

Solubilities of Nitrogen and Freon-23 in Alternative Halon Replacement Agents¹

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INTRODUCTION

As part of the USAF-sponsored halon replacement project, solubility measurements of nitrogen and Freon-23 in eleven potential halon replacement agents and evaluations of the thermodynamic properties of the agents are currently being conducted at NIST. The eleven agents proposed by the USAF are: FC-31-10, FC-318, HCFC-124, HFC-227, HFC-134a, FC-218, HCFC-22, HFC-125, HFC-236, FC-116, and HFC-32/HFC-125 azeotrope.

The determination of the solubility of nitrogen or Freon-23 (HFC-23) in the replacement agents is essential because nitrogen or Freon-23 is being considered as a pressurization gas; nitrogen is currently used in existing halon 1301 bottles. The purpose of using the pressurization gas is to expedite the discharge of the agent and to increase the penetration distance of the agent during discharge.

The other part of this task involves measurements of the thermodynamic properties of the agents. The objective is to determine what the final pressure of the vessel will be when the vessel, filled with either a pre-determined amount of pure agent or with agent and pressurization gas, is exposed to different ambient temperatures (from -60°C to 150°C). This information is extremely important because it will provide safety guidelines on the use of existing halon 1301 bottles for "drop-in" replacement agents. The amount of nitrogen or Freon-23 needed to pressurize the vessel plays a major role in the determination of the final pressure of the vessel because if the amount of pressurization gas is significant, a dangerously high pressure may result when the vessel is exposed to elevated temperatures. This paper reports the experimental measurements of the solubility of nitrogen or Freon-23 at room temperature in nine of the alternative agents. FC-116 was not included in this study because it is a gas at room temperature.

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EXPERIMENTAL METHOD

Figure 1 shows a schematic of the apparatus used for solubility measurements. The experimental apparatus includes a stainless steel vessel, a needle valve, a thermocouple, and a pressure transducer. The actual volume of the system was determined by pressurizing it with nitrogen to 4.02 MPa and then weighing it. Knowing the temperature, the pressure, and the mass of nitrogen, the volume was then calculated by using a generalized correlation for the compressibility factor [1]. The total volume of the apparatus was found to be $53.9 \pm 0.6 \text{ cm}^3$.

The experimental procedure is as follows. After evacuating the apparatus for at least 5 minutes, it was then connected to the agent supply bottle (not shown in Fig. 1). By immersing the apparatus in dry ice, liquid agent was dispensed through the needle valve into the vessel by condensing gaseous agent from the supply bottle. No attempt was made to remove noncondensable gases, if there were any, in the liquid agents. The total amount of agent used in each of the experiments was approximately equal to the amount required to fill one-third of the vessel volume with liquid. The apparatus was then weighed on an electronic balance with an accuracy of 0.05 gm to determine the actual mass of the agent. The vessel was pressurized with nitrogen or Freon-23 to approximately 4.1 MPa (600 psia) at room temperature by bubbling nitrogen or Freon-23 very slowly through the liquid agent. Shaking the vessel intermittently expedited equilibration of the final attainable pressure in the vessel. This value of pressure was selected in order to simulate a charging pressure commensurate with existing halon 1301 vessels. The amount of nitrogen or Freon-23 required to pressurize the vessel to the specified final pressure was then obtained by weighing the apparatus. This amount corresponded to the sum of the mass of nitrogen or Freon-23 in the vapor phase and that of the dissolved nitrogen or Freon-23 in the liquid agent.

The one-third fill capacity was chosen for this study to ensure that a liquid-filled condition would not be encountered during the course of heating the vessel [1]. After the liquid-filled condition, further heating would cause a very steep rise in pressure, a situation to be avoided.

RESULTS & DISCUSSION

Table 1 summarizes the experimental results for nitrogen. The values reported in the table are the average of two runs, which deviated less than 5% from each other. In all cases, the total amount of nitrogen required is less than 8% of the total mass of the agent.

