# Measured and predicted thermodynamic properties of selected halon alternative/nitrogen mixtures*

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Experimental measurements of selected thermodynamic properties of alternative agent/
nitrogen mixtures were performed. The selected alternatives were HFC-227ea ($C_3HF_7$),
$CF_3I$, FC-218 ($C_3F_8$), and HFC-125 ($C_2HF_5$); $CF_3Br$ was also included as a reference.
A thermodynamic model based on an extended corresponding states principle was
used. The model predictions were generally found to be within 10% or less of the
experimental measurements. The model can be used as a computational tool for
designers of fire extinguishers to obtain pressure–temperature relationships for selected
halon alternative/nitrogen mixtures. Published by Elsevier Science Ltd and IIR
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applications)

# Propriétés thermodynamiques mesurées et prévues pour une sélection de mélanges d' azote et de produits de remplacement de halons

*On a mesuré expérimentalement certaines propriétes thermodynamiques de mélanges d'
azote et de produits de remplacement. On a choisi comme produits de remplacement les
HFC-227ea (C3HF7), FC-218 (C3F8) et HFC-125 (C2HF5); le CF3BR a aussi été pris
à titre de référence. On a utilisé un modèle thermodynamique fondé sur le principe des états
correspondants étendu. On a trouvé que les prévisions générales du modèle se trouvaient
dans la limite de 10% autour des mesures expérimentales. On peut utiliser ce modèle comme
outil de calcul pour les concepteurs d'extincteurs d'incendie pour obtenir les relations
pression–température pour les mélanges d'azote et de produits de remplacement des halons.
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(Mots clés: incendie, halon, substitut, nitrogen, melange, propriete thermodynamique, calcul,
mesuré)

Current aircraft fire suppression bottles for in-flight fire protection are normally filled with liquid $CF_3Br$ (halon 1301) to about one-half of the bottle volume, and the bottle is then pressurized with nitrogen to a specified equilibrium pressure (typically 4.1 MPa) at room temperature. The purpose of using the pressur-ization gas is to expedite the discharge of the agent and to facilitate the dispersion of the agent. Without nitrogen pressurization, the bottle pressure, which is simply the vapor pressure of the agent, can be so low, especially at cold ambience, that there is not enough driving force to rapidly expel the agent from the bottle in case of a fire.

Due to its high ozone-depleting potential, $CF_3Br$ is now banned from production under the Montreal

**Table 1**　Selected thermophysical properties of halon alternatives

Tableau 1　*Propriétés thermodynamiques de produits de remplacement des halons*

| Agent | MW (kg/mol) | $T_b$ (°C) | $T_c$ (°C) | $P_c$ (MPa) | $P_{sat}$ (MPa) | $\rho_c$ (kg/m$^3$) | $\rho_l$ (kg/m$^3$) |
|---|---|---|---|---|---|---|---|
| HFC-227ea ($C_3HF_7$) | 0.170 | $-16.4^a$ | $101.9^a$ | $2.95^a$ | $0.46^a$ | $621^b$ | $1389^a$ |
| $CF_3I$ | 0.196 | $-22.0^c$ | $122.0^d$ | $4.04^d$ | $0.49^e$ | $871^d$ | $2106^f$ |
| FC-218 ($C_3F_8$) | 0.188 | $-36.8^a$ | $72.0^a$ | $2.68^a$ | $0.87^a$ | $629^g$ | $1251^a$ |
| HFC-125 ($C_2HF_5$) | 0.120 | $-48.6^a$ | $66.2^a$ | $3.63^a$ | $1.38^a$ | $571^h$ | $1190^a$ |
| $CF_3Br$ | 0.149 | $-57.8^a$ | $67.0^a$ | $4.02^a$ | $1.61^a$ | $745^i$ | $1551^a$ |

[a] From Gallagher *et al.*[4]
[b] From Great Lakes Chemical Corporation[5]
[c] From Kudchadker *et al.*[6]
[d] From Sladkov and Bogacheva[7]
[e] Estimated by the method of Lee and Kesler[8]
[f] Estimated by the modified Rackett method[8]
[g] From Braker and Mossman[9]
[h] From Allied Signal Inc.[10]
[i] From ASHRAE Inc.[11]

Protocol[1]. Alternatives are currently being sought to replace $CF_3Br$ for in-flight fire protection applications. Under the auspices of the U.S. Air Force, Navy, and Army, and the Federal Aviation Administration, the National Institute of Standards and Technology has been engaged in research in identifying potential short-term halon replacements[2,3]. As a result of that study, four halon alternatives (HFC-227ea, $CF_3I$, FC-218, and HFC-125) have been selected for potential in-flight fire protection applications.

The total pressure in the bottle is a complex function of ambient temperature because of the temperature dependence of the agent vapor pressure, the partial pressure of nitrogen in the gas ullage, and the solubility of nitrogen in the liquid agent. For $CF_3Br$, the bottle pressure–temperature relationship and the solubility of nitrogen in $CF_3Br$ have been well characterized. By contrast, such a relationship and solubility data are scarce or do not exist for some of the halon alternatives.

