

# Solution Theory Model for Thermophysical Properties of Refrigerant/Lubricant Mixtures

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*A general model for predicting the thermophysical properties of refrigerant/lubricant mixtures has been developed based on applicable theory for the excess Gibbs energy of nonideal solutions. In our approach, flexible thermodynamic forms are chosen to describe the properties of both the gas and liquid phases of refrigerant/lubricant mixtures. After an extensive study of models for describing nonideal liquid effects, the Wohl [3]-suffix equations, which have been extensively used in the analysis of hydrocarbon mixtures, have been developed into a general form applicable to mixtures where one component is a polyolester or alkylbenzene lubricant. We have developed a nonideal solution computer code, based on the Wohl model that predicts dew point or bubble point conditions over a wide range of composition and temperature and includes the calculation of the enthalpy and entropy of refrigerant/lubricant mixtures. Our present analysis includes the thermodynamic properties of an ideal solution mixture and the corrections due to nonideal solution behavior. These nonideal solution corrections are based on analysis of the excess Gibbs energy of the mixture. We find that these nonideal solution corrections are small (<4%) for most refrigerant/lubricant mixtures, except at very low temperatures. © 2009 American Institute of Chemical Engineers AIChE J, 55: 3241–3247, 2009*

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## Introduction

The addition of lubricants to refrigerants, either single component hydrofluorocarbons or the newer multicomponent blends, is necessary to reduce bearing friction and to minimize gas leakage at gaskets and fittings. The primary considerations in choosing a lubricant are its chemical compatibility with the refrigerant type and the required viscosity for

the service application. In particular, newer compressor designs incorporate closer bearing tolerances that make it imperative to maintain adequate film thickness for efficient and long-life operation. The refrigerant/lubricant thermophysical properties that are important in system and compressor design include viscosity, solubility, density, enthalpy, entropy, and dielectric strength. In the case of refrigerant blends, a new problem arises because the individual refrigerant components may exhibit different solubilities in the lubricant. These different component solubilities can give rise to fractionation (distillation) effects in the evaporator, condenser, or compressor sump that differ from the vapor-liquid equilibrium conditions in the absence of a lubricant.

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The effects of refrigerant/lubricant solution interactions may impact both cycle analysis and system performance. If these interactions are significant (nonideal solution behavior), they may result in detrimental performance and lower system operating efficiency.

In this study, an analysis of applicable theory for predicting the solubility of refrigerant-oil mixtures has been carried out. Models based on both nonideal solution theory and on an equation-of-state (EOS) have been developed and discussed in the literature.<sup>1</sup> Solution theory models require a large amount of experimental VLE data; EOS models involve the difficult task of describing the PVT behavior of two substances with drastically different boiling points. We have combined these two approaches by basing our pure refrigerant properties on an EOS model and our mixture properties on a solution theory model that includes refrigerant properties calculated from an EOS.

Several solution theory models have been described in the literature that relate nonideal behavior, as measured for example by the excess Gibbs energy, to composition, temperature, and pressure of the mixture.<sup>1</sup> Thomas and Pham<sup>2</sup> describe a model using the Flory-Huggins theory of solutions. Martz et al.<sup>3</sup> describe an approach based on modifications of the Wilson model of solutions. A solution theory model for refrigerant/lubricant mixtures that can be parameterized using the limited data sets for the solubility of refrigerant/lubricant pairs is necessary. Because of the large size differences between refrigerant and lubricant molecules, the model must account for differences in their effective molar volumes. In addition, the model should also be capable of predicting immiscible regions. Finally, the model should rely mainly on data for binary refrigerant/refrigerant and refrigerant/lubricant pairs. Ternary or higher mixture interaction parameters are difficult to extract from experimental solubility data and the most useful model will be based on a theoretical description of the interaction parameters that minimizes the need for such mixture data.

