PREDICTION OF REFRIGERANT THERMODYNAMIC PROPERTIES BY EQUATIONS OF STATE

Saturated Properties of Pure Compounds

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(First Received May 1992; accepted in revised form October 1992)

ABSTRACT

The ability of three equations of state (EOS) for calculating the thermodynamic properties of refrigerants has been studied for 35 pure component refrigerants. Three equations of state studied were the Soave-Redlich-Kwong (SRK), Peng-Robinson (PR) and Parameters From Group Contribution (PFGC).

For each refrigerant, the vapor pressure, saturated vapor volume, saturated liquid density, and heat of vaporization were calculated and compared with the values reported in the ASHRAE hand-book. For each refrigerant a range of temperature from about the triple point to the critical point was covered.

Specific EOS parameters such as acentric factor (for SRK and PR), b, s, E^{n}, E^{o}, E^{(i)} (for PFGC) were optimized to achieve better agreement between calculated values and the ASHRAE data.

The optimized acentric factors and PFGC parameters for several compounds are presented. Sample graphical error analyses are shown.

NOMENCLATURE

A, B, C and D : weighting factors
EOS : equation of state
HV : heat of vaporization
LD : liquid density
ND : number of data points
OF : objective function
PFGC : parameters from group contribution equation of state
PR : Peng-Robinson equation of state
PVT : Pressure-volume-temperature
SRK : Soave-Redlich-Kwong equation of state
INTRODUCTION

Equations of state (EOS) are widely used as a means of correlating and predicting thermodynamic properties. They are used as an integral part of all process simulators. The reliability and soundness of a process simulation depend to a significant degree on the accuracy of the equation of state used for thermodynamic and property calculations.

Because of the importance of EOS in correlating the thermodynamic properties extensive work has been done to develop new EOS or modify and improve existing EOS (1, 2, 3). Unfortunately there is a wide range of components and/or conditions that existing EOS can not cover well. In addition, most EOS have parameters that must be determined from experimental data before the EOS can be used for design purposes.

In order to use an EOS in a process simulator, an extensive and time consuming evaluation must be performed to confirm its accuracy, reliability and limitations in predicting thermodynamic properties. Sound evaluation of an EOS requires a valid and reliable Pressure-Volume-Temperature (PVT) and Vapor-Liquid-Equilibria (VLE) data bank for pure components and their mixtures. Since a large volume of data is involved, and almost all of the required calculations are iterative in nature, an efficient and easy to use computer package is a necessity for this work.

The objective of this paper was to evaluate the ability and, if necessary, improve the accuracy of three equations of state in predicting the saturated thermodynamic properties of pure refrigerants. A data bank based on the data reported in the ASHRAE handbook (4) was used as a basis for this work. A computer program, EOS *TAILOR (5), with graphics capability was used for evaluating and upgrading each of the equations of state under study. With the aid of EOS *TAILOR the following tasks were performed for the thirty five refrigerants.

1. The acentric factors of the pure refrigerants for the Peng-Robinson and Soave-Redlich-Kwong EOS were optimized to give the best prediction of vapor pressure for each component over a wide temperature range.
2. For each refrigerant the five parameters of the PFGC EOS were optimized to give the best calculation of vapor pressure, liquid density, vapor volume, and heat of vaporization.

THE EQUATIONS OF STATE

The three equations of state selected for evaluation were the Peng-Robinson (6), Soave-Redlich-Kwong (7) and Parameters From Group Contribution (8). The first two EOS have been applied successfully for light hydrocarbons and non-polar compounds and to some extent for refrigerants (9, 10). A revised version of the PFGC EOS was chosen because it is capable of handling systems containing one or more polar fluids (11) and has been reported to give satisfactory results when applied to a limited number of refrigerants (12). In the revised version of PFGC, in addition to treating each molecule as a group, the simple mixing rules are replaced by quadratic mixing rules. The revised version will be referred to as Parameters From Molecule Contribution (PFMC).

Appendices A through C present the equations for the PR, SRK and PFMC along with expressions for calculation enthalpy and fugacity or chemical potential. The mixing rules are also presented for each equation of state. Quadratic mixing rules as suggested by Moshfeghian and Maddox (11) were used for PFMC in the second part of this evaluation.

EOS PARAMETER OPTIMIZATION

One way of improving the accuracy of an equation of state in predicting saturated properties is to optimize the equation parameters. For example, the vapor pressure calculated by the PR or SRK is very sensitive to the value of the acentric factor used. A relatively very small change from the reported value can, in specific instances, cause dramatic decrease in errors in the calculated vapor pressure. In addition, the five parameters of PFMC must be determined from experimental data before it can be used for any thermodynamic calculations.

