A Model for Calculating Alternative Agent/Nitrogen Thermodynamic Properties

Jiann C. Yang, Marcia L. Huber', and Charles I. Boyer

Fire Science Division
Building and Fire Research Laboratory
and
'Thermophysics Division
'Chemical Science and Technology Laboratory
National Institute of Standards and Technology
Gaithersburg, MD 20899 U.S.A.
and
'Boulder, CO 80303 U.S.A.

ABSTRACT

A thermodynamic model based on the extended corresponding states principle has been developed to calculate the solubilities of nitrogen in five selected agents, HFC-227ea, CF_3I, FC-218, HFC-125, and CF_3Br and the pressure-temperature relationship for agent/nitrogen mixtures. The model only requires four pieces of input information: (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. Comparing to the experimental data obtained at 150 "C and -60 "C, the model predictions were generally found to be within 10% or less of the experimental measurements.

INTRODUCTION

As a continuation of the USAF/Navy/Army/FAA sponsored halon replacement project currently being conducted at the National Institute of Standards and Technology (NIST), the thermodynamic properties, in particular the pressure-temperature relationship for agent/nitrogen mixtures and nitrogen solubilities in agents, were further evaluated on the four agents, namely HFC-227ea, CF_3I, FC-218, and HFC-125, being considered for in-flight aircraft fire protection applications. Halon 1301 (CF_3Br) was also included in the study for the purpose of comparison.

A computer code, named PROFISSY (acronym for Properties of Fire Suppression Systems), was developed in the course of the study to facilitate the assimilation of the experimental data and to provide bottle design engineers a means to estimate pressure-temperature characteristics for the four selected agenthitrogen mixtures. Other agents can also be incorporated into the program by modifying the agent property database, if needed.

The computer code is based on a model known **as** "extended corresponding states" (ECS). This model has been quite successful in modeling the thermodynamic and transport properties of fluids. An early model of this type, known as the TRAPP model (Ely and Hanley, 1981a, 1981b, and 1983), has been successful in the prediction of hydrocarbon transport properties, including LNG (McCarty, 1982). Much of the development of TRAPP occurred in the early 1980's at the National Institute of Standards and Technology. Since that time, the model has been revised, improved, and used successfully to predict the properties of hydrocarbon mixtures (Ely, 1982; Huber and Ely, 1990; Friend, 1992), air (Ely, 1990), and CO_2-rich hydrocarbon mixtures (Sherman *et al.*, 1989), and forms the basis of two current Standard Reference Data Products (Huber and Ely, 1990; Friend, 1992). ECS has been used successfully to predict equilibrium properties such **as** density, heat capacity, speed of sound, entropy, enthalpy, Joule-Thomson coefficient, viscosity, and thermal conductivity. It 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 thennophysical properties of alternative refrigerants and their mixtures (Huber and Ely, 1992; Huber et al., 1992; Gallagher et af., 1995). 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, ρ 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 θ_j and ϕ_j are called shape factors, and subscript c denotes a critical property. In addition, we impose the condition that the compressibility factors of the fluids be equal, $Z_j^r = Z_o^r$. Other

dimensionless residual thermodynamic properties of a fluid can be derived from differentiation of Equation (1) and can be found in Huber and Ely (1994).

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 behaves as 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 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 (1973) modified 32 term Benedict-Webb-Rubin equation of state (MBWR-32) with coefficients **as** determined **by** Huber and McLinden (1992). 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 $a_n(T)$ is summarized in Table 1. 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 (1990). 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.* (1968) 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 (Huber and Ely, 1994) which results in density independent shape factors. It can be shown (Huber and Ely, 1994) that the vapor pressures and the saturated liquid densities of a fluid can be related to the reference fluid properties through the following equations,

$$p_{sat, j}(T_j) = p_{sat, o}(\frac{T_j}{f_j}) \frac{f_j}{h_j} \tag{13}$$

$$\rho_{sat, j}(T_j) = \rho_{sat, o}(\frac{T_j}{f_j}) \frac{1}{h_j} \tag{14}$$

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 (Reid *et al.,* 1987). Additional information on the procedure for obtaining shape factors can be found in Huber and Ely (1994).