In order to determine the solubility of nitrogen in the agent, measurements of nitrogen and agent concentrations in both phases are required. *Solubility* is defined as the mole fraction of nitrogen in liquid agent. The present experimental set-up does not have the provision for sampling the liquid and gas phases, but the mass of nitrogen that is dissolved in the liquid agent can be estimated by applying mass balances on the agent and nitrogen. Figure 2 is a schematic illustrating the various parameters used in the calculation. Initially, the vessel is filled with a pre-determined amount of agent, $m_{a,t}$, at temperature T

$$m_{a,t} = m_{a,v} + m_{a,l} = \rho_{a,v}V_v + \rho_{a,l}V_l \quad (1)$$

where m is the mass, subscript t represents total, subscript a represents agent, subscripts v and l represent vapor and liquid phases respectively, ρ is the saturation density of the agent, and V is the volume. Since $m_{a,t}$, V_t , $\rho_{a,v}$ and $\rho_{a,l}$ are known and $V_v = V_t - V_l$, the masses of agent in both liquid and vapor phases can be calculated by substituting $V_t - V_l$ for V_v and solving for V_l in Eq. (1).

The vessel is then pressurized with nitrogen until an equilibrium pressure at T is reached. Assuming that the dissolved gas (N_2) would not cause a significant change in the saturation liquid density of the agent and that the liquid agent is incompressible, the liquid mixture density can be approximated by the saturation liquid density of the pure agent. This approximation is reasonable if the amount of nitrogen dissolved in the liquid agent is much smaller than the mass of the liquid agent. From the experimental results, this appears to be the case for nitrogen in all the agents. If the vapor phase is further assumed to be ideal, then the total pressure P_t is given by

$$P_t = p_a + p_g \quad (2)$$

where p_a and p_g are the partial pressures of the agent and the pressurization gas respectively. From Raoult's law [2],

$$p_a = x_{a,l} P_{sat} = \frac{n_{a,l}}{n_{g,l} + n_{a,l}} P_{sat} \quad (3)$$

where $x_{a,l}$ is the mole fraction of the agent in the liquid phase, p_{sat} is the saturation vapor pressure of the agent at temperature T , $n_{g,l}$ is the number of moles of dissolved gas in the liquid phase, and $n_{a,l}$ is the number of moles of agent in the liquid phase. Furthermore, p_g can be calculated by

$$p_g = \frac{n_{g,v}RT}{V_v} = \frac{(n_{g,t} - n_{g,l})RT}{V_v} \quad (4)$$

where $n_{g,t}$ is the total moles of pressurization gas required to pressurize the vessel to a pressure P_t at a temperature T , and R is the universal gas constant. Substituting Eqs. (3) and (4) into Eq. (2), a quadratic equation for $n_{g,l}$ (unknown) is obtained.

$$n_{g,l}^2 + n_{g,l}(n_{a,l} - n_{g,t} + \frac{P_t V_v}{RT}) + n_{a,l}(\frac{P_t V_v}{RT} - \frac{p_{sat} V_v}{RT} - n_{g,t}) = 0 \quad (5)$$

Solving for $n_{g,l}$ (only one root is meaningful) and knowing $n_{g,v} = n_{g,t} - n_{g,l}$, the amount of nitrogen in both phases can be calculated. When no nitrogen is dissolved in the liquid agent, i.e., $n_{g,l} = 0$, $P_t = p_g + p_{sat}$ is recovered from Eq. (5).

The results and the parameters that are required to perform the calculation are shown in Table 2. The calculated solubilities are also tabulated in Table 2. Solubility ($x_{g,l}$) is calculated as follows.

$$x_{g,l} = \frac{n_{g,l}}{n_{g,l} + n_{a,l}} \quad (6)$$

For all the agents studied, the amount of nitrogen dissolved in the liquid agent was calculated to be less than 25% of the total amount of nitrogen added. Nitrogen has the highest solubility in FC-31-10, whereas it dissolves insignificantly in HCFC-22. Nitrogen was found to be less soluble in the azeotrope (a mixture of HFC-125 and HFC-32) than in pure HFC-125.