The initial amount of nitrogen that is required to pressurize a fire extinguisher with a specified amount of a halon alternative to a specified equilibrium total pressure at room temperature, and the variations of the total vessel pressure as a result of the fire extinguisher being exposed to different operating ambient temperatures are both critical for fire suppressant suppliers. The purpose of this study was to address these two issues. More specifically, the first objective was to measure the amount of nitrogen to pressurize the bottle to 2.75 or 4.12 MPa at room temperature (with an initial amount of liquid halon alternative in the bottle before nitrogen pressurization corresponding to approximately one-half or two-thirds of the vessel volume). These two pressures are common for most in-flight applications. The second objective was to determine the final pressure of the extinguisher bottle when it was subsequently exposed to two extreme temperatures (−60 and 150°C) which are
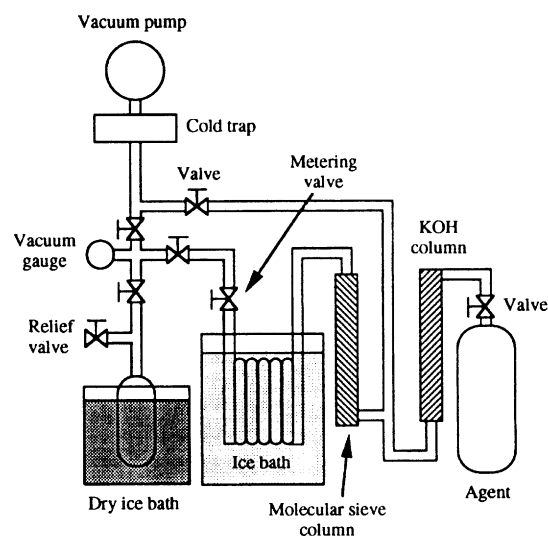


**Figure 1**　Schematic of $CF_3I$ purification system

Figure 1　*Schéma de système de purification pour $CF_3I$*

considered to be the lowest and highest operating temperatures for in-flight fire protection. $CF_3Br$ was also included in this study for the purposes of reference and comparison with the four alternative agents.

In addition, a thermodynamic model based on an extended corresponding state was used to predict the pressure–temperature relationship of the halon alternative/nitrogen mixtures and the initial amount of nitrogen that is required to pressurize the vessel to a specified initial total fill pressure at room temperature. The calculated results were compared and validated with experimental measurements. The model is intended to be used as a computational tool for designers of fire extinguishers to facilitate their design calculations.

For the purpose of reference, selected thermophysical properties of the four selected agents are tabulated in *Table 1* where MW is the molecular

weight, $T_b$ is the normal boiling point, $T_c$ is the critical temperature, $P_{sat}$ is the saturation vapor pressure at 25°C, $P_c$ is the critical pressure, $\rho_c$ is the critical density, and $\rho_l$ is the saturated liquid density at 25°C.

## Apparatus and procedure

### Agent preparation

Before the agent was dispensed into the test vessel, it was degassed to remove any dissolved non-condensable gases which might be present in the liquid agent. The detailed degassing procedure can be found in Gann[3]. Because the initial batch of $CF_3I$ was found contaminated with trace amounts of HI, $CO_2$, $H_2O$, and $I_2$, a purification system was constructed in order to remove impurities which might be present in other batches. The purification system is shown schematically in *Figure 1*. After the entire system was evacuated, the agent vapor passed through a column packed with potassium hydroxide whose main function was to remove HI, then through a molecular sieve filter to remove water vapor and carbon dioxide, and finally through a stainless steel coil which was immersed in an ice bath to remove $I_2$. The purified vapor was then retrieved by condensation in a stainless steel container. The collected agent was again subjected to degassing to further remove any non-condensable gases. The agents were obtained from Great Lakes Chemical Corporation* (HFC-227ea, $CF_3Br$), Allied-Signal (HFC-125), 3M Specialty Chemicals (FC-218), and Pacific Scientific ($CF_3I$).

### Total amount of nitrogen

To measure the total amount of nitrogen required to pressurize the vessel to a specified equilibrium pressure at room temperature, the experimental set-up consists of a stainless steel (SS 304) vessel equipped with a needle valve for dispensing the agent and nitrogen, a K-type thermocouple, and a pressure transducer with a resolution of 6.9 kPa. The total volume of the apparatus was determined to have a mean of 52.2 cm$^3$ with a standard deviation of 0.3 cm$^3$.

The experimental procedure was as follows. The apparatus was evacuated to 1.33 Pa for at least 10 minutes. The set-up was then connected to the agent supply bottle. The vessel was placed in a Dewar flask and chilled with dry ice before gaseous agent was dispensed through the needle valve into the vessel. Liquid agent was obtained by condensing the agent vapor, and the total amount was metered by placing the vessel and the Dewar flask on an electronic balance. When the amount of agent reached the target

mass, the needle valve was closed. The vessel was then removed from the Dewar flask, warmed to room temperature, and weighed on an electronic balance with an uncertainty of 0.1 g to determine the actual mass in the system. The nitrogen gas supply line was then connected to the vessel. The supply line was evacuated for at least 5 minutes before initiating a slow flow of nitrogen. The needle valve was then opened to allow nitrogen to bubble slowly through the liquid agent until an equilibrium pressure of approx. 2.8 MPa was reached. Shaking the vessel intermittently and vigorously and repetitive bubbling of nitrogen was required before the final equilibrium pressure was attained. The amount of nitrogen needed to pressurize the vessel was obtained by weighing the apparatus. This amount corresponded to the sum of the mass of nitrogen in the gas ullage of the vessel and that dissolved in the liquid agent. The charged vessel was then ready for the cold temperature experiments, as described in the next section. When the cold experiments were completed, the charged vessel was warmed to room temperature and was pressurized with more nitrogen to approx. 4.1 MPa. The amount of nitrogen was then determined, and the vessel was ready for another cold temperature experiment.