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 reduced with the use of the binary interaction parameters.

CALCULATION PROCEDURE

The computer code PROFISSY was developed with the primary purpose of helping fire suppression bottle designers or users to obtain temperature-pressure characteristics of the bottle contents. 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 report, 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

Table 1.   Temperature dependence of the MBWR-32 coefficients

---

$a_1 = RT$

$a_2 = b_1 T + b_2 T^{1/2} + b_3 + b_4/T + b_5/T^2$

$a_3 = b_6 T + b_7 + b_8/T + b_9/T^2$

$a_4 = b_{10} T + b_{11} + b_{12}/T$

$a_5 = b_{13}$

$a_6 = b_{14}/T + b_{15}/T^2$

$a_7 = b_{16}/T$

$a_8 = b_{17}/T + b_{18}/T^2$

$a_9 = b_{19}/T^2$

$a_{10} = b_{20}/T^2 + b_{21}/T^3$

$a_{11} = b_{22}/T^2 + b_{23}/T^4$

$a_{12} = b_{24}/T^2 + b_{25}/T^3$

$a_{13} = b_{26}/T^2 + b_{27}/T^4$

$a_{14} = b_{28}/T^2 + b_{29}/T^3$

$a_{15} = b_{30}/T^2 + b_{31}/T^3 + b_{32}/T^4$

---

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. The flash calculation can be generally stated as follows:

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 (a) where x is the liquid mole fraction and y is the vapor mole fraction. The solution of the problem requires mass balance and vapor-liquid equilibrium calculations. A detailed computational procedure can be found in Prausnitz et al. (1980) and Walas (1985). In our case, the calculation procedure is slightly different depending on whether (1) the amount of nitrogen ($n_{g,i}$) or (2) the total initial charge pressure (P_i) is given.

In Case (1), with V_i, T_i, $n_{a,i}$, and $n_{g,i}$ given, we calculate P_i, x_g, y_g, and α, 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_i, T_i, $n_{i,a}$, and P_i, then $n_{g,i}$, x_g, y_g, and α are calculated. Irrespective of Case (1) or (2), bubble point and dew point calculations (see e.g., Prausnitz et al., 1980) need be carried out to ensure that the flash calculations are performed in the two-phase region. Below the bubble point, the mixture is a subcooled liquid; in this case, $x_i = z_i$. Above the dew point, the mixture is a superheated vapor; in this case $y_i = z_i$.

Once the initial conditions of the vessel are established, calculations of temperature-pressure characteristics can proceed. In this case, given V_i, $n_{a,i}$, and $n_{g,i}$, we want to calculate P_f, x_g, y_g, and a 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, 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.

MODEL VALIDATION

Experimental data have been obtained to validate and compare to the model predictions. Details of the experimental methods and results can be found in Yang et al. (1995). In the following, the

comparisons of a subset of the experimental data to the model calculations are presented. The cases shown below correspond to an initial amount of liquid agent occupying two-thirds of the vessel volume. The calculations were performed with the two binary interaction parameters (k_{ij} and l_{ij}) set equal to zero.

Nitrogen solubilities

Table 2 summarizes the experimental results obtained under an initial total pressure (P_i) of approximately 2.8 MPa or 4.1 MPa at room temperature ($T_i = 23 \pm 1$ "C). The predicted nitrogen mass in the fifth column and the solubilities of nitrogen ($x_{g,i}$) in the agent under T_i and P, in the last column of Table 2 were obtained using PROFISSY. The calculations were performed with $m_{a,t}$, P_i, V_t ($= 52.2$ cm^3), and T_i as input. The solubility is defined as the mole fraction of dissolved nitrogen in the liquid agent/nitrogen mixture at pressure P,. The predicted nitrogen mass compares favorably with the measured value even without taking k_{ij} and l_{ij} into consideration.