Since the solubility of nitrogen is very small, i.e., $x_{g,l} \rightarrow 0$, Henry's law is applicable to nitrogen. Henry's law is given by

$$p_g = Hx_{g,l} \quad (7)$$

where H is the Henry's constant and is a function of temperature. From Eqs. (4) and (6), Henry's constants can be calculated and are tabulated in Table 2. Solubility of nitrogen at the same temperature but at a different partial pressure of nitrogen can be estimated if H is known.

Table 3 shows some of the recent results for Freon-23. The values reported in the table are the average of two runs, which deviated less than 7% from each other. Since the work is still in progress, the results from only four agents are presented.

Experimental results from FC-31-10, HFC-227, HFC-134a, and HCFC-22 show that the amount of Freon-23 needed to pressurize the vessel to ≈ 4.1 MPa is as much as or greater than that of the agent in the vessel. Under such conditions (for example HCFC-22), a pressure greater than 12 MPa (1750 psig) was measured when the vessel was heated to $\approx 50^\circ\text{C}$. Such an increase in pressure at elevated temperatures was caused by an increase in the amount of Freon-23 in the ullage of the vessel due to a decrease in solubility of Freon-23 in the liquid agent. If the vessel had been exposed to an ambient temperature of 150°C , a pressure higher than 20.6 MPa (3000 psig) could have easily been attained. If Freon-23 were to be selected as the pressurization gas, extreme care should be taken in the design of the bottle for the replacement agent, especially when the bottle may be exposed to a high temperature environment.

The above approximate calculation of solubility is not appropriate for Freon-23 because a significant amount of Freon-23 is dissolved in the liquid agent, as implied by the total amount of Freon-23 required to pressurize the vessel (see Table 3). Given the amount of Freon-23 and that of the agent at a specified temperature and pressure, a detailed vapor-liquid equilibrium (VLE) calculation is necessary in order to calculate the distributions of Freon-23 and agent in both the liquid and vapor phases [2, 3]. A suitable equation of state and some form of mixing rules are required. Recently, the Patel-Teja cubic equation of state [4] was found to correlate VLE data of various refrigerant mixtures better than other cubic equations of state [5]. Current effort is directed to the application of the Patel-Teja equation to VLE calculations of mixtures of Freon-23 and agents.

CONCLUDING REMARKS

The amount of nitrogen dissolved in all the agents was found to be very small. However, preliminary results of the four agents studied revealed that a considerable amount of Freon-23 was needed to pressurize the vessel, implying that the solubility of Freon-23 in the liquid agent

was much greater than that of nitrogen. Preliminary results suggested that at elevated temperature an extremely high pressure could result in the vessel if Freon-23 was used as a pressurization gas.

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Table 1. Experimental conditions and the amount of nitrogen needed to pressurize the vessel to P at T when the fill volume fraction is $1/3$.

| Agent | T (K) | P (MPa) | N_2 (gm) | Agent (gm) | N_2 /Agent |
|-----------|---------|-----------|------------|------------|--------------|
| FC-31-10 | 296 | 4.15 | 2.0 | 27.8 | 0.072 |
| FC-318 | 297 | 4.16 | 2.0 | 28.0 | 0.071 |
| HCFC-124 | 296 | 4.16 | 1.9 | 25.2 | 0.075 |
| HFC-227 | 297 | 4.16 | 1.8 | 26.3 | 0.068 |
| HFC-134a | 296 | 4.15 | 1.8 | 22.8 | 0.079 |
| FC-218 | 296 | 4.14 | 1.7 | 26.6 | 0.064 |
| HCFC-22 | 295 | 4.12 | 1.4 | 21.4 | 0.065 |
| HFC-125 | 296 | 4.21 | 1.5 | 24.3 | 0.062 |
| Azeotrope | 297 | 4.17 | 1.3 | 20.7 | 0.063 |

Table 2. Parameters used to calculate the amount of nitrogen in both liquid and vapor phases, the calculated amount (gm) of nitrogen in both phases ($m_{g,l}$, $m_{g,v}$), the calculated solubilities ($x_{g,l}$), and the calculated Henry's constants (H).