### Agent/nitrogen mixture measurements

For low temperature (−60°C) measurements, the experimental set-up discussed above was used. After the total amount of nitrogen in the vessel was determined, the filled vessel was immersed in a heat transfer fluid which was chilled by two immersion coolers to −60°C. The final vessel pressure was recorded from the pressure transducer read-out at least 1 hour later, after the internal temperature had reached thermal equilibrium with the bath temperature.

For high temperature (150°C) measurements, a different set-up was constructed because the vessel used in the cold temperature experiments could not withstand the pressure that resulted from the high temperature condition. The apparatus is shown schematically in *Figure 2*. It consisted of a stainless steel (SS 316) high pressure liquid level sight gage, a magnetic pump/mixer, a pressure transducer, and taper seal high pressure valves. Heating was achieved by placing the test apparatus in a temperature controlled oven. The internal volume of the entire system was determined by evacuating the system followed by introducing distilled water into the system from a beaker. The amount of water required to fill the system was then determined from the loss of weight of the beaker, and the internal system volume was calculated to have an average of 42.6 cm$^3$ with a standard deviation of 0.2 cm$^3$. The height of each window on the pressure vessel was also calibrated in terms of the volume percent of liquid to facilitate the filling process by measuring the amount of water required to fill up to each window. In order to
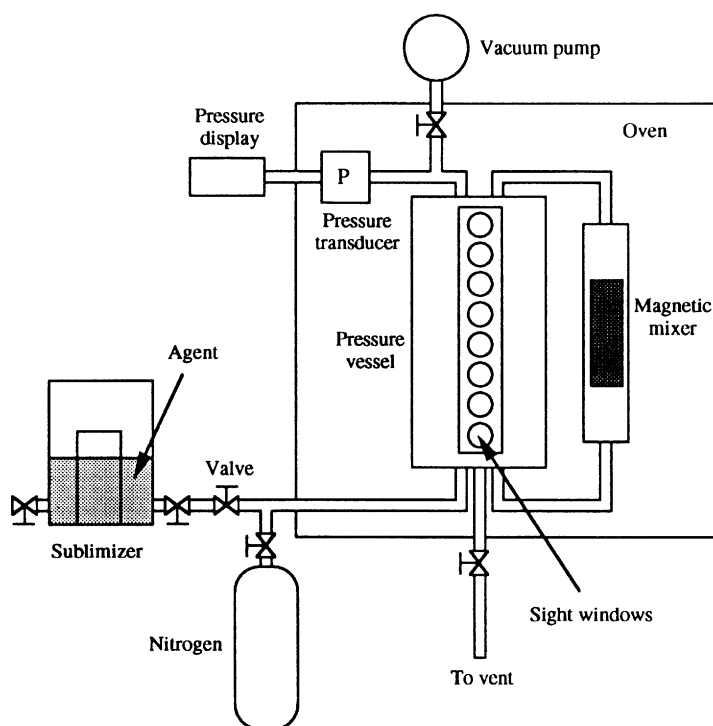
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**Figure 2** Apparatus for high temperature experiments

Figure 2 *Appareil pour les expériences à haute température*

minimize photolysis of CF₃I, agent filling was performed under a darkroom safelight. In addition, when CF₃I was used in a test, caution was taken to prevent stray room light from getting into the oven.

To perform an experiment, the entire system was first evacuated for at least half an hour before liquid agent was dispensed into the vessel. Then, the pressurization of the vessel with nitrogen to a specified equilibrium pressure (approx. 2.8 MPa) at room temperature was initiated with the magnetic pump running to facilitate the mixing of nitrogen with the agent. The oven was then turned on, and the test apparatus was heated to 150°C. Because of space limitation, it was not possible to insert a thermocouple into the vessel to monitor the internal temperature. To ensure that thermal equilibrium had been reached, two thermocouples were placed at two different locations on the vessel wall, and the final pressure was recorded only when the two thermocouple readings were within 1.0°C of the set temperature of the oven and the final pressure maintained a steady reading for at least half an hour. The apparatus was then cooled back to room temperature, pressurized with nitrogen to approx. 4.1 MPa, and heated to 150°C, where the equilibrium pressure was recorded.

**Modeling thermodynamic properties of agent/nitrogen mixtures**

The thermodynamic properties of agent/nitrogen mixtures are calculated using a computer program

PROFISSY (acronym for Properties Of Fire Suppression Systems). The program incorporates a model known as 'extended corresponding states' (ECS). This model has been quite successful in modeling the thermodynamic and transport properties of fluids. ECS is a powerful method, applicable to the entire range of fluid states, from dense liquid to dilute gas, as well as to the supercritical fluid regime. It may be used with only minimal information on a fluid: the critical point, the normal boiling point, and the molecular weight. Additional information on a fluid, such as vapor pressures, saturated liquid densities, and liquid viscosities can be used to refine the model predictions.

Recently ECS models have been used to model thermophysical properties of alternative refrigerants and their mixtures[12-14]. In this work, we extended the model to calculate the thermodynamic properties of agent/nitrogen mixtures.

*Extended corresponding states model*

The central idea of extended corresponding states is that all points on the *PVT* surface of any fluid may be represented by scaling the *PVT* surface of a reference substance. These 'scale factors' involve the critical properties of the fluid of interest and the reference fluid, and may also be functions of temperature and density.

