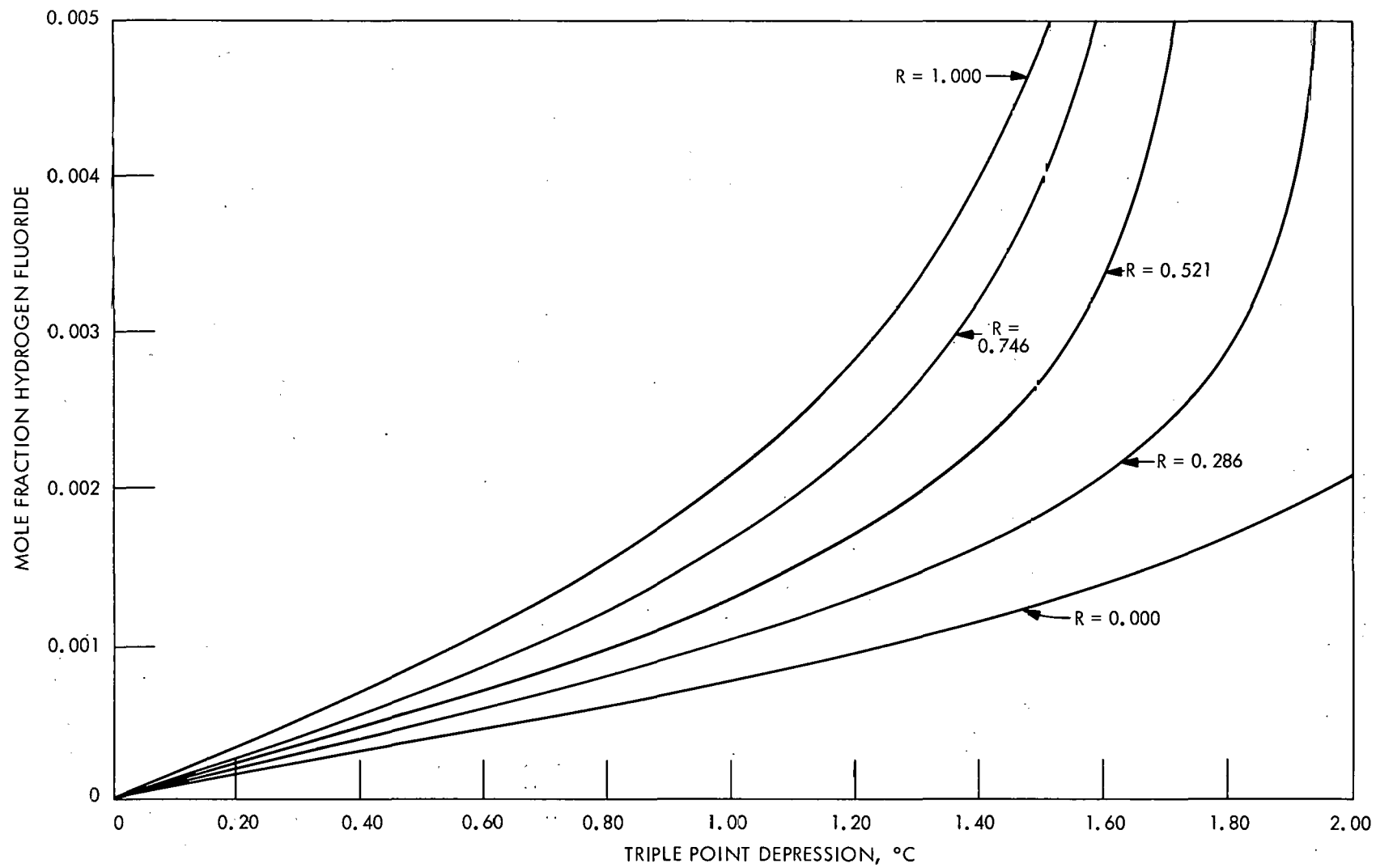| Ratio of Liquid Volume to Total Volume	1.0	0.8	0.6	0.4	0.2	0.0
Triple Point Depression, °C	Mole Fractions Hydrogen Fluoride					
0.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1	0.0012	0.0010	0.0009	0.0008	0.0006	0.0005
0.2	0.0029	0.0023	0.0017	0.0016	0.0013	0.0012
0.3	0.0047	0.0037	0.0028	0.0025	0.0023	0.0019
0.4	0.0066	0.0053	0.0040	0.0036	0.0031	0.0026
0.5	0.0087	0.0071	0.0053	0.0046	0.0039	0.0033
0.6	0.0108	0.0090	0.0067	0.0057	0.0047	0.0041
0.7	0.0130	0.0110	0.0082	0.0069	0.0056	0.0048
0.8	0.0157	0.0131	0.0098	0.0081	0.0065	0.0055
0.9	0.0182	0.0153	0.0117	0.0095	0.0074	0.0062
1.0	0.0211	0.0180	0.0139	0.0111	0.0083	0.0069
1.1	0.0246	0.0211	0.0163	0.0130	0.0095	0.0078
1.2	0.0285	0.0247	0.0192	0.0146	0.0108	0.0089
1.3	0.0331	0.0290	0.0228	0.0167	0.0122	0.0100
1.4	0.0390	0.0342	0.0268	0.0190	0.0138	0.0110
1.5	0.0479	0.0420	0.0321	0.0220	0.0155	0.0124
1.6	--	--	0.0418	0.0261	0.0174	0.0139
1.7	--	--	--	0.0322	0.0199	0.0154
1.8	--	--	--	--	0.0231	0.0172
1.9	--	--	--	--	0.0280	0.0190
2.0	--	--	--	--	0.0500	0.0210
2.1	--	--	--	--	--	0.0236
2.2	--	--	--	--	--	0.0278