Agent/Nitrogen Mixtures

The experimental results for agent/nitrogen mixtures at -60 "C are shown in Table 3. In all cases, the combined standard uncertainty of the measurement was found to be less than 0.1 MPa. Tabulated in the fifth column are the predicted final pressures using PROFISSY. The calculations were performed with $V_t = 52.2$ cm^3, and the initial conditions given in the table. In general, the predicted values were all found to be within 8% of the measured values.

The results for high temperature (150 "C) measurements are shown in Table 4. The combined standard uncertainty, in all cases, was estimated to be less than 0.2 MPa. The predictions were obtained with $V_t = 42.6$ cm^3. The errors between the predicted and measured final pressures were found to be less than 10%.

In **summary,** the model pressure predictions were generally found to be within 10% or less of the measured values; however, the current code tends to **underestimate** the final pressures at elevated temperatures in some cases.

ACKNOWLEDGEMENTS

REFERENCES

Ely, J.F. and Hanley, H.J.M., A *Computer Program for the Prediction of Viscosity and Thermal Conductivity in Hydrocarbon Mixtures,* **NBS** Technical Note 1039, U.S. Department of Commerce, Washington, DC 1981.

Ely, J.F. and Hanley, H.J.M., "Prediction of Transport Properties. 1. Viscosity of Fluids and Mixtures," *Ind. Eng. Chem. Fundam.* **20,** 323 (1981).

Ely, J.F., "Prediction of Dense Fluid Viscosities in Hydrocarbon Mixtures," *Proc. 61st Gas Processors Association,* pp. 9-17 (1982).

Ely, J.F. and Hanley, H.J.M., "Prediction of Transport Properties. 2. Thermal Conductivity of Pure Fluids and Mixtures," *Ind. Eng. Chem. Fundam.* **22,** 90 (1983).

Ely, J.F., "A Predictive, Exact Shape Factor Extended Corresponding States Model for Mixtures," *Advances in Cryogenic Engineering 35,* 1511 (1990).

Friend, D.G., *NIST Standard Reference Database 14: NIST Mixture Property Database,* U.S. Department of Commerce, Washington, DC, Version 9.08, 1992.

Table 2.   Amount of nitrogen ($m_{g,t}$) required to pressurize mixture to P_i at T_i (= 23 $\pm$
1 °C) with an initial amount of liquid agent corresponded to two-thirds of the
vessel volume

Agent	Agent, $m_{a,t}$ (g)	P_i (MPa)	Nitrogen, $m_{g,t}$ (g)	Predicted $m_{g,t}$ (g)	Solubility, $x_{g,t}$ (predicted)
HFC-227ea	48.7	2.87	1.1	1.16	0.082
	48.7	2.98	1.2	1.21	0.086
	48.7	4.25	1.8	1.81	0.127
	48.7	4.25	1.8	1.82	0.127
CF$_3$I	72.8	2.77	0.9	1.02	0.054
	72.7	2.79	0.9	1.02	0.054
	72.8	4.14	1.4	1.62	0.086
	72.7	4.16	1.4	1.63	0.086
FC-218	44.1	2.94	1.0	1.07	0.096
	44.2	2.93	1.0	1.06	0.096
	44.1	4.36	1.6	1.81	0.161
	44.2	4.29	1.6	1.75	0.157
HFC-125	41.9	2.70	0.8	0.79	0.051
	41.8	2.85	0.8	0.83	0.055
	41.9	4.18	1.5	1.56	0.104
	41.8	4.18	1.5	1.51	0.102
CF$_3$Br	54.9	2.92	0.7	0.76	0.048
	54.8	2.87	0.7	0.74	0.046
	54.9	4.25	1.4	1.48	0.094
	54.8	4.25	1.4	1.49	0.094

Gallagher, J., Huber, M.L., Morrison, G., and McLinden, M.O., *NIST Standard Reference Database 23: NIST Thermodynamic Properties of Refngeranr and Refrigerant Mixtures,* U.S. Department of Commerce, Washington, DC, Version 5.0, 1995 (in preparation).