The basic equation in the extended corresponding states theory relates the dimensionless residual

Helmholtz free energy of a pure fluid, denoted by subscript *j*, to that of a reference fluid, denoted by subscript o, whose thermodynamic properties are known, in principle, with great accuracy:

$$a_j^r(\rho_j, T_j) = a_o^r(\rho_o, T_o) \tag{1}$$

where the residual Helmholtz free energy is defined as

$$a^r = \frac{A(\rho, T) - A^*(\rho, T)}{RT} \tag{2}$$

In the above two equations, $A$ is the Helmholtz free energy, the asterisk indicates an ideal gas state value, $\rho$ is the molar density, $T$ is the absolute temperature, and $R$ is the universal gas constant. The temperature and molar density of the fluid $j$ are scaled with the corresponding values for the reference fluid o according to the following two equations:

$$T_o = \frac{T_j}{f_j} \tag{3}$$

$$\rho_o = \rho_j h_j \tag{4}$$

where the scale factors $f_j$ and $h_j$ are called the equivalent substance reducing ratios. In extended corresponding states between two pure fluids *j* and o, they are related to the critical parameters of the two fluids, namely

$$f_j = \frac{T_{c,j}}{T_{c,o}} \theta_j(\rho_j, T_j) \tag{5}$$

$$h_j = \frac{\rho_{c,o}}{\rho_{c,j}} \phi_j(\rho_j, T_j) \tag{6}$$

where the functions $\theta_j$ and $\phi_j$ are called shape factors, and subscript c denotes a critical property. In addition, the condition that the compressibility factors of the fluids be equal, $Z_j^r = Z_o^r$, is imposed. Other dimensionless residual thermodynamic properties of a fluid can be derived form differentiation of Equation (1) and can be found in Huber and Ely[15].

To calculate properties of mixtures using extended corresponding states, we use what is known as a 'one-fluid' mixture model. The properties of a mixture are found by first assuming the mixture to be a single hypothetical pure fluid (subscript *x*) through the use of some mixing and combining rules. In this way, the properties of the hypothetical pure fluid are then found by scaling with a single reference fluid o.

$$a_{mix}^r(\rho, T, [x_j]) = a_x^r(\rho_x, T_x) = a_o^r(\rho_o, T_o) \tag{7}$$

In order to obtain the equivalent substance reducing ratios, $f_x$ and $h_x$, for the hypothetical pure fluid, we use the van der Waals one-fluid mixing rules,

$$h_x = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j h_{ij} \tag{8}$$

$$f_x h_x = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j f_{ij} h_{ij} \tag{9}$$

and the combining rules,

$$f_{ij} = \sqrt{f_i f_j}(1 - k_{ij}) \tag{10}$$

$$h_{ij} = \frac{(h_i^{1/3} + h_j^{1/3})^3 (1 - l_{ij})}{8} \tag{11}$$

where *x* is the mole fraction, *n* is the number of components, subscripts *i* and *j* refer to component *i* and *j* respectively, $k_{ij}$ and $l_{ij}$ are the binary interaction parameters that may be non-zero when $i \neq j$ and $k_{ii}$ and $l_{ii}$ are defined to be zero. The parameters are generally found empirically by fitting experimental data. However, in order to test the robustness of the ECS model without resorting to the experimental data which have to be obtained *a priori*, the binary interaction parameters are set equal to zero in the model.

Several factors contribute to the ability of the ECS model to accurately predict thermophysical properties. Two important factors are the choice of the reference fluid and the determination of the shape factors. It is important to have a very well characterized empirical reference fluid equation of state. The reference fluid used in this work is HFC-134a (1,1,1,2-tetrafluoroethane) which is represented by the Jacobsen–Stewart[16] modified 32 term Benedict–Webb–Rubin equation of state (MBWR-32) with coefficients as determined by Huber and McLinden[17]. This equation has been used extensively to represent the properties of hydrocarbons, common inorganics, and most recently refrigerants. Its functional form is essentially a polynomial in density and temperature and is given by

$$p = \sum_{n=1}^{9} a_n(T)\rho^n + e^{-(\rho/\rho_c)^2} \sum_{n=10}^{15} a_n(T)\rho^{2n-17} \tag{12}$$

The temperature dependence of the $a_n(T)$ for the reference fluid HFC-134a is tabulated in Huber and Ely[15]. Equation (12), when applied to HFC-134a, typically reproduces the pressures within 0.4% and the density within 0.2%. Exceptions are large density deviations in the near critical region, and large pressure errors in the low-temperature compressed liquid region near the saturation boundary.

The accuracy one obtains from ECS models also depends on how well the shape factors are determined. The shape factors are functions of both density and temperature. In principle, if one has accurate, analytical equations of state for the two fluids, the exact shape factors relating them can be found, as discussed by Ely[18]. However, often only one fluid (the reference) has an accurate, analytical equation of state available. In this situation, one usually assumes an empirical form for the shape factors. Leach *et al.*[19] expressed the shape factors as weak functions of temperature and density using the acentric factor as a third correlating parameter. Since the shape factors are much stronger functions of temperature than density and most of the data which are available for refrigerants are for the saturation boundary, we have chosen a different

approach utilizing information along the saturation boundary of the fluids[15] which results in density independent shape factors. It can be shown[15] that the vapor pressures and the saturated liquid densities of a fluid can be related to the reference fluid properties through the following equations

$$p_{\text{sat},j}(T_j) = p_{\text{sat},0}\left(\frac{T_j}{f_j}\right)\frac{f_j}{h_j} \tag{13}$$

$$\rho_{\text{sat},j}(T_j) = \rho_{\text{sat},0}\left(\frac{T_j}{f_j}\right)\frac{1}{h_j} \tag{14}$$

where subscript sat refers to a property of a fluid along the saturation boundary. Equations (13) and (14) are simultaneously solved to obtain $f_j$ and $h_j$ along the saturation boundary. Vapor pressures and saturated liquid densities are provided from empirical correlations of data, if available, or from estimations[8]. Additional information on the procedure for obtaining shape factors can be found in Huber and Ely[15].

