DETERMINATION OF NITROGEN SOLUBILITY IN SUPERPRESSURIZED HFC-227ea, HFC- 236fa, AND HFC-125

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INTRODUCTION

Bromochlorofluorocarbons (halons), developed in the 1930s, have unique properties. They are low in toxicity, nonflammable, noncorrosive, and compatible with other materials. In addition, they have thermodynamic and physical properties that make them ideal fire extinguishing agents and explosion suppressants for protection of high-value equipment. They are used in handheld portable extinguishers, total-flooding systems, and local application systems.

The atmospheric stability of these compounds, coupled with their bromine and/or chlorine content, has linked them to depletion of the earth's protective ozone layer. As a result, these compounds have been phased out of production. DuPont has developed alternative compounds with improved environmental properties, HFC-227ea (DuPont FE-227®), HFC-236fa (DuPont FE-36®) and HFC-125 (DuPont FE-25®), as replacements for Halon 1301 (bromotrifluoromethane).

Like Halon 1301, its replacements, HFC-227ea, **HFC-236fa,** and HFC-125, do not have sufficient vapor pressure to assure complete and effective discharge into the protected area. The discharge time would vary greatly with ambient temperature, and the agent would vaporize, or boil off in the piping. This would result in a poor discharge and distribution of the agent. To achieve a constant discharge of the agent, it is superpressurized with nitrogen or other inert gas. Superpressurization of the agent in the container results in some of the nitrogen going into solution in the agent. The solubility affects the filling density, the flow in the piping, and the discharge at the nozzle. To design a fire extinguishing system properly, the nitrogen solubility in the agent must be understood.

Solubilities of nitrogen in three of the Halon 1301 replacements (HFC-227ea HFC-236fa, and HFC-125), were measured using a semi-automated vapor-liquid-equilibrium static cell. The data were reduced using a modified Peng-Robinson equation of state. The Henry's law constants, the weights of nitrogen required for superpressurization of **HFC-227ea, HFC-236fa,** and HFC-I25, and pertinent isometric diagrams were calculated using the same equation of state.

EXPERIMENTAL SECTION

Chemicals. The HFC-227ea, **HFC-236fa,** and HFC-125 used in this work were manufactured by DuPont. The purities were greater than 99.999%. The nitrogen (99.998% purity) used in this work was manufactured by MG Industries. All were used without any further purification. The HFCs were degassed prior to making the solubility measurements.

Experimental Apparatus. Figure 1 shows the schematic diagram of a semi-automated vapor-liquid-equilibrium static cell, which was used to measure solubilities of nitrogen. The 71 cm^3 sapphire VLE (vapor-liquid-equilibrium) cell is immersed in a constant temperature bath (a glass beaker filled with silicone oil). The bath is controlled with an Eurotherm 2604 to ±0.01 °C. The temperature of the bath is measured to the same accuracy using a Hart 1502A thermometer with a Hart 5614 RTD. The VLE cell is connected by a heat traced 1/16 in. stainless steel tubing to a Paroscientific quartz pressure transducer (model 31K), which can be heated up to 107 °C. The pressure transducer and the connecting tubing are heated to a temperature at least 10 °C higher than the bath temperature.