Solution theory models are generally reliable under the temperature and pressure conditions normally encountered in system operation. For operation near the critical point of a refrigerant, however, an EOS model applied to the refrigerant/lubricant mixture would be desirable. Yokozeki<sup>4</sup> compared the usefulness of several cubic EOS models for refrigerant/lubricant mixtures. However, previous studies have illustrated the difficulties and errors that arise with an EOS approach because the mixture involves components with very different vapor pressures. Because the vapor pressure and critical data of high molecular weight lubricants are usually unknown, several group-contribution models have been used to estimate these data. A compilation of several EOS models that have been proposed is given by Huber et al.<sup>5</sup>

We have examined experimental solubility data for R-134a/POE 220 mixtures that were obtained from a leading lubricant supplier.<sup>6</sup> In addition, we have analyzed experimental solubility and heat capacity data for R-22/AB 150 and R-22/AB 300 mixtures. (R-134a and R-22 are the ASHRAE designations for 1,1,1,2-tetrafluoroethane and chlorodifluoromethane.) These data were obtained from lubricant suppliers<sup>7</sup> and from published technical bulletins on the properties of alkylbenzenes.<sup>8,9</sup> We note here that the combinations, R-134a/POE 220, R-22/AB 150, and R-22/AB 300,

do not exhibit immiscibility over the temperature range of the available experimental data. The pentaerythritol ester (POE 220) studied here has both branched and straight chain molecules, with an average molecular weight of ~700. AB 150 and AB 300 are branched chain alkylbenzenes with average molecular weights of 330 and 375, respectively. The solubility data were reduced to pressure-composition isotherms, as required for rigorous thermodynamic solution modeling. These new data were analyzed and included in our final thermodynamic model. Additional refrigerant/lubricant mixtures can be added as experimental lubricant heat capacity data become available.

In this study we have analyzed the refrigerant/lubricant mixtures R-134a/POE 320, R-22/AB 150, and R-22/AB 300. Data were collected from several sources on the thermodynamic properties of these refrigerant/lubricant binary pairs. These data included solubility, viscosity, thermal heat capacity, and density for both pure refrigerant and lubricant, and for mixtures ranging in composition from 30 to 100% mass fraction refrigerant. We have developed a nonideal solution computer code (NISC), based on the Wohl model, that predicts dew point or bubble point conditions over a wide range of composition and temperature and includes the calculation of the enthalpy and entropy of refrigerant/lubricant mixtures. This code has also been generalized to include the calculation of enthalpy and entropy for any refrigerant/lubricant mixture for which specific heat data for the lubricant are known. For pure refrigerants or refrigerant mixtures, such as R-404A and R-410A, the code permits calculation of all thermodynamic properties, including enthalpy and entropy. In addition, pressure effects on the refrigerant properties have been included by an equation-of-state treatment of the liquid compressibility. Our present analysis includes the thermodynamic properties of an ideal solution mixture and the corrections due to nonideal solution behavior. These nonideal solution corrections are based on analysis of the excess Gibbs energy of the mixture. We find that these nonideal solution corrections are small (<4%) for most refrigerant/lubricant mixtures, except at very low temperatures. The NISC computer code that incorporates these modifications has been tested over a temperature range from -40 to +80°C and over a wide composition range. An analysis of our calculated versus available experimental properties indicates an average error of <1%. The present model, with the incorporation of experimental heat capacity data for the lubricants, can be used to analyze other refrigerant/lubricant mixtures. The computer code has been modified to permit direct input of heat capacity data for any lubricant, as data become available.

## Mathematical Models of Refrigerant/Lubricant Mixtures

The vapor-liquid equilibria of a mixture can be described in terms of the component fugacities in the liquid and vapor phases.<sup>1</sup> At equilibrium, we have

$$f_i^v = y_i P_T \phi_i^v = f_i^l = x_i \gamma_i P_i^s \phi_i^l \mathcal{F}_i \quad (1)$$

where  $y_i$ , vapor phase molar composition of component  $i$ ;  $P_T$ , total system pressure at temperature  $T$ ;  $\phi_i^v$ , vapor phase

fugacity coefficient which, for moderate pressure, can be estimated from second virial coefficient data;  $x_i$ , liquid phase molar composition of component  $i$ ;  $\gamma_i$ , liquid phase activity coefficient of component  $i$ ;  $P_i^V$ , vapor pressure of pure component  $i$  at temperature  $T$ ;  $\phi_i^*$ , fugacity coefficient for pure  $i$  at the system  $T$  and  $P$ ; and  $\mathcal{F}_i^\ell$ , Poynting factor for compressibility of the liquid phase.