We do not yet have extensive results on the performance of the ECS model for predicting the density of agent/nitrogen mixtures; however, our experience with hydrocarbon mixtures and with refrigerant mixtures gives us confidence that generally the densities of the liquid phase are accurate to within 3%. This number can be improved with the use of the binary interaction parameters.

*Calculation procedure*

The computer code was developed with the primary purpose of helping fire suppression bottle designers or users to obtain temperature–pressure characteristics of the bottle. In other words, given a vessel ($V_t$) charged with agent and nitrogen at room temperature, one would like to know what the final vessel pressure will be when the vessel is exposed to a different temperature. In this aspect, only the information which is pertinent to the problem is provided in the output although the computer program can perform other thermodynamic property calculations.

The first step in the calculation is to determine the initial conditions of the vessel, that is, to determine the compositions of the liquid and vapor phases, the fraction of the mixture (agent/nitrogen) that will be in the vapor phase, and the amount of nitrogen required to pressurize the vessel or the initial total pressure of the vessel given an initial amount of nitrogen. To perform such calculations, it is required that the amount of agent, the fill temperature, the vessel size, and the total pressure of the vessel or the amount of nitrogen in the vessel be known. The calculation is essentially a flash calculation at fixed $T$ and $P$.

Given a mixture, in this case agent/nitrogen, whose bulk compositions ($z_j$) are known at $T$ and $P$, determine $x_j$, $y_j$, and fraction vaporized ($\alpha$), where $x$ is the liquid mole fraction and $y$ is the vapor mole fraction. A detailed computational procedure can be found in Prausnitz *et al.*[20] and Walas[21]. In our case,

the calculation is slightly different depending on whether (1) the amount of nitrogen ($n_{g,t}$) or (2) the total initial charge pressure ($P_i$) is given.

In Case (1), with $V_t$, $T_i$, $n_{a,t}$, and $n_{g,t}$ given, we calculate $P_i$, $x_g$, $y_g$, and $\alpha$, where $n$ is the number of moles and subscripts, t, g, and a represent total, nitrogen, and agent respectively. Note that for a binary system $x_a$ and $y_a$ are known once $x_g$ and $y_g$ are determined. In Case (2), knowing $V_t$, $T_i$, $n_{t,a}$, and $P_i$, then $n_{g,t}$, $x_g$, $y_g$, and $\alpha$ are calculated. Irrespective of Case (1) or (2), bubble point and dew point calculations (see e.g. Prausnitz *et al.*[20]) need be carried out to ensure that the flash calculations are performed in the two-phase region.

Once the initial conditions of the vessel are established, calculations of temperature–pressure characteristics can proceed. In this case, given $V_t$, $n_{a,t}$, and $n_{g,t}$, we want to calculate $P_f$, $x_g$, $y_g$, and $\alpha$ at $T_f$ if the resulting condition is in a two-phase region. The computational procedure is similar to Case (1) above. If the resulting condition in the vessel is in a single-phase region, then straightforward $PVT$ calculations will provide $P_f$ given $V_t$, $T_f$, and $z_i$ ($= x_i$ or $y_i$).

Only four pieces of information are required to run the program: (1) agent mass, (2) vessel volume, (3) fill temperature, and (4) either nitrogen mass needed to pressurize the vessel, or the fill pressure of the vessel. The current version of the program only supports the agents used in this study although other agents can be incorporated into the program by modifying the property database.

**Results and discussion**

In the following discussion, all the predictions from the thermodynamic model were obtained by setting the binary interaction parameters, $k_{ij}$ and $l_{ij}$, equal to zero.

*Total amount of nitrogen*

*Table 2* summarizes the experimental results obtained under an initial total pressure ($P_i$) at $T_i = 23°C \pm 1°C$ and with an initial amount of liquid agent corresponding to one-half of the vessel volume. For all the agents evaluated, the amounts of nitrogen ($m_{g,t}$) required to pressurize the vessel to $\sim 2.8$ and $\sim 4.1$ MPa were found experimentally to be less than 4 and 6% of the total mass of the agent ($m_{a,t}$), respectively. The predicted nitrogen mass under $T_i$ and $P_i$ were obtained using PROFISSY. The calculations were performed with $m_{a,t}$, $P_i$, $V_t$, and $T_i$ as input. In most cases, the predicted nitrogen mass compares favorably with the measured value even without taking $k_{ij}$ and $l_{ij}$ into consideration.

*Table 3* tabulates the experimental results as well as the predictions obtained when the initial amount of liquid agent corresponded to two-thirds of the vessel

**Table 2** Amount of nitrogen ($m_{g,t}$) required to pressurize mixture to $P_i$ at $T_i$ = 23°C ± 1°C with an initial amount of liquid agent corresponding to one-half of the vessel volume