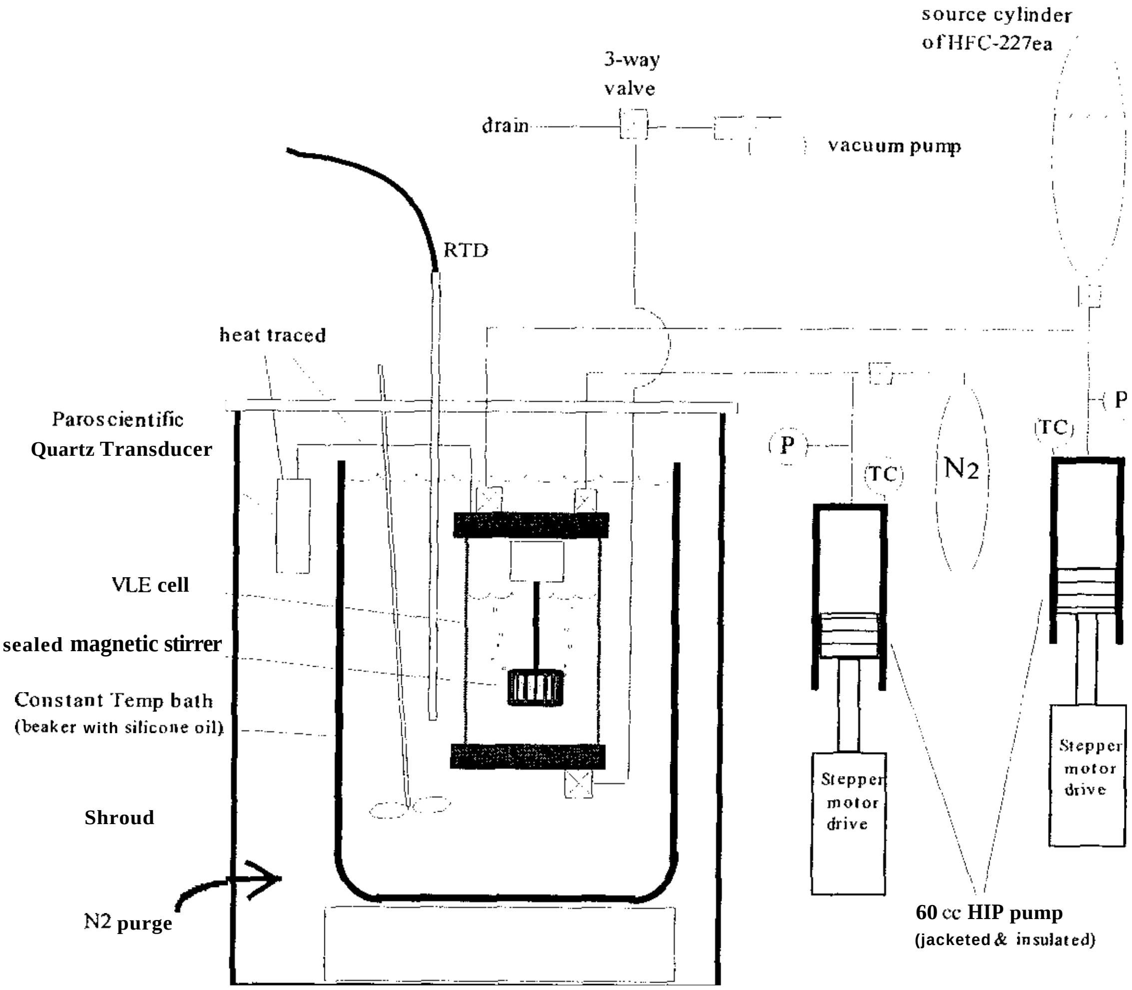

Figure 1. Schematic diagram of the experimental apparatus.

Prior to connecting the source cylinder of a fire extinguishing agent to the system, the agent in the source cylinder is degassed by repeated freeze-pump-thaw cycles using liquid nitrogen to freeze the sample. The VLE cell, the pressure transducer, the HIP pumps, and all connecting lines are evacuated after the source cylinder and the nitrogen cylinder are connected to the system and prior to loading the agent and nitrogen into two HIP pumps. The HIP pumps are kept at 24 °C by circulating a constant temperature fluid through the insulated jackets using a Neslab circulating bath. The shaft of each HIP pump is driven by a stepper motor, which is computer controlled. A Setra pressure transducer (Model 225, 0-3000 psia) and a Heise pressure transducer (Model 901B, 0-800 psia) are used to measure the pressure of agent and the pressure of nitrogen in the HIP pumps, respectively.

The agent is loaded into its HIP pump while the shaft of the pump is driven down by its stepper motor to the full capacity of the pump. The valve of the source cylinder is then closed, and the shaft of the HIP pump is moved to a position such that the pressure of the agent in the HIP pump is at least 50 psi higher than the vapor pressure of the agent at either the cell temperature or the pump temperature, whichever is higher. The agent is loaded into the cell while the shaft of the pump moves up. After the agent is loaded into the cell, the shaft is positioned such that the pressure of the agent in the HIP pump is the same as before the loading. The amount of the agent loaded into the cell is calculated from the volume displacement of the shaft and the density of the agent at the pump temperature and pressure.