For  $\phi_i^V = \gamma_i = \phi_i^* = \mathcal{F}_i^\ell = 1.0$ , this analysis reduces to ideal solution behavior (Raoult's Law). Choosing a fixed value of the system temperature, the fugacity coefficients are evaluated in terms of the vapor phase virial expansion as follows:

$$\ln \phi_i^V = \frac{P_T}{RT} \left[ 2 \sum_j y_j B_{ij} - B_{\text{mix}} \right]; \quad B_{\text{mix}} = \sum_i \sum_j y_i y_j B_{ij} \quad (2)$$

where  $B$  is the second virial coefficient and  $y$  is the molar fraction in the vapor phase. Correspondingly, for pure component  $i$ , we have

$$\ln \phi_i^* = \frac{B_{ii} P_T}{RT} = Z_{ii} - 1. \quad (3)$$

The Poynting factor,  $\mathcal{F}_i^\ell$ , is normally negligible for moderate pressures but may be estimated from molar volume data for pure liquid component  $i$ :

$$\ln \mathcal{F}_i^\ell = \int_{P_i^V}^{P_T} \frac{V_i^\ell}{RT} dP = \frac{V_i^\ell (P_T - P_i^V)}{RT}. \quad (4)$$

Finally, we combine the fugacity coefficients and Poynting factor into a correction term,  $F_i$ , as

$$F_i = \exp \left[ \frac{B_{ii} P_T}{RT} + \frac{V_i^\ell (P_T - P_i^V)}{RT} - \frac{P_T}{RT} \left( 2 \sum_j y_j B_{ij} - B_{\text{mix}} \right) \right]. \quad (5)$$

The vapor-liquid equilibria for component  $i$  (Eq. 1) can then be written as

$$y_i P_T = x_i \gamma_i P_i^V F_i. \quad (6)$$

The correction term,  $F_i$ , can be evaluated from liquid density and second virial coefficient data for pure refrigerants. One convenient source is the tabulation given in the NIST REFPROP database. (Newer and more accurate versions of the NIST code are available that are not based on the EOS used in this work. They are not as convenient for the modeling of refrigerant/lubricant mixtures.)<sup>10</sup> The difficult part of this analysis is the representation of the liquid phase activity coefficients,  $\gamma_i$ . These liquid activity coefficients may be extracted from experimental data or estimated using group additivity models such as UNIFAC.<sup>11</sup> The latter approach is difficult at present due to limited knowledge of the chemical formulations of the POEs and the lack of reliable functional group interaction parameters.

Preliminary evaluation of the nonideal behavior of several refrigerant/lubricant binary mixtures indicated both positive

and negative deviations from ideal solution behavior. Many of the proposed forms for liquid phase activity coefficients cannot mathematically represent such behavior. The Wilson model<sup>12</sup> for the excess Gibbs energy, for example, is not applicable over the entire refrigerant/lubricant composition range. Various modifications of the Wilson model have been proposed, including those described in the literature as the Heil et al.,<sup>13</sup> NRTL,<sup>14</sup> and T-K<sup>15</sup> equations. All of these equations represent local composition models in an attempt to incorporate effects of molecular size and mixture concentration. These derivations, however, are mainly empirically based and can lead to computed solution parameters that lack physical meaning. After an extensive study of models for describing nonideal liquid phase effects, the Wohl [3]-suffix equations<sup>16</sup> were chosen. Using the Wohl [3]-suffix expansion, the excess Gibbs energy can be represented as:

$$\frac{g^E}{RT \sum_j x_j q_j} = 2 \sum_{\substack{i,j \\ i \neq j}}^n a_{ij} z_i z_j + 3 \sum_{\substack{i,j \\ i \neq j}}^n a_{ijj} z_i^2 z_j + 6 \sum_{\substack{i,j,k \\ i \neq j \neq k}}^n a_{ijk} z_i z_j z_k \quad (7)$$

where  $z_i$ , generalized volume fraction ( $q$ -fraction) =  $\frac{x_i q_i}{\sum_j x_j q_j}$ ;