Tableau 2  *Quantité d'azote* ($m_{g,t}$) *nécessaire pour pressuriser un mélange à la pression* $P_i$ *et à la température* $T_i$ *= 23°C ± 1°C avec une quantité de liquide initiale correspondant à la moitié du volume du récipient*

| Agent | Agent, $m_{a,t}$ (g) | $P_i$ (MPa) | $m_{g,t}$ (g) (measured) | $m_{g,t}$ (g) (predicted) | Difference[a] (%) |
|---|---|---|---|---|---|
| HFC-227ea | 36.5 | 2.90 | 1.2 | 1.24 | 3.3 |
|  | 36.6 | 2.93 | 1.2 | 1.26 | 5.0 |
|  | 36.5 | 4.29 | 1.9 | 1.95 | 2.6 |
|  | 36.6 | 4.28 | 1.9 | 1.94 | 2.1 |
| CF₃I | 54.9 | 2.87 | 1.0 | 1.15 | 15.0 |
|  | 54.8 | 2.87 | 1.1 | 1.15 | 5.0 |
|  | 54.9 | 4.21 | 1.6 | 1.79 | 12.0 |
|  | 54.8 | 4.21 | 1.7 | 1.78 | 4.7 |
| FC-218 | 33.2 | 2.89 | 1.0 | 1.07 | 7.0 |
|  | 33.1 | 2.89 | 1.1 | 1.07 | 2.7 |
|  | 33.2 | 4.27 | 1.8 | 1.77 | 1.7 |
|  | 33.1 | 4.31 | 1.8 | 1.80 | 0.0 |
| HFC-125 | 31.3 | 2.78 | 0.9 | 0.81 | 10.0 |
|  | 31.1 | 2.79 | 0.8 | 0.81 | 1.3 |
|  | 31.3 | 4.24 | 1.6 | 1.62 | 1.3 |
|  | 31.1 | 4.23 | 1.6 | 1.61 | 0.6 |
| CF₃Br | 40.9 | 2.89 | 0.7 | 0.75 | 7.1 |
|  | 40.7 | 2.87 | 0.6 | 0.75 | 25.0 |
|  | 40.9 | 4.29 | 1.4 | 1.53 | 9.3 |
|  | 40.7 | 4.29 | 1.4 | 1.53 | 9.3 |

[a] Difference (%) = $|m_{g,t}$(measured) $- m_{g,t}$(predicted)$| \times 100/m_{g,t}$(measured)

**Table 3** Amount of nitrogen ($m_{g,t}$) required to pressurize mixture to $P_i$ at $T_i$ (= 23°C ± 1°C) with an initial amount of liquid agent corresponding to two-thirds of the vessel volume

Tableau 3  *Quantité d'azote* ($m_{g,t}$) *nécessaire pour pressuriser un mélange à la pression* $P_i$ *et à la température* $T_i$ *= 23°C ± 1°C avec une quantité de liquide initiale correspondant aux deux tiers du volume du récipient*

| Agent | Agent, $m_{a,t}$ (g) | $P_i$ (MPa) | $m_{g,t}$ (g) (measured) | $m_{g,t}$ (g) (predicted) | Difference[a] (%) |
|---|---|---|---|---|---|
| HFC-227ea | 48.7 | 2.87 | 1.1 | 1.16 | 5.5 |
|  | 48.7 | 2.98 | 1.2 | 1.21 | 0.8 |
|  | 48.7 | 4.25 | 1.8 | 1.81 | 0.6 |
|  | 48.7 | 4.25 | 1.8 | 1.82 | 1.1 |
| CR₃I | 72.8 | 2.77 | 0.9 | 1.02 | 13.3 |
|  | 72.7 | 2.79 | 0.9 | 1.02 | 13.3 |
|  | 72.8 | 4.14 | 1.4 | 1.62 | 15.7 |
|  | 72.7 | 4.16 | 1.4 | 1.63 | 16.4 |
| FC-218 | 44.1 | 2.94 | 1.0 | 1.07 | 7.0 |
|  | 44.2 | 2.93 | 1.0 | 1.06 | 6.0 |
|  | 44.1 | 4.36 | 1.6 | 1.81 | 13.1 |
|  | 44.2 | 4.29 | 1.6 | 1.75 | 9.4 |
| HFC-125 | 41.9 | 2.70 | 0.8 | 0.79 | 1.3 |
|  | 41.8 | 2.85 | 0.8 | 0.83 | 3.8 |
|  | 41.9 | 4.18 | 1.5 | 1.56 | 4.0 |
|  | 41.8 | 4.18 | 1.5 | 1.51 | 0.7 |
| CF₃Br | 54.9 | 2.92 | 0.7 | 0.76 | 8.6 |
|  | 54.8 | 2.87 | 0.7 | 0.74 | 5.7 |
|  | 54.9 | 4.25 | 1.4 | 1.48 | 5.7 |
|  | 54.8 | 4.25 | 1.4 | 1.49 | 6.4 |

[a] Difference (%) = $|m_{g,t}$(measured) $- m_{g,t}$(predicted)$| \times 100/m_{g,t}$(measured)

volume. The measured and predicted nitrogen masses, in most cases, differ by less than 15%. For all the agents evaluated, the amount of nitrogen required to pressurize the vessel was found experimentally to be less than 3 (~2.8 MPa) and 4% (~4.1 MPa) of the total mass of the agent.