Optimization of requisite EOS parameters was achieved through the use of EOS *TAILOR (5). The objective function was to minimize the sum of the squares of multiproperty errors. For pure refrigerants the following form was used:

\[
OF = \sum_{i=1}^{ND} \left[ A \left( \frac{VP_E - VP_C}{VP_E} \right)^2 + B \left( \frac{LD_E + LD_C}{VP_E} \right)^2 \right] + C \left( \frac{VV_E - VV_C}{VV_E} \right) + D \left( \frac{HV_E - HV_C}{HV_E} \right)^2 \] 

(1)
Weighting factors A through D were used to emphasize accuracy in calculating a specific property. In the case of the PR and SRK equations, B, C and D were set equal to zero. For PFMC a value of 2 for A and a value of unit for B, C and D was used.

Using the above optimization technique, the PR acentric factor, SRK acentric factor and the PFMC parameters for thirty five refrigerants have been determined. Table 1 presents typical optimized EOS parameters for several refrigerants.

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**EVALUATIONS**

Based on the optimized parameters, vapor pressure, saturated vapor volume, saturated liquid density and heat of vaporization for the 35 refrigerants over a wide temperature range were calculated and compared with the values reported in the ASHRAE hand-book (4). Table 2 presents the chemical stoichiometric formula and ASHRAE designated refrigerant number for the refrigerants evaluated in this study. Table 2 also contains the number of data points and temperature range which were covered for each refrigerant in this evaluation.

38
Table 2
List of Refrigerants and Reduced Temperature Range Studied in This Evaluation.

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For each saturated property, the percent error defined as:

\[
\text{Percent Error} = \left\{ \frac{\text{ASHRAE Value} - \text{Calculated Value}}{\text{ASHRAE Value}} \right\} \times 100
\]

was calculated and plotted as a function of reduced temperature (absolute temperature of system divided by the critical temperature). Typical percent errors for properties calculated in this manner using the three EOS are presented in Figs. 1 through 12 for C$_2$H$_2$F$_4$, NH$_3$, and CHF$_3$.

Figs. 1, 5 & 9 present the error in calculated vapor pressure of C$_2$H$_2$F$_4$, NH$_3$, and CHF$_3$, respectively. As can be seen from these three figures, all three EOS give relatively low errors. However, for low temperature, i.e., for a reduced temperature of less than 0.55 for C$_2$H$_2$F$_4$, the PR and SRK results are not as good as for PFMC. At higher temperature, the PR and PFMC give essentially the same quality of agreement between calculated and the values reported in the ASHRAE handbook. The SRK gives poor results for C$_2$H$_2$F$_4$ at low reduced temperature. This same kind of behavior for calculated vapor pressure was observed for all of the refrigerants evaluated.

Figs. 2, 6 & 10 present the error in heat of vaporization for the same three refrigerants. With the exception of high reduced temperature, i.e., greater than 0.95, all three EOS give good agreement with the values reported in the ASHRAE handbook.

Fig. 1: Error in Liquid Vapor Pressure of C$_2$H$_2$F$_4$ Calculated by the SRK, PR and PFMC.
Fig. 2: Error in Latent Heat Vaporization of $C_2H_2F_4$ Calculated by the SRK, PR and PFMC.

Fig. 3: Error in Saturated Vapor Volume of $C_2H_2F_4$ Calculated by the SRK, PR and PFMC.
Fig. 4: Percent Error in Saturated Liquid Density of C₂H₂F₄ Calculated by the SRK, PR and PFMC.

Fig. 5: Error in Vapor Pressure of NH₃ Calculated by the SRK, PR and PFMC.
Fig. 6: Error in Latent Heat of Vaporization of NH$_3$ Calculated by the SRK, PR and PFMC.

Fig. 7: Error in Saturated Vapor Volume of NH$_3$ Calculated by the SRK, PR and PFMC.
Fig. 8: Error in Saturated Liquid Density of NH₃ Calculated by the SRK, PR and PFMC.

Fig. 9: Error in Vapor Pressure of CHF₃ Calculated by the SRK, PR and PFMC.
Fig. 10: Error in Latent Heat of Vaporization of CHF$_3$ Calculated by the SRK, PR and PFMC.

Fig. 11: Error in Saturated Vapor Volume of CHF$_3$ Calculated by the SRK, PR and PFMC.
Fig. 12: Percent Error in Saturated Liquid Density of CHF₃ Calculated by the SRK, PR and PFMC.