= effective volume of species  $i$  upon collision. The  $a_{ij}$ ,  $a_{ijj}$ ,  $a_{ijk}$  are the interaction parameters describing binary and ternary interaction strengths. For binary pairs, this leads to the following form for the liquid phase activity coefficients:

$$\ln \gamma_1 = z_2^2 \left[ A_{12} + 2z_1 \left( \frac{q_1}{q_2} A_{21} - A_{12} \right) \right];$$

$$\ln \gamma_2 = z_1^2 \left[ A_{21} + 2z_2 \left( \frac{q_2}{q_1} A_{12} - A_{21} \right) \right] \quad (8)$$

$A_{12}$  and  $A_{21}$  are defined as follows:

$$A_{12} = q_1(2a_{12} + 3a_{122}); \quad A_{21} = q_2(2a_{12} + 3a_{112}) \quad (9)$$

We note that  $A_{12} \neq A_{21}$  in this analysis. Equation 8 was used to reduce the experimental solubility data for all mixtures that are currently in the NISC code. All of the required  $A_{ij}$  can be evaluated from the binary pair data. The  $q_i$  are treated as free parameters in the fit to experimental data and are not constrained as mole or volume fractions. For most binary systems that we have studied, they are remarkably close to the  $q$ -fractions of the UNIFAC model.

For a nonideal mixture, the total molar enthalpy of the refrigerant/lubricant mixture can be written as:

$$h_{\text{TOT}} = x_R h_R + x_L h_L + h^{\text{XS}}. \quad (10)$$

In Eq. 10,  $h_R$  and  $h_L$  refer to the enthalpy of pure refrigerant and pure lubricant;  $h^{\text{XS}}$  is the excess enthalpy due to mixing. The properties of the pure refrigerants, R-134a and R-22, were obtained from the Carnahan-Starling-Desantis (CSD) equation-of-state as outlined in Version 5 of the NIST REFPROP program.<sup>10</sup> More recent versions of the REFPROP code are available that are not based on the CSD equation-of-state. However, they are not as convenient as the

CSD equation-of-state for developing a model describing the properties of refrigerant/lubricant mixtures.

The CSD equation-of-state (EOS) can be written as:

$$\frac{PV}{RT} = \frac{1 + y + y^2 - y^3}{(1 - y)^3} - \frac{a}{RT}; \quad y = \frac{b(T)}{V} \quad (11)$$

$$a(T) = a_0 \exp(a_1 T + a_2 T^2); \quad b(T) = b_0 + b_1 T + b_2 T^2.$$

The usual mixture rules for this EOS are

$$a_{\text{mix}} = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} (1 - f_{ij}); \quad b_{\text{mix}} = \sum_i \sum_j x_i x_j b_{ij} \quad (12)$$

The volume cross term,  $b_{ij}$ , can be written as:

$$b_{ij} = \frac{1}{8} [b_{ii}^{1/3} + b_{jj}^{1/3}]^3. \quad (13)$$

The empirical mixture term,  $f_{ij}$ , is obtained from analysis of experimental PVT data.

The properties of the pure lubricant were obtained from data supplied by manufacturers.<sup>8,9,17</sup> These data included heat capacity data in the form:

$$C_p = \frac{A}{\rho(T)^{1/2}} [B + CT + DT^2],$$

$$\rho(T) = A + BT + CT^2. \quad (14)$$

The enthalpy of the pure refrigerant was developed from the REPROP code. In terms of the EOS given in Eq. 11, the refrigerant enthalpy can be written as:

$$h_R(T, P(V)) - h_R(\text{ref}) = \frac{b \left( \frac{\partial a}{\partial T} \right) T - a \left( \frac{\partial b}{\partial T} \right) T - ab}{b^2} \ln \left( \frac{V + b}{V} \right),$$

$$+ \frac{a \left( \frac{\partial b}{\partial T} \right) T - ab}{b(V + b)} + \frac{RT(4V^2 - 2V\beta) \left( \beta - \left( \frac{\partial \beta}{\partial T} \right) T \right)}{(V - \beta)^3}; \quad \beta = \frac{b}{4}. \quad (15)$$