Nitrogen is filled from the nitrogen cylinder to the other HIP pump to a pressure that is higher than the targeted cell pressure. The valve of the nitrogen cylinder is closed. Nitrogen is then loaded into the cell in the same way as the agent. The amount of nitrogen loaded into the cell is calculated from the volume displacement of the shaft and the nitrogen density at the pump temperature and pressure. The density of nitrogen is calculated from Benedict-Webb-Robin equation of state [1]. For each solubility experiment, the amount of agent loaded into the cell is approximately equivalent to 58 cm^3 at cell temperature. Vapor pressure of the agent as well as successive isothermal pressures for solutions of different nitrogen concentrations are measured.

DATA REDUCTION

The loadings of a agent (component 1) and nitrogen (component 2) are converted to equilibrium vapor and liquid phase compositions by accounting for the amount of each component in the vapor phase. The material balance equations for data reduction are as follows:

$$n^L + n^V = n_1 + n_2 \qquad (1)$$

$$n_1 = x_1 n^L + y_1 n^V \qquad (2)$$

$$V_T = n^L v^L + n^V v^V \qquad (3)$$

where n_i is the number of moles of component i charged to the cell,

n^α is the total number of moles in phase α

v^α is the molar volume of phase α

x_1 and y_1 are the liquid and vapor mole fractions of component 1

V_T is the total volume of the cell

An expression for the number of moles in the liquid phase is derived from Eq. (1) and (3):

$$n^L = [\,(n_1 + n_2)\, v^V - V_T]/(v^V - v^L) \qquad (4)$$

and an expression for the mole fraction of component 1 is derived from Eq. (1) and (2):

$$x_1 = [n_1 - (n_1 + n_2 - n^L) y_1]/n^L \qquad (5)$$

A solution for x_1 is found at the temperature of interest by a conventional vapor-liquid equilibrium calculation in which the equilibrium pressure and y_1 are first determined from the temperature and an initial estimate for x_1. Eq. (4) and (5) are then used to update the estimated value of x_1. This iterative procedure is repeated until x_1 converges to a single value. In this calculation, the vapor and liquid fugacities of each component, as well as v^L and v^V, are obtained from the Peng-Robinson equation of State [2]:

$$P = RT/(v-b) - a/[v(v+b)+b(v-b)] \qquad (6)$$

$$a = \Sigma\,\Sigma\, x_i x_j\, a_{ij} \quad a_{ij} = (a_{ii}\ a_{jj})^{1/2}\,(1 - KA) \qquad (7)$$

$$b = \Sigma\,\Sigma\, x_i x_j\, b_{ij} \quad b_{ij} = (b_{ii} + b_{jj})/2 \qquad (8)$$

Peng-Robinson equations of state (PREOS) parameters for a pure fire extinguishing agent, a_{11} and b_{11}, are obtained from vapor pressure and liquid density at each temperature of interest. PREOS parameters for nitrogen, a_{22} and b_{22}, are obtained from its acentric factor and critical properties as originally proposed by Peng and Robinson [2]. At each temperature, the binary parameter, KA, is obtained by minimizing $[1/N\ \Sigma\,(P_{exp}/P_{calc}-1)^2]^{1/2}$. Once KA is reduced from the measured solubility data, the Henry's law constants for nitrogen in an agent, the weights of nitrogen required for superpressurization of an agent, and pertinent isometric diagrams are calculated using PR EOS.

RESULTS AND DISCUSSION

N_2 in HFC-227ea. Pressures were measured as a function of overall mixture composition at 69.76 °F (20.98 °C). These pressures (P_{exp}), the calculated pressures (P_{calc}), the corrected equilibrium mole fractions of nitrogen in liquid phase (x_2), and the calculated equilibrium mole fractions of nitrogen in vapor phase (y_2) are given in Table 1. The isothermal pressure-composition plot is shown in Figure 2. The data for nitrogen and HFC-227ea at 68 "F, published by J. S. Lim and J-D. Kim [3], are also shown in the figure. Lim and Kim used a gas chromatograph to analyze both the liquid and vapor samples taken from the equilibrium cell.

The Henry's law constant for a gas in an agent is the ratio of the fugacity of the gas to the mole fraction of the gas dissolved in the agent at infinite dilution. $H_{2,1} = f_2/x_2$ as $x_2 \to 0$.