Figs. 3, 7 & 11 present errors in saturated volume for the same three compounds. Again, with the exception of high reduced temperature, i.e. greater than 0.97, all three EOS give good agreement with the values reported in the ASHRAE hand-book.

Errors in saturated liquid density for the same three compounds are presented in Figs. 4, 8 & 12. With the exception of C₂H₂F₄, PFMC gives much better agreement with the reported values in ASHRAE.

Table 3 presents the summary of the error analysis between the calculated properties and reported values in the ASHRAE hand-book (4) for the thirty five refrigerants. Table 3 indicates that, with the exception of liquid density, all three EOS give good agreement with the reported values in the ASHRAE hand-book. The accuracy of all three EOS in predicting saturated vapor volume and heat of vaporization is essentially the same. However, PFMC has better accuracy in predicting vapor pressure and liquid density. With the exception of C₂H₂F₄, H₂ and He, PFMC does a very good job of predicting liquid density. The PR is second after PFMC in predicting vapor pressure and liquid density. Table 3 also indicates that the SRK is the least accurate in terms of predicting the saturated properties for the refrigerants studied.
Table 3

Comparison of Saturated Properties Calculated by Three Equations of State

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**AA = Average Absolute Percent Error**
CONCLUSIONS

For the thirty five pure components refrigerants studied, the summary of errors indicates that all three EOS considered perform well when applied to predict saturated vapor pressure, saturated vapor volume, and heat of vaporization. The accuracy for prediction of liquid density is not as good as one would desire, but this is a common characteristic of the three equations of state studied. The lack of accuracy for prediction of liquid density is more pronounced in the case of the SRK and PR.

Between the three EOS considered PFMC gives a much better performance as is expected because the PR and SRK are not applicable to compounds such as H₂O and NH₃.

Based on this evaluation, application of PFMC or PR for calculating vapor pressure, saturated vapor volume or latent heat of refrigerant is recommended. For saturated liquid density calculation a method such as that proposed by Hankinson and Thomson (15) is recommended.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support for Dr. Moshfeghian's sabbatical year that was provided by Shiraz University, the Gas Processors Association, and Chemical Engineering Consultants. Inc.

REFERENCES


APPENDIX A

Peng-Robinson EOS

Peng and Robinson proposed their equation in 1976 as follows (6):

\[ P = \frac{RT}{V - b} - \frac{a}{V(V + b) + b(V - b)} \] (1)

or in dimensionless form as

\[ Z' - (1 - B) Z' + (A - 3B^2 - 2B) Z - (AB - B^2 - B') = 0 \] (2)

where

\[ A = (aP/R^2 T^2) \] (3)
\[ B = (bP/RT) \] (4)
\[ Z = (PV/RT) \] (5)
\[ a_i = \alpha_i a_c_i \] (6)
\[ b_i = b_c i \] (7)
\[ \alpha_i \frac{1}{2} = 1 + k_i (1 - T_{ri} \frac{1}{2}) \] (8)
\[ b_{c i} = 0.778RT_{c i}/P_{c i} \] (9)
\[ a_{c i} = 0.42724 (R^2 T_{c i}^2/P_{c i}) \] (10)
\[ k_i = 0.37464 + 1.54226w_i - 0.26992w_i^2 \] (11)

\[ b = \sum_{i} y_i b_i \] (12)

\[ a = \sum_{i} \sum_{j} y_i y_j (a_i a_j) \frac{1}{2} (1 - k_{i j}) \] (13)

The expression for departure of enthalpy from ideal gas state can be expressed as

\[ \frac{(H - H^o)/RT = 1 - Z - \frac{A}{2 \sqrt{2} B} (1 + D/a) \ln \frac{Z + 2.414B}{Z - 0.414B} }{2} \] (14)

where

\[ D = \sum_{i} \sum_{j} m_i y_i y_j (a_i a_j T_{r j}) \frac{1}{2} (1 - k_{i j}) \] (15)

The fugacity coefficient can be obtained from

\[ \ln (\mathcal{Z}) = (b_i / b) (Z-1) - \ln (Z - B) - \frac{A}{(2 + 2 \sqrt{2} B)} (b_i / b - 2A_i / a) \]

\[ \ln \left( \frac{Z + 2.414B}{Z - 0.414B} \right) \] (17)
where
\[ A_i = \sum_{j} y_i (a_i a_j)^{\frac{1}{2}} (1 - k_{i,j}) \] \hspace{1cm} (18)