Figure 6

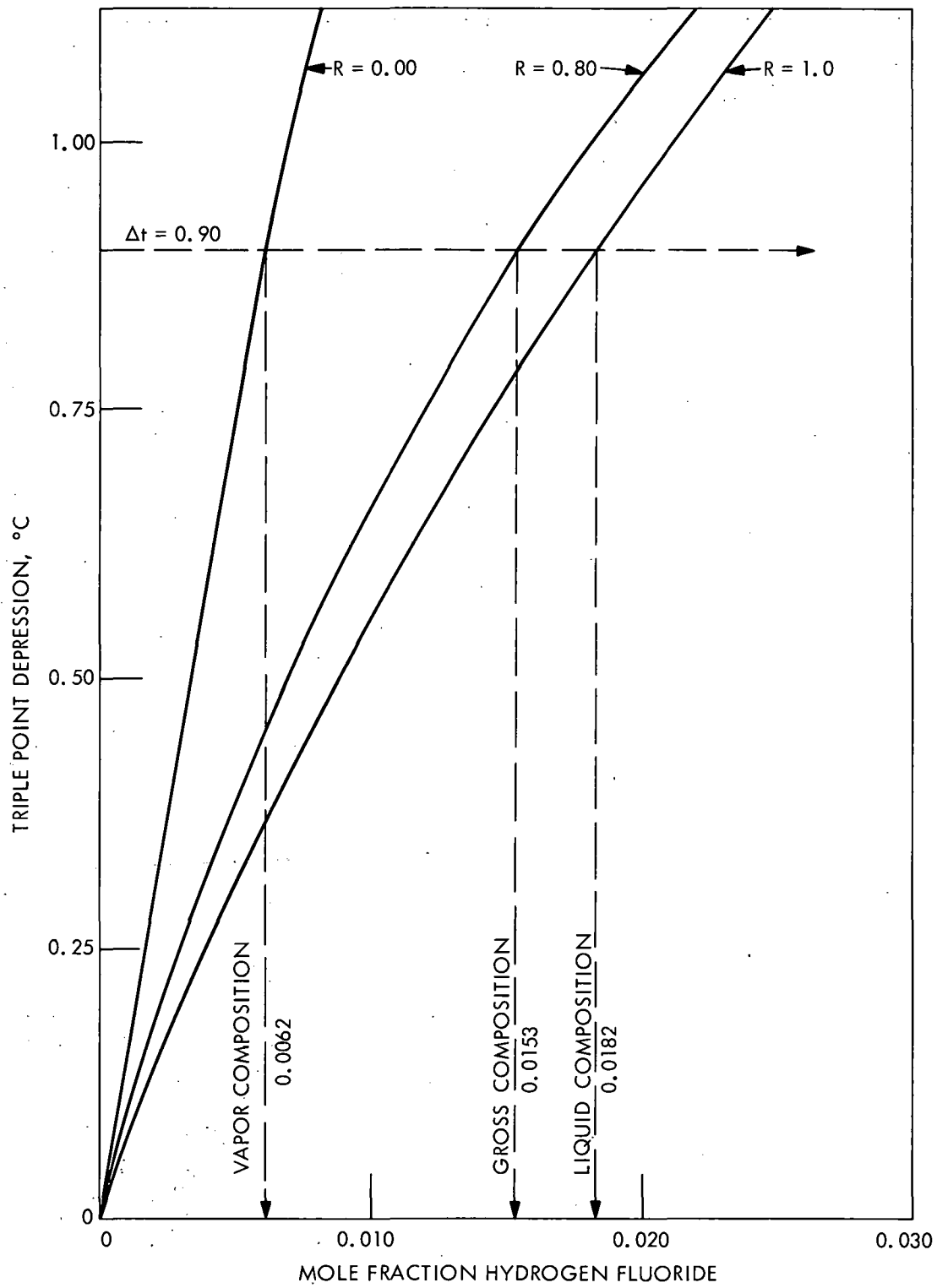MOLYBDENUM HEXAFLUORIDE-HYDROGEN FLUORIDE TRIPLE POINT CURVES

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Figure 7A

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

If such a system as described above were liquid-sampled and gravimetrically analyzed for mole fraction molybdenum hexafluoride, the obtained result would represent the liquid phase only. Since material was withdrawn at the liquid composition, the gross composition remaining in the container after sampling would now be different, and the composition of the liquid and vapor phase would readjust to the new conditions.

To estimate the change resulting in the gross, liquid, and vapor compositions due to withdrawing a liquid portion of the solution, assume that 345 grams of liquid were withdrawn from the solution represented by the dashed lines in figure 7A. Thus the container now has 115 grams of solution with a ratio of liquid to total volume of $115/(2.55)(225) = 0.20$. To determine the gross, liquid, and vapor compositions of the remaining solution after the withdrawal, generate a line parallel to the triple point depression axis from the intersection $(\Delta t = 0.90, R = 0.20)$ to the intersection with $R = 0.80$. 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 liquid composition: 0.0091 mole fraction hydrogen fluoride. The intersection with the curve $R = 0.20$ is the gross composition: 0.0041 mole fraction. And the intersection with the curve $R = 0.0$ is the vapor composition: 0.0035 mole fraction. This procedure is illustrated in figure 7B. Identical results may be obtained by determining the triple point depression after withdrawing the sample (estimated graphically in figure 7A by $\Delta t = 0.52$). After determining the triple point depression, Equation 2 may be used to solve for the desired compositions.

Figure 8 is a graphic presentation of the expected gross, liquid, and vapor compositions of a typical molybdenum hexafluoride-hydrogen fluoride 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.