Figure 3 shows the Henry's law constant for nitrogen in HFC-227ea from -40 to 180 °F calculated using PREOS with a slightly temperature dependent binary parameter KA. KA was reduced from measured nitrogen solubility in HFC-227ea at 69.76 °F and at four other temperatures, which are not reported here. Figure 3 also shows the ratio of the partial pressure of nitrogen to the mole fraction of nitrogen dissolved in HFC-227ea at infinite dilution, which is quite different from the Henry's law constant at the same temperature. The Henry's law constant reduced from data reported [3] is also shown in Figure 3

TABLE 1. VAPOR-LIQUID EQUILIBRIUM PRESSURES AND PHASE COMPOSITIONS FOR HFC-227ea(1) + N2(2) MIXTURES AT 69.76 °F (20.98 "C).

X_2	Calc. Y_2	P_{exp}/psia	P_{calc}/psia	P_{exp}/P_{calc}-1
0.00000	0.0000	58.19	58.19	
0.00981	0.3813	101.03	100.87	-1.62E-03
0.02097	0.5594	149.73	149.70	-2.18E-04
0.03230	0.6531	199.69	199.60	-4.73E-04
0.04411	0.7119	252.02	251.96	-2.34E-04
0.05541	0.7493	302.79	302.38	-1.37E-03
0.06671	0.7759	353.34	353.15	-5.50E-04
0.07904	0.7973	408.87	408.86	-2.19E-05
0.09097	0.8129	463.04	463.12	1.73E-04
0.10751	0.8291	538.69	538.89	3.69E-04
0.12054	0.8386	598.51	599.00	8.12E-04
0.13129	0.8450	648.13	648.94	1.25E-03

In fire suppression applications, nitrogen is often added to a cylinder of fire extinguishing agent to increase the pressure. This is called "superpressurization." The weight of nitrogen required to pressurize a given amount of HFC-227ea to 360 psig and 600 psig at 70 °F was calculated using PREOS and is shown in Table 2. Isometric diagrams of HFC-227ea superpressurized to 360 psig and 600 psig at 70 °F are shown in Figures 4 and 5. The temperature at which the cylinder of superpressurized HFC-227ea is liquid full is the temperature at which the calculated saturation density of the liquid of loading composition equals the loading density. At temperatures below the liquid full temperature, the points on the isometric diagram were calculated by solving VLE and material balance equations at the same time, and the pressures of the cylinder are approximately the same for different HFC-227ea fill densities. At temperatures above the liquid full temperature, the pressures of the cylinder are a strong function of temperature and fill density. The density of the compressed liquid mixture (of loading composition) calculated from PREOS was corrected by ρ(227ea)/ρ(227ea,EOS), the ratio of actual to calculated density for HFC-227ea at the same temperature and pressure.

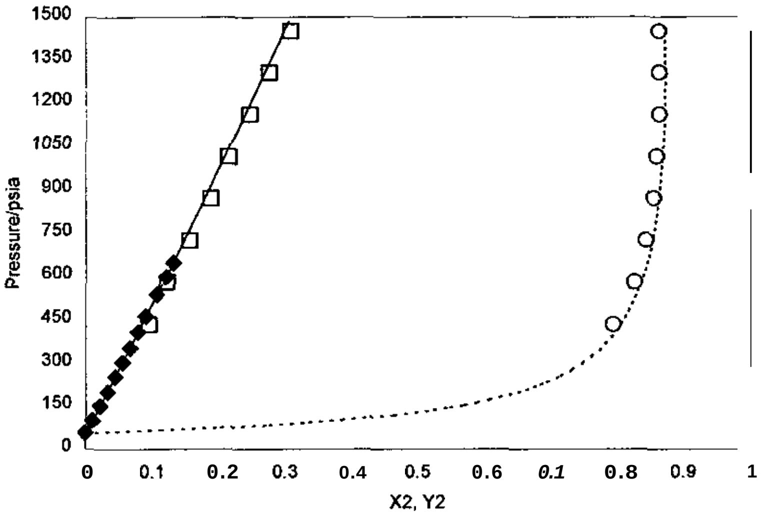

Figure 2. Vapor-liquid equilibrium pressures and phase compositions for HFC-227ea (1) + nitrogen (2) at 20.98 °C or 69.76 °F. The solid and broken lines are the calculated liquid and vapor coexistence curves, respectively; solid symbols denote measured pressures. The open squares and circles are data at 68 °F [3].