*Agent/nitrogen mixtures*

The experimental results for agent/nitrogen mixtures at −60°C with an initial volume of liquid agent corresponding to one-half of the vessel volume are shown in *Table 4*. In all cases, the combined standard

**Table 4** Initial conditions at $T_i = 23°C \pm 1°C$ and final pressures ($P_{f,c}$) at $-60°C \pm 1°C$ for agent/nitrogen mixtures (half-filled volume)

Tableau 4 *Conditions intiales à* $T_i = 23°C$ *et pressions finales à* $-60°C \pm 1°C$ *pour des mélanges agent/azote (remplissage à moitié)*

| Agent | $m_{a,t}$ (g) | $P_i$ (MPa) | $P_{f,c}$ (MPa) (measured) | $P_{f,c}$ (MPa) (predicted) | Difference[a] (%) |
|---|---|---|---|---|---|
| HFC-227ea | 36.5 | 2.90 | 1.69 | 1.70 | 0.6 |
| | 36.6 | 2.93 | 1.72 | 1.71 | 0.6 |
| | 36.5 | 4.29 | 2.59 | 2.60 | 0.4 |
| | 36.6 | 4.28 | 2.58 | 2.61 | 1.2 |
| CF₃I | 54.9 | 2.87 | 1.71 | 1.61 | 5.9 |
| | 54.8 | 2.87 | 1.71 | 1.62 | 5.3 |
| | 54.9 | 4.21 | 2.62 | 2.49 | 5.0 |
| | 54.8 | 4.21 | 2.61 | 2.47 | 5.4 |
| FC-218 | 33.2 | 2.89 | 1.44 | 1.39 | 3.5 |
| | 33.1 | 2.89 | 1.43 | 1.38 | 3.5 |
| | 33.2 | 4.27 | 2.34 | 2.23 | 4.7 |
| | 33.1 | 4.31 | 2.38 | 2.27 | 4.6 |
| HFC-125 | 31.3 | 2.78 | 1.11 | 1.07 | 3.6 |
| | 31.1 | 2.79 | 1.11 | 1.08 | 2.7 |
| | 31.3 | 4.24 | 2.10 | 2.04 | 2.9 |
| | 31.1 | 4.23 | 2.09 | 2.03 | 2.9 |
| CF₃Br | 40.9 | 2.89 | 1.04 | 1.02 | 1.9 |
| | 40.7 | 2.87 | 1.00 | 1.02 | 2.0 |
| | 40.9 | 4.29 | 1.95 | 1.94 | 0.5 |
| | 40.7 | 4.29 | 1.99 | 1.97 | 1.0 |

[a] Difference (%) = $|P_{f,c}$(measured) $- P_{f,c}$(predicted)$| \times 100/P_{f,c}$(measured)

**Table 5** Initial conditions at $T_i = 23°C \pm 1°C$ and final pressures ($P_{f,c}$) at $-60°C \pm 1°C$ for agent/nitrogen mixtures (two-thirds-filled volume)

Tableau 5 *Conditions intiales à* $T_i = 23°C$ *et pressions finales à* $-60°C \pm 1°C$ *pour des mélanges agent/azote (remplissage aux deux tiers)*

| Agent | $m_{a,t}$ (g) | $P_i$ (MPa) | $P_{f,c}$ (MPa) (measured) | $P_{f,c}$ (MPa) (predicted) | Difference[a] (%) |
|---|---|---|---|---|---|
| HFC-227ea | 48.7 | 2.87 | 1.66 | 1.67 | 0.6 |
| | 48.7 | 2.98 | 1.70 | 1.73 | 1.8 |
| | 48.7 | 4.25 | 2.55 | 2.57 | 0.8 |
| | 48.7 | 4.25 | 2.51 | 2.59 | 3.2 |
| CF₃I | 72.8 | 2.77 | 1.60 | 1.52 | 5.0 |
| | 72.7 | 2.79 | 1.64 | 1.53 | 6.7 |
| | 72.8 | 4.14 | 2.49 | 2.43 | 2.4 |
| | 72.7 | 4.16 | 2.62 | 2.41 | 8.0 |
| FC-218 | 44.1 | 2.94 | 1.41 | 1.41 | 0.0 |
| | 44.2 | 2.93 | 1.39 | 1.38 | 0.7 |
| | 44.1 | 4.36 | 2.32 | 2.32 | 0.0 |
| | 44.2 | 4.29 | 2.30 | 2.27 | 1.3 |
| HFC-125 | 41.9 | 2.70 | 1.08 | 1.06 | 1.9 |
| | 41.8 | 2.85 | 1.10 | 1.11 | 0.9 |
| | 41.9 | 4.18 | 2.06 | 2.05 | 0.5 |
| | 41.8 | 4.18 | 2.02 | 1.99 | 1.5 |
| CF₃Br | 54.9 | 2.92 | 1.05 | 1.04 | 1.0 |
| | 54.8 | 2.87 | 1.02 | 1.02 | 0.0 |
| | 54.9 | 4.25 | 1.94 | 1.94 | 0.0 |
| | 54.8 | 4.25 | 1.90 | 1.96 | 3.2 |

[a] Difference (%) = $|P_{f,c}$(measured) $- P_{f,c}$(predicted)$| \times 100/P_{f,c}$(measured)

uncertainty of the measurement was found to be less than 0.1 MPa. Comparing to the vapor pressure of a pure agent at $-60°C$, the measurements showed that there were still significant residual pressures in the vessel. These residual pressures are deemed necessary to expel the cold liquid agents if the vessels are discharged (in case of a fire) under such extremely low temperature. The fifth column in the table tabulates the predicted final pressures. The calculations were performed with the initial conditions given in the table. In general, the predicted values were all found to be within 6% of the measured values.