For the lubricant, retaining terms quadratic in temperature, integration of the heat capacity yields the following equation:

$$h_L = \int \left( \frac{\partial H}{\partial T} \right)_P dT + \int \left( \frac{\partial H}{\partial P} \right)_T dP + \text{constant},$$

$$= \int C_p dT + \text{constant},$$

$$= AT + \frac{1}{2} BT^2 + \frac{1}{3} CT^3 - h_L(\text{ref}). \quad (16)$$

The pressure dependent term in Eq. 16 is small for liquids. It was included for the refrigerant enthalpy through the CSD-EOS. For the lubricant it can be estimated from liquid phase compressibility data, where available. The excess enthalpy of the mixture can be written as:

$$h^{\text{XS}} = x_R \bar{h}_R^{\text{XS}} + x_L \bar{h}_L^{\text{XS}} \quad (17)$$

where the barred terms represent partial molar quantities. The excess enthalpy of a mixture component can be related to the activity coefficients expressed in the Eq. 8 by the thermodynamic relation:

$$\left[ \frac{\partial (g^{\text{XS}}/T)}{\partial T} \right]_{P, x_i} = -\frac{h^{\text{XS}}}{T^2} = R \sum_i x_i \left( \frac{\partial \ln \gamma_i}{\partial T} \right)_{P, x_i}. \quad (18)$$

Carrying out the indicated differentiation, we find

$$-\frac{\bar{h}_R^{\text{XS}}}{RT^2} = z_L^2 \left\{ \left( \frac{\partial A_{12}}{\partial T} \right) + 2z_R \left[ \left( \frac{q_1}{q_2} \right) \left( \frac{\partial A_{21}}{\partial T} \right) - \left( \frac{\partial A_{12}}{\partial T} \right) \right] \right\}$$

$$= z_L^2 \left\{ A_{121} + 2A_{122}T + 2z_R \left[ \left( \frac{q_1}{q_2} \right) \right. \right.$$

$$\left. \left. \times (A_{211} + 2A_{212}T) - (A_{121} + 2A_{122}T) \right] \right\}$$

$$-\frac{\bar{h}_L^{\text{XS}}}{RT^2} = z_R^2 \left\{ \left( \frac{\partial A_{21}}{\partial T} \right) + 2z_L \left[ \left( \frac{q_2}{q_1} \right) \left( \frac{\partial A_{12}}{\partial T} \right) - \left( \frac{\partial A_{21}}{\partial T} \right) \right] \right\}$$

$$= z_R^2 \left\{ A_{221} + 2A_{212}T + 2z_L \left[ \left( \frac{q_2}{q_1} \right) \right. \right.$$

$$\left. \left. \times (A_{121} + 2A_{122}T) - (A_{211} + 2A_{212}T) \right] \right\} \quad (19)$$

The parameters,  $q_1/q_2$ ,  $A_{121}$ ,  $A_{122}$ ,  $A_{211}$ , and  $A_{212}$  are developed from mixture solubility data.

The total molar entropy of the mixture can be written as:

$$s = x_R s_R + x_L s_L - R[x_R \ln x_R + x_L \ln x_L] + s^{\text{XS}} \quad (20)$$

where  $s^{\text{XS}}$  is the nonideal excess entropy of the mixture, in addition to the entropy due to component mixing. The entropy of the pure refrigerant was developed from the REFPROP code.

In terms of the EOS given in Eq. 11, the refrigerant entropy can be written as

$$S_R(V, T) - S_R(\text{ref}) = \frac{b \left( \frac{\partial a}{\partial T} \right) - a \left( \frac{\partial b}{\partial T} \right)}{b^2} \ln \left( \frac{V + b}{V} \right)$$

$$+ \frac{a \left( \frac{\partial b}{\partial T} \right)}{b(V + b)} - \frac{R\beta(4V - 3\beta)}{(V - \beta)^2} - \frac{RT \left( \frac{\partial \beta}{\partial T} \right) (4V^2 - 2V\beta)}{(V - \beta)^3}. \quad (21)$$