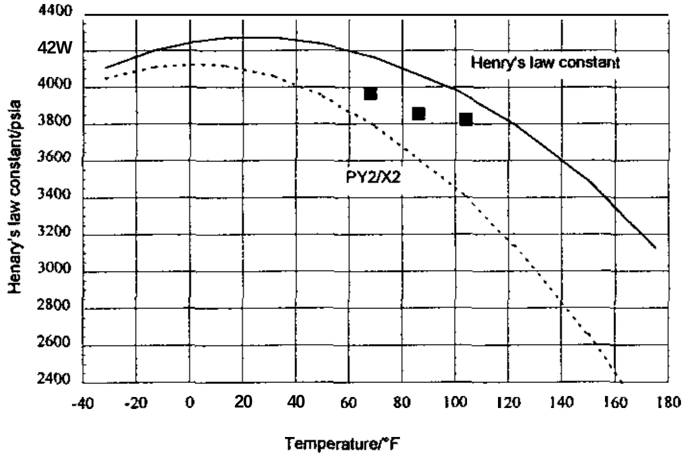

Figure 3. Henry's law constant for nitrogen in HFC-227ea and ratio of nitrogen partial pressure to mole fraction of nitrogen in HFC-227ea at infinite dilution. Symbols denote the Henry's law constant reduced from data [3].

TABLE 2. WEIGHT OF NITROGEN REQUIRED FOR SUPERPRESSURIZATION OF HFC-227EA.

Weight of nitrogen per lb of HFC-227ea at 70°F		
Fill Density lb/ft³	Amount of Superpressure 360 psig	Amount of Superpressure 600 psig
	oz	oz
40	0.534	0.944
45	0.463	0.819
50	0.407	0.718
55	0.361	0.636
60	0.323	0.568
65	0.291	0.511
70	0.263	0.461
75	0.239	0.418

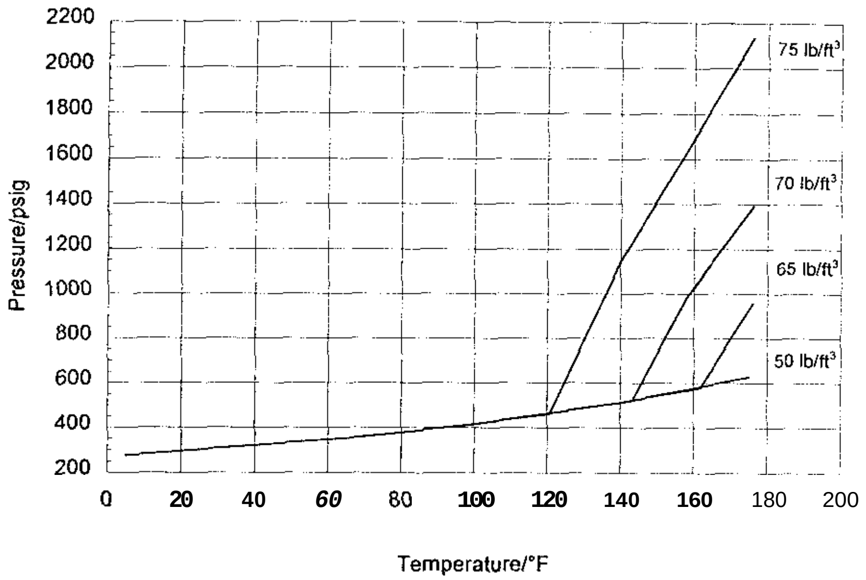

Figure 4. Isometric diagram – HFC-227ea pressurized with nitrogen to 360 psig at 70 °F.

N_2 in HFC-125 and HFC-236fa. Solubilities of nitrogen in HFC-125 and HFC-236fa at four temperatures each were measured and reduced using PREOS. Figures 6 to 11 and Tables 3 and 4 show the calculated Henry's **law** constants, the ratios of the partial pressures to the mole fractions of nitrogen in liquid at infinite dilution, the weights of nitrogen required for superpressurization of HFC-125 and HFC-236fa to 360 psig and 600 psig at 70 "F, and the pertinent isometric diagrams.

ACKNOWLEDGMENTS

The assistance of David J. Bateman, Howard **S.** Hammel, and Daniel W. Moore in providing background information on **fire** extinguishing agents is gratefully acknowledged. The assistance of Dr. William Schotte and James Sturgis in designing the experimental apparatus, and the careful experimental work of Gary Brown and David Guntrum, who assisted with the measurements, are also greatly appreciated.