Huber, M.L. and Ely, J.F., *NIST Standard Reference Database 4: NIST Thermophysical Properties of Hydrocarbon Mixtures,* U.S. Department of Commerce, Washington, DC 1990.

Huber, M.L. and McLinden, M.O., "Thermodynamic Properties of R134a (1,1,1,2-tetrafluoroethane)," *Proc* 1992 *International Refrigeration Conference,* Purdue University, July 14-17, 453 (1992).

Huber, M.L. and Ely, J.F., "Prediction of Viscosity of Refrigerants and Refrigerant Mixtures," *Fluid Phase Equilibria 80,* 239 (1992).

Huber, M.L., Friend, D.G., and Ely, J.F., "Prediction of the Thermal Conductivity of Refrigerants and Refrigerant **Mixtures,**" *Fluid Phase Equilibria 80,* 249 (1992).

Table 3.   Initial conditions at $T_i = 23 \pm 1\,°C$ and final pressures $(P_{f,c})$ at $-60 \pm 1\,°C$
for agent/nitrogen mixtures (two-thirds filled volume)

Agent	$m_{a,t}$ (g)	P_i (MPa)	$P_{f,c}$ (MPa) (measured)	$P_{f,c}$ (MPa) (predicted)	error' (%)
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
CF$_3$I	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
CF$_3$Br	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

'error (%) = | $P_{f,c}$(measured) - $P_{f,c}$(predicted) | x 100 / $P_{f,c}$(measured)

Huber, M.L. and Ely, J.F., "**A** Predictive Extended Corresponding States Model for Pure and Mixed Refrigerants Including an Equation of State for R134a," *Int. J. Refrig.* **17,** 18 (1994).

Jacobsen, R.T. and **Stewart,** R.B., "Thermodynamic Properties of Nitrogen Including Liquid and Vapor Phases from 63 K to 2000 K with Pressures to 10,000 Bar," **J. Phys. Chem. Ref Data 2,** 757 (1973).

Leach, J.W., Chappelear, P.S., and Leland, T.W., "Use of Molecular Shape Factors in Vapor Liquid Equilibrium Calculations with the Corresponding States Principle," *AIChE Journal 14,* 568 (1968).

McCarty, R.D., "Mathematical Models for the Prediction of Liquified-Natural-Gas Densities," **J. Chem. Thermodynamics 14,** 837 (1982).

Prausnitz, J.M., Anderson, T.F., Grens, E.A., Eckert, C.A., Hsieh,R., and O'Connell, J.P., *Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria,* Prentice-Hall,

Table **4.** Initial conditions at $T_i = 23 \pm 1\ °C$ and final pressures $(P_{f,h})$ at $150 \pm 1\ °C$ for agent hitrogen mixtures (two-thirds filled volume)

Agent	$m_{a,t}$ (g)	P_i (MPa)	$P_{f,h}$ (MPa) (measured)	$P_{f,h}$ (MPa) (predicted)	error[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_3I	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_3Br	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]error (%) = | $P_{f,h}$(measured) - $P_{f,h}$(predicted) | x 100 / $P_{f,h}$(measured)

New Jersey, 1980.

Reid, R.C., Prausnitz, J.M., and Sherwood, K.T., *The Physcial Properties of Gases and Liquids,* 3rd ed., McGraw-Hill, New York, 1977.

Sherman, G.J., Magee, J.W., and Ely, J.F., "PVT Relationships in a Carbon Dioxide Rich Mixture with Ethane," *Int. J. Thermophysics 10,* 47 (1989).

Walas, S.M., *Phase Equilibrium in Chemical Engineering,* Butterworth, Boston, 1986.

Yang, J.C., Vazquez, I., Boyer, C., Breuel, B.D., Huber, M.L., and Weber, L., NIST Special Publication, 1995 (in preparation).