For the lubricant, integration of the heat capacity data yields the following equation:

$$S_L = \int \left( \frac{\partial S}{\partial T} \right)_P dT + \int \left( \frac{\partial S}{\partial P} \right)_T dP + \text{constant},$$

$$= \int \frac{C_p}{T} dT + \text{constant}$$

$$= A \ln T + BT + \frac{1}{2} CT^2 - S_L(\text{ref}). \quad (22)$$

where the pressure dependent term is small for liquids. It is included for the refrigerant through the CSD-EOS and estimated from compressibility data for the lubricant, where available. The excess entropy can now readily be developed from the thermodynamic relation:

$$s^{\text{XS}} = \frac{h^{\text{XS}} - g^{\text{XS}}}{T} \quad (23)$$

**Table 1. Calculated Enthalpy and Entropy for R-22/AB 300 Mixtures**  
( $H_{\text{mix}}$  and  $S_{\text{mix}}$  are the Total Enthalpy and Entropy of the Mixture)

Temp. (°C)	$H_{\text{mix}}$ (kJ/kg)	$S_{\text{mix}}$ (kJ/kg K)	$H_{\text{mix}}E$ (Btu/lb)	$S_{\text{mix}}E$ [Btu/lb-R]	$X_r$ (mass)
-40.0	131.4165	0.7287	0.0000	0.0000	0.0
-20.0	165.1945	0.8677	14.5316	0.0332	0.0
-00.0	200.0000	1.0000	29.5053	0.0648	0.0
20.0	235.8321	1.1266	44.9207	0.0951	0.0
40.0	272.6897	1.2482	60.7771	0.1242	0.0
60.0	310.5717	1.3654	77.0744	0.1522	0.0
80.0	349.4771	1.4788	93.8119	0.1793	0.0
-40.0	138.5465	0.7814	0.9864	0.0075	0.2
-20.0	170.3320	0.9112	14.6609	0.0386	0.2
-00.0	203.1471	1.0349	28.7782	0.0681	0.2
20.0	237.0288	1.1532	43.3545	0.0964	0.2
40.0	272.0407	1.2671	58.4169	0.1236	0.2
60.0	308.3050	1.3770	74.0182	0.1499	0.2
80.0	346.1160	1.4839	90.2849	0.1755	0.2
-40.0	144.0851	0.8052	1.2881	0.0082	0.4
-20.0	173.5934	0.9248	13.9829	0.0368	0.4
-00.0	204.1097	1.0386	27.1113	0.0640	0.4
20.0	235.7096	1.1475	40.7059	0.0900	0.4
40.0	268.5206	1.2524	54.8215	0.1151	0.4
60.0	302.7889	1.3539	69.5641	0.1393	0.4
80.0	339.1036	1.4532	85.1870	0.1631	0.4
-40.0	148.5886	0.8204	1.1446	0.0068	0.6
-20.0	175.6346	0.9289	12.7800	0.0327	0.6
-00.0	203.6518	1.0322	24.8333	0.0574	0.6
20.0	232.7541	1.1310	37.3534	0.0810	0.6
40.0	263.1335	1.2261	50.4229	0.1037	0.6
60.0	295.1596	1.3184	64.2009	0.1258	0.6
80.0	329.7167	1.4092	79.0677	0.1475	0.6
-40.0	152.3481	0.8306	0.6809	0.0042	0.8
-20.0	176.7985	0.9276	11.1997	0.0273	0.8
-00.0	202.1725	1.0197	22.1159	0.0494	0.8
20.0	228.6222	1.1078	33.4948	0.0704	0.8
40.0	256.4040	1.1927	45.4468	0.0907	0.8
60.0	286.0110	1.2752	58.1840	0.1104	0.8
80.0	318.6225	1.3571	72.2138	0.1300	0.8
-40.0	155.6025	0.8344	0.0000	0.0000	1.0
-20.0	177.3671	0.9194	9.3633	0.0203	1.0
-00.0	200.0000	1.0000	19.1002	0.0396	1.0
20.0	223.6920	1.0770	29.2927	0.0580	1.0
40.0	248.7634	1.1512	40.0787	0.0757	1.0
60.0	275.8312	1.2236	51.7236	0.0930	1.0
80.0	306.3697	1.2962	64.8615	0.1104	1.0