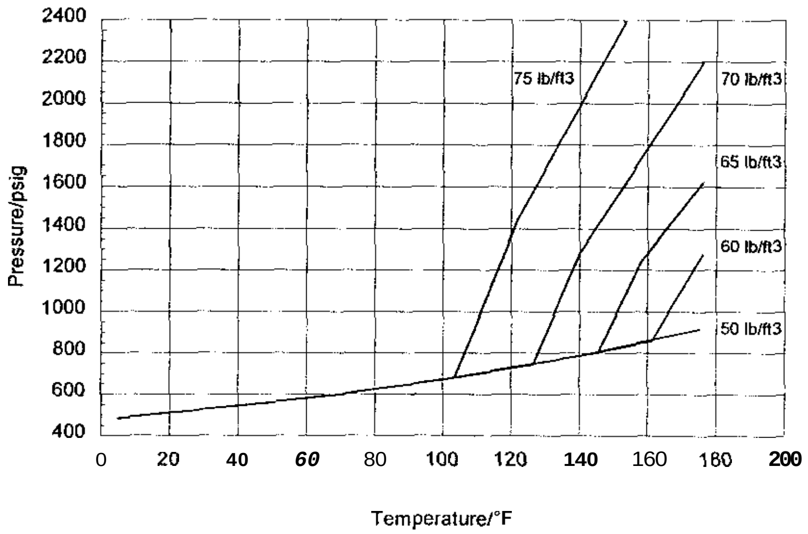

Figure 5. Isometric diagram – HFC-227ea pressurized with nitrogen to 600 psig at 70 °F

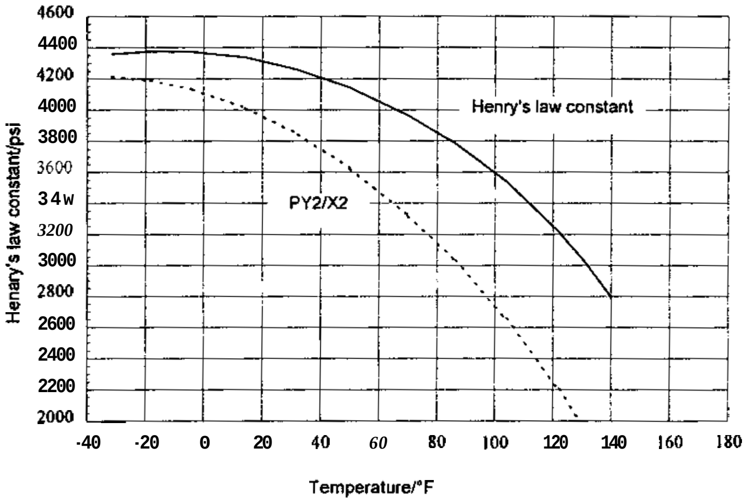

Figure 6. Henry's law constant for nitrogen in HFC-125 and ratio of nitrogen partial pressure to mole fraction of nitrogen in HFC-125 at infinite dilution.

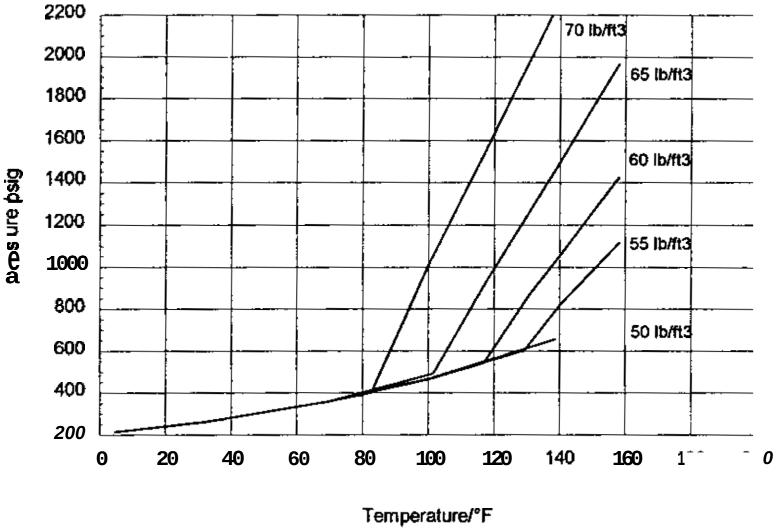

Figure 7. Isometric diagram – HFC-125 pressurized with nitrogen to 360 psig at 70 °F.