**NOMENCLATURE**

- **A**: dimensionless parameter defined by (Equation 3)
- **B**: dimensionless parameter defined by (Equation 4)
- **a**: interaction parameter
- **b**: molecular volume
- **H**: enthalpy
- **P**: absolute pressure
- **T**: absolute temperature
- **R**: universal gas constant
- **V**: molar volume
- **w**: acentric factor
- **Z**: compressibility factor defined by (Equation 5)
- \( \varnothing \): fugacity coefficient

**SUBSCRIPTS & SUPERSCRIPTS**

- **L**: liquid phase property
- **V**: vapor phase property
- **c**: critical property
- **i**: component i
- **j**: component j
- **r**: reduced property

**APPENDIX B**

**Soave-Redlich-Kwong EOS**

Soave (5) version of the Redlich-Kwong EOS is as follows (5):

\[ P = \frac{RT}{V - b} - \frac{a}{V(V + b)} \] \hspace{1cm} (1)

or in dimensionless form as

\[ Z^3 - Z^2 + (A - B - B^2) Z - AB = 0 \] \hspace{1cm} (2)
where

\[ A = (aP/R^2T^3) \]  
(3)
\[ B = (bP/RT) \]  
(4)
\[ Z = (PV/RT) \]  
(5)
\[ a_i = \alpha_i \alpha_c i \]  
(6)
\[ b_i = b_c i \]  
(7)
\[ \alpha_i^{1/2} = 1 + m_i (1 - T_{r,i}^{1/2}) \]  
(8)
\[ b_{c,i} = 0.08667RT_{c,i}/P_{c,i} \]  
(9)
\[ a_{c,i} = 0.42747 \left( R^2T_{c,i}^2/P_{c,i} \right) \]  
(10)
\[ m_i = 0.37464 + 1.54226w_i - 0.26992w_i^2 \]  
(11)
\[ b = \sum_{i} y_i b_i \]  
(12)
\[ a = \sum_{i} \sum_{j} y_i y_j (a_i a_j)^{1/2} (1 - k_{i,j}) \]  
(13)
\[ A_i = \sum_{j} y_i (a_i a_j)^{1/2}(1 - k_{i,j}) \]  
(14)
\[ \beta = \sum_{i} \sum_{j} y_i y_j (p_{i,j} + q_{i,j}) (1 - k_{i,j}) \]  
(15)
\[ p_{i,j} = (a_{c,i} a_j)^{1/2} m_i/(2T_{c,i} T_{r,i}) \]  
(16)
\[ q_{i,j} = (a_{c,i} a_j)^{1/2} m_i/(2T_{c,j} T_{r,j}) \]  
(17)

The expression for departure of enthalpy from ideal gas state can be expressed as

\[ (H - H^o)/RT = Z - 1 - [A/B - \beta/(Rb)] \ln (1 + B/Z) \]  
(18)

The fugacity coefficient can be obtained from

\[ \ln (\Omega_i) = (b/b) (Z - 1) - \ln(Z-B) - (A/B) [2A_i/a - b_i/b] \ln(1 + B/Z) \]  
(19)

The expression for departure of entropy from ideal gas state is

\[ (S - S^o)/R = \sum_{i} y_i \ln(\Omega_i) - (H-H^o)/RT + \sum_{i} y_i \ln y_i + \ln(p/p^o) \]  
(20)

The vapor liquid equilibria is defined by

\[ K_i = \Omega_i^L/\Omega_i^V \]  
(21)
NOMENCLATURE

A : dimensionless parameter defined by (Equation 3)
B : dimensionless parameter defined by (Equation 4)
a : interaction parameter
b : molecular volume
K : vapor liquid equilibria ratio
H : enthalpy
P : absolute pressure
T : absolute temperature
R : universal gas constant
V : molar volume
w : acentric factor
Z : compressibility factor defined by (Equation 5)
Ω : fugacity coefficient

SUBSCRIPTS & SUPERSCRPTS

L : liquid phase property
V : vapor phase property
c : critical property
i : component i
j : component j
r : reduced property
° : ideal gas state

APPENDIX C

PFMC EOS (11)

The dimensionless form compressibility factor is

\[ Z = 1 - \frac{(s/x) \ln (1 - x) - s + 12bx \sum \Gamma_i \left( \frac{1 - \sum_j \Gamma_j \theta_{n,j}}{1 - x + x \sum_j \Gamma_j \theta_{n,j}} \right)}{n} \]  

(1)

\[ b = \sum_i \sum_j y_i y_j (b_i b_j)^{0.5} k_{i,j} \]  

(2)

\[ c c \]

\[ s = \sum_i \sum_j y_i y_j (s_i s_j)^{0.5} l_{i,j} \]  

(3)