where the excess Gibbs energy is related to Eq. 8 through the relation

$$g^{\text{XS}} = RT[x_R \ln \gamma_R + x_L \ln \gamma_L] \quad (24)$$

This analysis for enthalpy and entropy uses the Wohl [3]-suffix model that has previously been developed for the solution activity coefficients.<sup>18,19</sup> Our work expands this model to include enthalpy and entropy properties, currently applied to the R-134a/POE 220, R-22/AB 150, and R-22/AB 300 systems, but expandable to include other mixtures by incorporation of lubricant thermal heat capacity data. This new formulation has been developed into a computer code that, in its present form, describes the thermodynamic properties of these mixtures over the entire composition range and has been tested for the temperature range -40 to +80°C.

## Results and Discussion

In this study, we have analyzed in detail the thermophysical properties of the R-134a/POE 220, R-22/AB 150, and

R-22/AB 300 refrigerant/lubricant mixtures. The development of a rigorous thermodynamic treatment of mixture enthalpy and entropy is included in this study. Our approach is based on the treatment of nonideal solutions using thermodynamic excess functions that can be related to measured mixture solubility parameters. We find that the nonideal corrections to the enthalpy and entropy ( $h^{\text{XS}}$  and  $s^{\text{XS}}$ ) of these refrigerant/lubricant systems are small (<4.0%), except at very low temperatures. However, these nonideal solution (excess functions) corrections have been incorporated into the final NISC computer code for thermodynamic completeness. In addition to the refrigerant/lubricant mixtures discussed earlier, the NISC code has been generalized to include enthalpy and entropy estimates for many pure refrigerants and refrigerant blends that are now being used as CFC (chlorofluorocarbon) replacements.

We have examined the pressure corrections to the thermodynamic properties, enthalpy, and entropy, for refrigerants through use of the VIT subroutine available in REFPROP. The pressure corrections, as illustrated in Eqs. 16 and 22 are small for pure refrigerant (<0.1%). There are currently no



**Table 2. Calculated Enthalpy and Entropy for R-134a/POE 220 Mixtures**  
( $H_{xsm}$  and  $S_{xsm}$  are Nonideal Mixture Solution Terms)