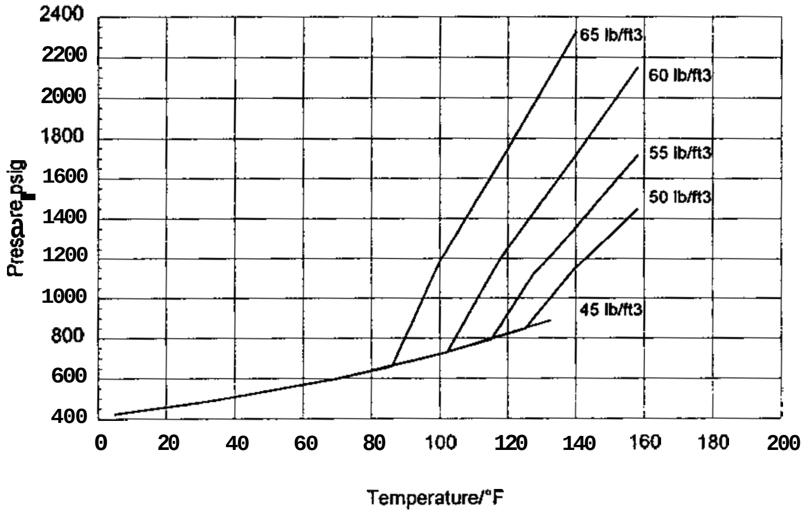

Figure 8. Isometric diagram – HFC-125 pressurized with nitrogen to 600 psig at 70 °F.

TABLE 3. WEIGHT OF NITROGEN REQUIRED FOR SUPERPRESSURIZATION OF HFC-125.

Weight of nitrogen per lb of HFC-125 at 70°F		
Fill Density **lb/ft^3**	**Amount of Superpressure** **360 psig**	**Amount of Superpressure** **600 psig**
	oz	**oz**
40	0.346	0.777
45	0.303	0.680
50	0.269	0.602
55	0.240	0.539
60	0.217	0.485
65	0.197	0.441
70	0.190	0.424
75	0.180	

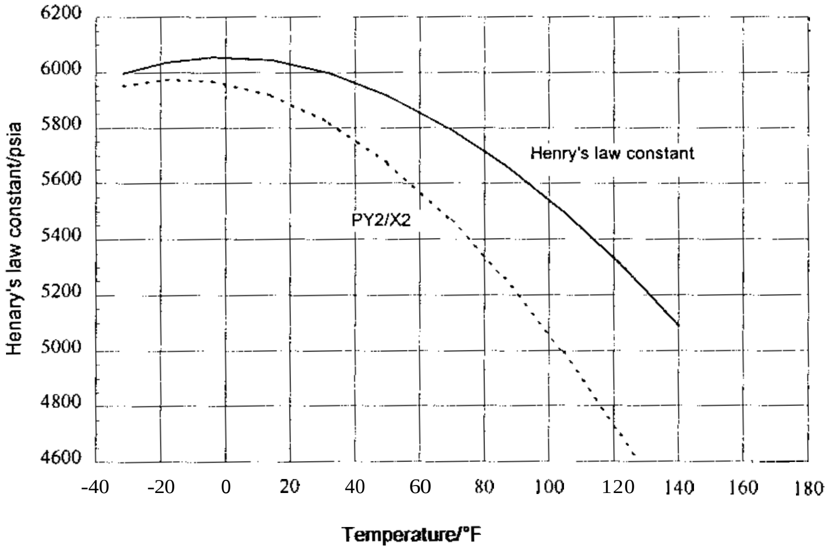

Figure 9. Henry's **law** constant for nitrogen in HFC-236fa and ratio **of** nitrogen partial pressure to mole fraction of nitrogen in HFC-236fa at infinite dilution.