ACKNOWLEDGEMENTS
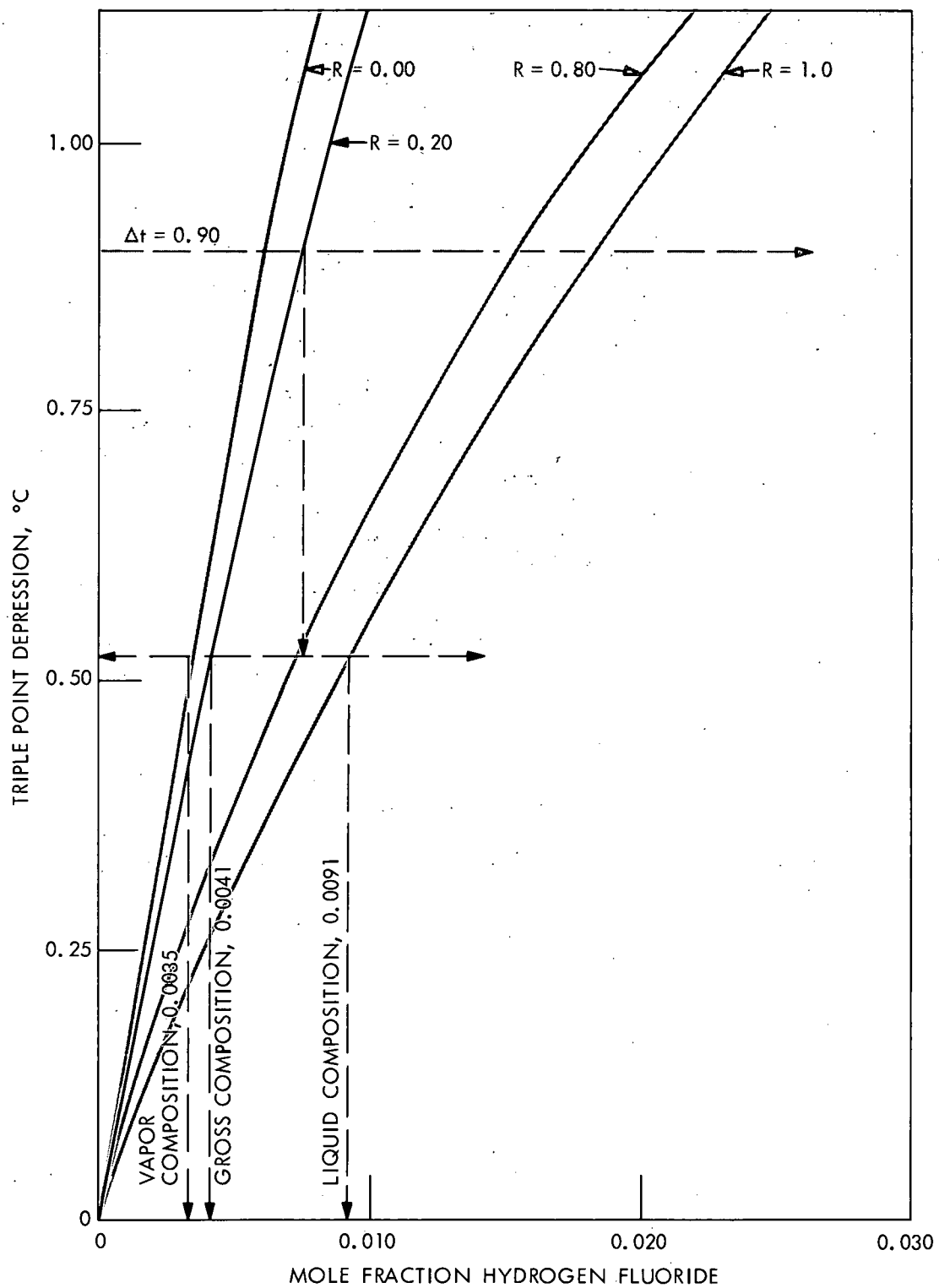
Figure 7B

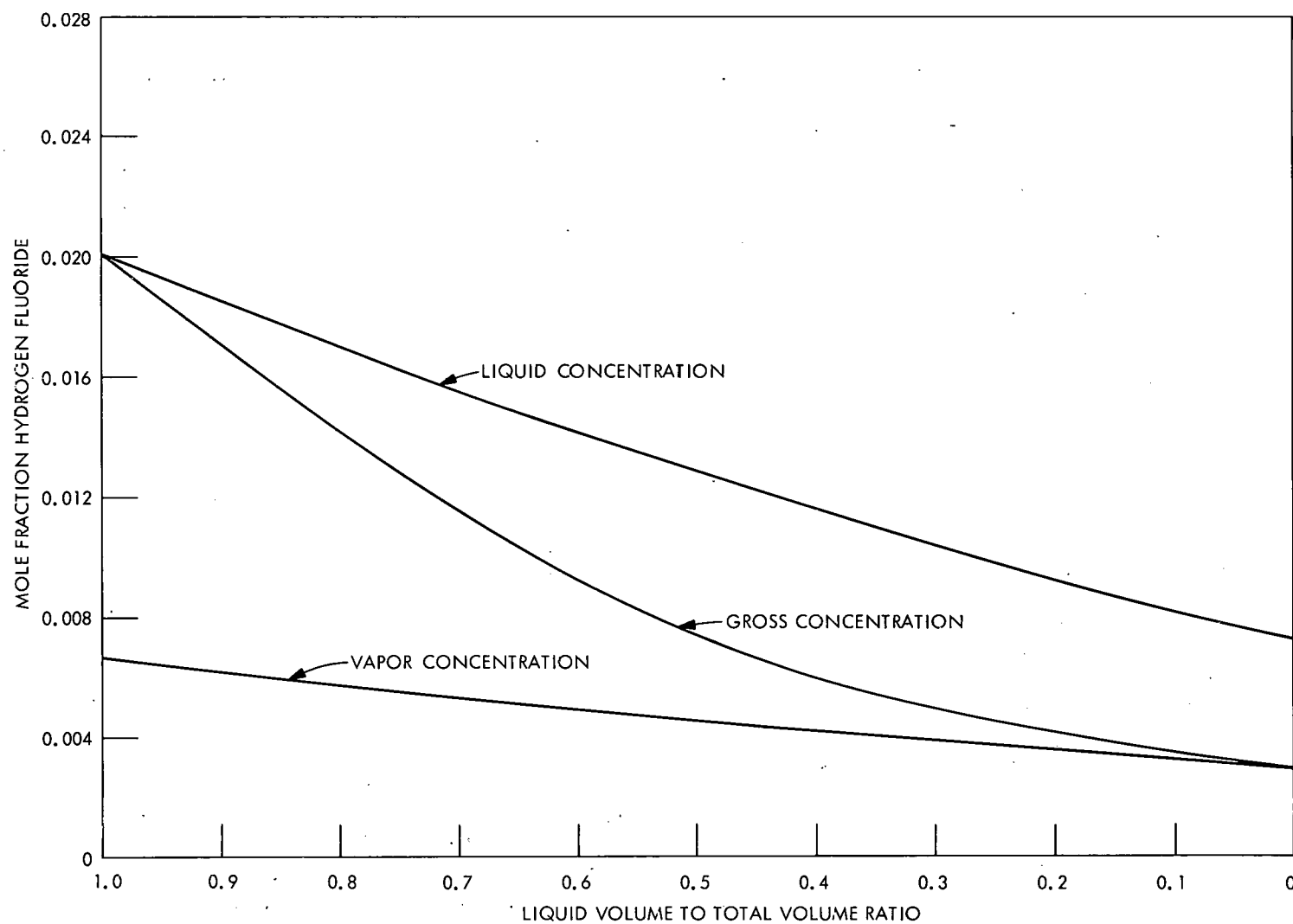GROSS, VAPOR, AND LIQUID COMPOSITION OF THE SYSTEM MoF_6-HF

Figure 8

MOLE FRACTION HYDROGEN FLUORIDE DISTRIBUTION FOR
A TYPICAL MoF_6-HF SOLUTION

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