Temp. (°C)	$X_r$ (mass)	$H_{mix}$ (kJ/kg)	$S_{mix}$ (kJ/kg K)	$H_{mix}E$ (Btu/lb)	$S_{mix}E$ (Btu/lb-R)	$H_{xsm}$ (kJ/kg)	$S_{xsm}$ (kJ/kg K)
-40.0	0.00	135.5112	0.6871	0.0000	0.0000	0.0000	0.0000
-20.0	0.00	166.9693	0.8451	13.5336	0.0378	0.0000	0.0000
0.0	0.00	200.0015	1.0002	27.7444	0.0748	0.0000	0.0000
20.0	0.00	234.6319	1.1531	42.6427	0.1114	0.0000	0.0000
40.0	0.00	270.8848	1.3044	58.2391	0.1475	0.0000	0.0000
60.0	0.00	308.7858	1.4544	74.5444	0.1834	0.0000	0.0000
80.0	0.00	348.3610	1.6036	91.5701	0.2190	0.0000	0.0000
-40.0	0.20	135.2314	0.7202	-1.3881	0.0020	-3.2266	-0.0085
-20.0	0.20	165.4170	0.8666	11.5980	0.0370	-3.0591	-0.0079
0.0	0.20	197.3068	1.0107	25.3173	0.0715	-2.6944	-0.0065
20.0	0.20	230.9679	1.1530	39.7987	0.1055	-2.1046	-0.0044
40.0	0.20	266.4871	1.2940	55.0794	0.1392	-1.2618	-0.0016
60.0	0.20	304.0060	1.4345	71.2204	0.1728	-0.1382	0.0060
80.0	0.20	343.8579	1.5751	88.3651	0.2063	1.2942	0.0109
-40.0	0.40	138.7434	0.7466	-1.1450	0.0024	-2.6614	-0.0085
-20.0	0.40	167.4163	0.8806	11.1904	0.0345	-2.5666	-0.0081
0.0	0.40	197.6774	1.0117	24.2090	0.0658	-2.3235	-0.0072
20.0	0.40	229.6025	1.1406	37.9435	0.0966	-1.9106	-0.0057
40.0	0.40	263.3065	1.2679	52.4433	0.1271	-1.3066	-0.0037
60.0	0.40	299.0126	1.3944	67.8044	0.1573	-0.4900	-0.0012
80.0	0.40	337.3268	1.5211	84.2876	0.1876	0.5605	0.0019
-40.0	0.60	142.9223	0.7712	-0.6149	0.0024	-1.4293	-0.0059
-20.0	0.60	170.0700	0.8927	11.0643	0.0315	-1.4197	-0.0059
0.0	0.60	198.6565	1.0107	23.3625	0.0597	-1.3441	-0.0056
20.0	0.60	228.7614	1.1259	36.3139	0.0872	-1.1924	-0.0050
40.0	0.60	260.5224	1.2391	49.9778	0.1143	-0.9547	-0.0043
60.0	0.60	294.2399	1.3510	64.4834	0.1410	-0.6212	-0.0032
80.0	0.60	330.7873	1.4633	80.2065	0.1678	-0.1817	-0.0020
-40.0	0.80	146.8506	0.7931	-0.1926	0.0018	-0.4478	-0.0028
-20.0	0.80	172.5225	0.9022	10.8517	0.0279	-0.4741	-0.0029
0.0	0.80	199.5111	1.0074	22.4624	0.0530	-0.4892	-0.0030
20.0	0.80	227.9031	1.1093	34.6769	0.0774	-0.4913	-0.0030
40.0	0.80	257.8630	1.2088	47.5660	0.1012	-0.4783	-0.0029
60.0	0.80	289.7714	1.3068	61.2933	0.1246	-0.4481	-0.0028
80.0	0.80	324.7730	1.4051	76.3514	0.1481	-0.3987	-0.0027
-40.0	1.00	150.2452	0.8103	0.0000	0.0000	0.0000	0.0000
-20.0	1.00	174.5034	0.9072	10.4361	0.0232	0.0000	0.0000
0.0	1.00	200.0000	1.0000	21.4050	0.0453	0.0000	0.0000
20.0	1.00	226.8350	1.0893	32.9497	0.0667	0.0000	0.0000
40.0	1.00	255.2054	1.1758	45.1549	0.0874	0.0000	0.0000
60.0	1.00	285.5779	1.2606	58.2215	0.1076	0.0000	0.0000
80.0	1.00	319.3744	1.3461	72.7611	0.1281	0.0000	0.0000

compressibility data for the lubricants POE 220, AB 150, and AB 300. The pressure correction to the lubricant thermodynamic enthalpy and entropy is estimated to be small, based on compressibility data of similar chemical structures. However, a POE lubricant molecule is near polymer-like and compressibility effects will become important at some higher level of pressure than that considered in the present study. For studies of the dielectric constant of refrigerant/lubricant mixtures, this pressure correction could be very important since the loading pressure in bearings is typically much higher than the range of fluid system pressures that are involved in typical refrigerant circulation patterns. An analysis of the compressibility coefficient for long chain hydrocarbon molecules, similar to POEs, is discussed by Cutler et al.<sup>20</sup>

The thermodynamic analysis described in the section above has been reduced to FORTRAN computer code and incorporated into the NISC refrigerant/lubricant solution code. This code has been checked for typical input options, such as  $(x,T)$ ,  $(P,T)$ , and for arrays of temperature and composition as input. This NISC code calculates enthalpy and entropy in both SI (kJ/kg, kJ/kg K) and engineering (IP)

(Btu/lb, Btu/lb-F) units. Because these thermodynamic functions are typically not absolute, the standard convention used in REFPROP and other refrigerant data sources has been used. In this convention, the enthalpy and entropy are, respectively, 200 kJ/kg and 1.0 kJ/kg K, at 0.0°C in SI units, and 0.0 Btu/lb and 0.0 Btu/lb-F at -40°C in I/P units. Tables 1 and 2 illustrate calculated values of these properties for a range of temperatures and pressures.

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