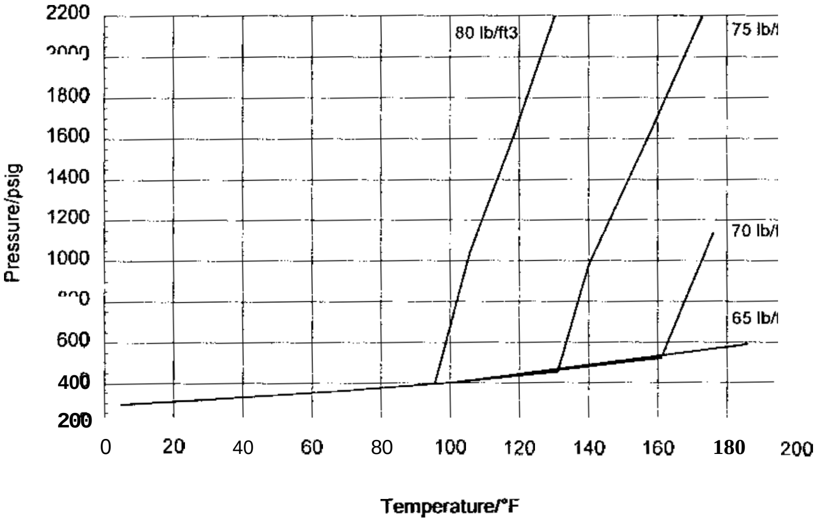

Figure 10. Isometric diagram – HFC-236fa pressurized with nitrogen to 360 psig at 70 “F.

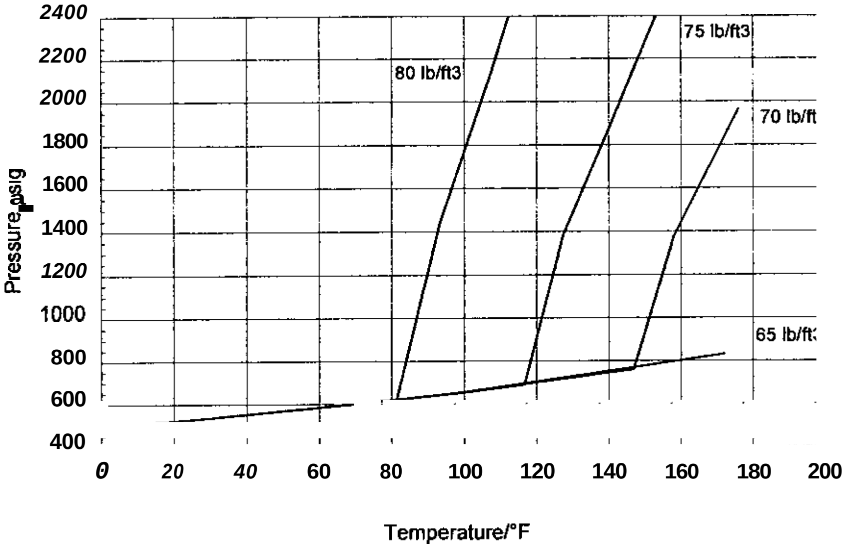

Figure 11. Isometric diagram – HFC-236fa pressurized with nitrogen to 600 psig at 70 °F.

TABLE 4. WEIGHT OF NITROGEN REQUIRED FOR SUPERPRESSURIZATION OF HFC-236fa.

	Weight of nitrogen per lb of HFC-236fa at 70°F	
Fill Density lb/ft^3	**Amount of Superpressure 360 psig**	**Amount of Superpressure 600 psig**
	oz	**oz**
40	0.528	0.899
45	0.452	0.770
50	0.392	0.666
55	0.342	0.581
60	0.301	0.511
65	0.266	0.451
70	0.236	0.400
75	0.211	0.355
80	0.188	0.316

REFERENCES

1. Reid, C. R. Prausnitz, J.M., and Sherwood, T. K., "The Properties of Gases and Liquids," Third Edition, Chapter 3, ***Pressure- Volume-Temperature Relationships of Pure Gases and Liquids,*** McGraw-Hill Book Company, 43-50,1977.
2. Peng, D.-Y., and Robinson, D. B., "A New Two-Constant Equation of State," ***Ind. Eng.*** Chem. ***Fundam.***, *15*, 59-64, 1976.
3. Lim, J. S., and Kim, J.-D., "Vapor-Liquid Equilibria of the Binary Systems Nitrogen + Bromotrifluoromethane, + Bromochlorodifluoromethane, + 1,1,1,2,3,3,3-Heptafluoropropane, and + Trifluoroiodomethane from 293.2 to 313.2 K and 30 to 100 bar," *J.* ***Chem. Eng. Data., 42,*** 112-115, 1997.