In equations 2 & 3 \( y_i \) is the mole fraction of molecule \( i \) and \( k_{ij} \) and \( l_{ij} \) are the binary interaction coefficients between molecules \( i \) and \( j \) which are determined from the experimental VLE data. The fraction of molecular volume for group \( j \), \( \Gamma_j \), is
\[ \Gamma_j = \frac{c}{\sum_i y_i m_i j b_j}/b \]  

The interaction energy function between groups \( j \) and \( n \) is
\[ \theta_{jn} = \exp(-E_{jn}/RT) \]  

\( E_{jn} \), the interaction energy parameter between groups \( j \) and \( n \) is given by
\[ E_{jn} = a_{jn} (E_j + E_n)/2 \]  

The binary interaction coefficient, \( a_{jn} \), in equation (6) is defined as a linear function of temperature.
\[ a_{jn} = p_{jn} + q_{jn} T/1000 \]  

The energy term, \( E_j \), is calculated by
\[ E_j = E_j^0 + E_j^1 [283.2/T - 1] + E_j^2 [(283.2/T)^2 - 1] \]  

In the above equations, \( b_j, s_j, E_j^0, E_j^1 \) and \( E_j^2 \) are the parameters of group \( j \) which are determined from experimental PVT data for pure compounds.

Based on the quadratic mixing rule the expression for chemical potential, \( \mu_i \) is derived to be
\[ \frac{\mu_i}{RT} = S_i (1 - 1/x) \ln (1 - x) - B_i [1 - s - (s/x) \ln(1 - x)] - \ln(Z) \]
\[ \frac{g}{12} \sum \frac{m_{in} b_n \ln \left[ \frac{1 - x + x \Sigma_j \Gamma_j \theta_{nj}}{\Gamma_n \sum_j \left( \frac{b_j - \Sigma_j m_i j b_j \Gamma_j \theta_{nj}}{1 - x + x \Sigma_j \Gamma_j \theta_{nj}} \right) \right]}{\theta_{nn}} \]  

where \( B_i \) and \( S_i \) are defined as:
\[ B_i = (b - \Sigma J_j (b_j b_j)^{a_j} k_{jj})/b \]  
\[ S_i = s - \Sigma J_j (s_j s_j)^{a_j} k_{jj} \]  

The chemical potential is related to the fugacity coefficient by:
\[ \mu_i - \mu_i^\circ = RT \ln(\zeta_i) \]  

The expression for departure of entropy from ideal gas state is
\[ (S - S^\circ)/R = \sum_i n_i \ln (\zeta_i) - [(H - H^\circ)/RT + \sum_i n_i \ln y_i + \ln (p/p^\circ)] \]
The vapor liquid equilibria is defined by

\[ K_i = \frac{\mathcal{O}_i^l}{\mathcal{O}_i^v} \]  

(14)

**NOMENCLATURE**

- \( a_{jn} \) : binary interaction coefficient of energy term between molecules \( j \) and \( n \)
- \( b \) : molecular volume of system, m\(^3\)/kgmole
- \( b_i \) : molecular volume of component \( i \), m\(^3\)/kgmole
- \( B_i \) : term defined by (Equation 10)
- \( c \) : number of component in system
- \( E_{ij} \) : energy term of group \( j \)
- \( E_{jn} \) : interaction energy term between groups \( j \) and \( n \)
- \( E^g_{ij} \) : energy parameter in (Equation 8)
- \( E^l_{ij} \) : energy parameter in (Equation 8)
- \( E_r \) : energy parameter in (Equation 8)
- \( g \) : number of groups in system
- \( H \) : enthalpy
- \( m_{ij} \) : number of group \( j \) in molecule \( i \)
- \( k_{ij} \) : binary interaction coefficient between molecules \( i \) and \( j \) for \( b \)
- \( l_{ij} \) : binary interaction coefficient between molecules \( i \) and \( j \)
- \( p_{jn} \) : binary parameter between groups \( j \) and \( n \)
- \( q_{jn} \) : binary parameter between groups \( j \) and \( n \)
- \( R \) : universal gas constant
- \( s_i \) : degrees of freedom of component \( i \)
- \( S_i \) : term defined by (Equation 11)
- \( T \) : temperature of system, K
- \( v \) : volume of system, m\(^3\)/kgmole
- \( x \) : equal to \( b/v \)
- \( y_i \) : mole fraction of component \( i \)
- \( Z \) : compressibility factor
- \( \Gamma_j \) : fraction of volume of group \( j \)
- \( \theta_{jn} \) : energy parameter between groups \( j \) and \( n \)
- \( \mathcal{O}_j \) : fugacity coefficient of component \( i \)
- \( \mu_i \) : chemical potential for component \( i \)