**Table 6** Initial conditions at $T_i$ = 23°C ± 1°C and final pressures ($P_{f.h}$) at 150°C ± 2°C for agent/nitrogen mixtures (half-filled volume)

Tableau 6   *Conditions initiales à* $T_i$ = 23°C ± 1°C *et pressions finales (*$P_{f.h}$*) à* 150°C ± 2°C *pour des mélanges agent/azote (remplissage à moitié)*

| Agent | $m_{a.t}$ (g) | $P_i$ (MPa) | $P_{f.h}$ (MPa) (measured) | $P_{f.h}$ (MPa) (predicted) | Difference[a] (%) |
|---|---|---|---|---|---|
| HFC-227ea | 28.3 | 2.76 | 10.70 | 10.39 | 2.9 |
|  | 30.3 | 2.81 | 11.25 | 10.95 | 2.7 |
|  | 28.3 | 4.29 | 13.58 | 13.25 | 2.4 |
|  | 30.3 | 4.19 | 14.43 | 14.00 | 3.0 |
| CF$_3$I | 43.2 | 2.75 | 10.38 | 10.55 | 1.6 |
|  | 43.2 | 2.74 | 10.22 | 10.35 | 1.3 |
|  | 43.2 | 4.13 | 12.71 | 13.03 | 2.5 |
|  | 43.2 | 4.16 | 12.92 | 13.05 | 1.0 |
| FC-218 | 28.9 | 2.85 | 12.13 | 11.90 | 1.9 |
|  | 29.1 | 2.76 | 11.84 | 11.76 | 0.7 |
|  | 28.9 | 4.16 | 14.64 | 14.44 | 1.4 |
|  | 29.1 | 4.25 | 14.73 | 14.59 | 1.0 |
| HFC-125 | 26.4 | 2.79 | 14.45 | 14.43 | 0.1 |
|  | 26.1 | 2.78 | 14.35 | 14.41 | 0.4 |
|  | 26.4 | 4.18 | 17.32 | 17.56 | 1.4 |
|  | 26.1 | 4.21 | 17.20 | 17.36 | 0.9 |
| CF$_3$Br | 34.9 | 2.80 | 14.32 | 14.04 | 2.0 |
|  | 34.9 | 4.22 | 17.11 | 16.90 | 1.2 |

[a] Difference (%) = $|P_{f.h}$(measured) − $P_{f.h}$(predicted)$|$ × 100/$P_{f.h}$(measured)

**Table 7** Initial conditions at $T_i$ = 23°C ± 1°C and final pressures ($P_{f.h}$) at 150°C ± 1°C for agent/nitrogen mixtures (two-thirds-filled volume)

Tableau 7   *Conditions initiales à* $T_i$ = 23°C ± 1°C *et pressions finales (*$P_{f.h}$*) à* 150°C ± 2°C *pour des mélanges agent/azote (remplissage aux deux tiers)*

| Agent | $m_{a.t}$ (g) | $P_i$ (MPa) | $P_{f.h}$ (MPa) (measured) | $P_{f.h}$ (MPa) (predicted) | Difference[a] (%) |
|---|---|---|---|---|---|
| HFC-227ea | 38.4 | 2.80 | 15.56 | 14.57 | 6.4 |
|  | 39.7 | 2.78 | 16.77 | 15.34 | 8.5 |
|  | 38.4 | 4.14 | 19.19 | 17.71 | 7.7 |
|  | 39.7 | 4.29 | 20.54 | 18.87 | 8.1 |
| CF$_3$I | 57.3 | 2.76 | 13.79 | 14.34 | 4.0 |
|  | 58.6 | 2.79 | 14.42 | 15.08 | 4.6 |
|  | 57.3 | 4.23 | 17.62 | 18.38 | 4.3 |
|  | 58.6 | 4.10 | 18.25 | 18.41 | 0.9 |
| FC-218 | 37.4 | 2.88 | 16.39 | 16.24 | 0.9 |
|  | 37.3 | 2.78 | 16.51 | 16.68 | 1.0 |
|  | 37.4 | 4.16 | 20.03 | 20.01 | 0.1 |
|  | 37.3 | 4.23 | 19.99 | 19.94 | 0.3 |
| HFC-125 | 34.6 | 2.76 | 20.13 | 20.37 | 1.2 |
|  | 32.3 | 2.86 | 18.87 | 18.94 | 0.4 |
|  | 34.6 | 4.16 | 24.25 | 24.71 | 1.9 |
|  | 32.3 | 4.18 | 22.39 | 22.87 | 2.1 |
| CF$_3$Br | 44.4 | 2.76 | 18.92 | 18.68 | 1.3 |
|  | 45.6 | 2.76 | 20.19 | 19.69 | 2.5 |
|  | 44.4 | 4.18 | 22.91 | 22.82 | 0.4 |
|  | 45.6 | 4.21 | 23.22 | 23.31 | 0.4 |

[a] Difference (%) = $|P_{f.h}$(measured) − $P_{f.h}$(predicted)$|$ × 100/$P_{f.h}$(measured)

*Table 5* summarizes the results obtained from experiments at −60°C using an initial liquid agent volume equivalent to two-thirds of the vessel volume. Considerable final pressures in the vessel were also noted at −60°C. The comparisons between predicted and measured final pressures indicate that overall the differences were within 8% for all the agents.

The results for high temperature (150°C) measurements are shown in *Tables 6* and *7* for initial conditions corresponding to one-half and two-thirds filled volumes, respectively. The combined standard uncertainty, in all cases, was estimated to be less than 0.2 MPa. For these two experimental conditions, the differences between the predicted and measured final pressures were found to be within 10%.

## Conclusions

Experimental measurements of selected thermodynamic properties of selected halon alternative (HFC-227ea, CF$_3$I, FC-218, and HFC-125)/nitrogen mixtures have been performed. A thermodynamic model which is based on extended corresponding states was used to predict thermodynamic properties of halon alternative/nitrogen mixtures and to help fire suppression bottle designers to facilitate the calculations of bottle temperature–pressure relationships. Comparing to the experimental measurements, the predictions from the model were generally found to be within 10% of the measured values.

## Acknowledgements

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