| Agent | $\rho_{a,l}$ (kg/m ³) | $\rho_{a,v}$ (kg/m ³) | P_{sat} (MPa) | $m_{g,l}$ (gm) | $m_{g,v}$ (gm) | $x_{g,l}$ | H (MPa) |
|-----------|--------------------------------------|--------------------------------------|--------------------|-------------------|-------------------|-----------|--------------|
| FC-31-10 | 1505 | 27.3 | 0.25 | 0.38 | 1.62 | 0.108 | 36.5 |
| FC-318 | 1504 | 27.0 | 0.30 | 0.43 | 1.57 | 0.102 | 38.0 |
| HCFC-124 | 1363 | 22.5 | 0.36 | 0.33 | 1.57 | 0.062 | 61.6 |
| HFC-227 | 1400 | 36.3 | 0.45 | 0.30 | 1.50 | 0.068 | 55.1 |
| HFC-134a | 1214 | 30.2 | 0.62 | 0.34 | 1.46 | 0.054 | 66.1 |
| FC-218 | 1333 | 83.4 | 0.84 | 0.32 | 1.38 | 0.084 | 40.3 |
| HCFC-22 | 1206 | 40.7 | 0.96 | N.S.* | 1.40 | - | - |
| HFC-125 | 1201 | 84.0 | 1.31 | 0.28 | 1.22 | 0.054 | 55.4 |
| Azeotrope | 1045 | 59.3 | 1.63 | 0.19 | 1.11 | 0.024 | 107.8 |

* not significant $O(10^{-4})$

Table 3. Experimental conditions and the amount of Freon-23 needed to pressurize the vessel to P at T when the fill volume fraction is 1/3.

| Agent | T (K) | P (MPa) | Freon-23 (gm) | Agent (gm) | Freon-23 /Agent |
|----------|------------|--------------|------------------|---------------|--------------------|
| FC-31-10 | 296 | 4.15 | 28.8 | 27.9 | 1.03 |
| HFC-227 | 297 | 4.17 | 30.4 | 26.3 | 1.16 |
| HFC-134a | 296 | 4.16 | 31.9 | 22.7 | 1.41 |
| HCFC-22 | 295 | 4.31 | 30.8 | 22.8 | 1.35 |

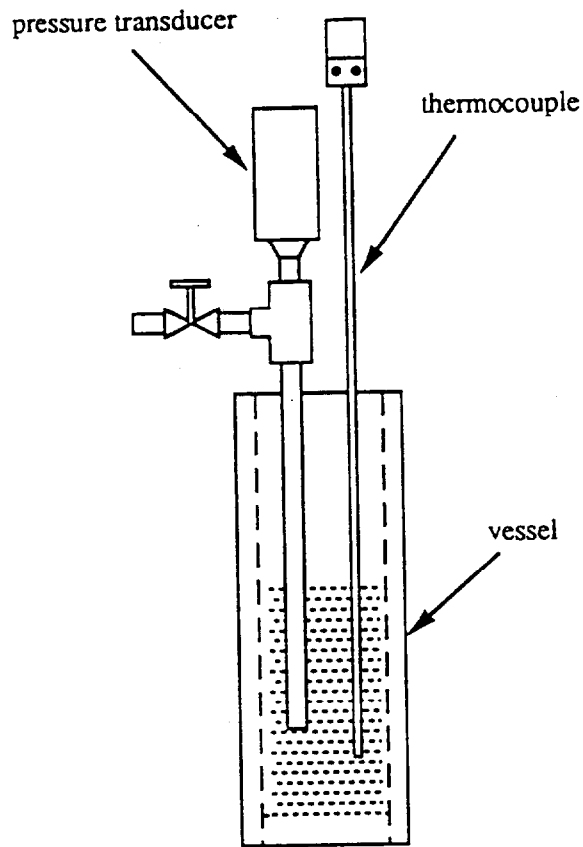


Fig. 1 Set-up for solubility measurement.

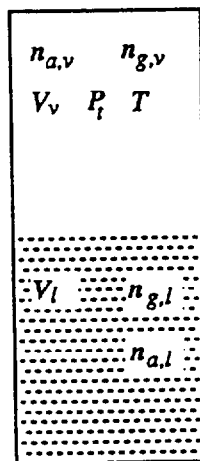


Fig. 2 Schematic showing the various parameters used in the calculation.

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