PREDICTION OF REFRIGERANT THERMODYNAMIC PROPERTIES BY EQUATIONS OF STATE

Saturated Properties of Pure Compounds

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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, $E^{(0)}$ $E^{(1)}$, $E^{(2)}$ (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-tempterature
SRK   : Soave-Redlich-Kwong equation of state

VLE	: vapor-liquid equilibrium (or equilibria)
VP	: vapor pressure
VV	: vapor volume

SUBSCRIPTS

C	: calculated property
E	: experimental property
i	: data point i

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 neccessary, 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.

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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:

$$OF = \sum_{i=1}^{ND} [A \left(\frac{VP_E - VP_C}{VP_E} \right)2 + B \left(\frac{LD_E + LD_C}{VP_E} 2 \right)$$

$$+ C \frac{VV_E - VV_C}{VV_E} + D \left(\frac{HV_E - HV_C}{HV_E} \right)2] i \qquad (1)$$

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.

Table 1

Optimum Parameters for the Soave-Redlich-Kwong, Peng-Robinson and Parameters from Molecule Contributions Equations of State for Refrigerants.

Compound	Acentric Factor		PFMC Parameters				
	SRK	PR	b (ft³/ lbmol)	s	E^0/R (°R)	E^1/R (°R)	E^2/R (°R)
CCl_2F_2	0.17884	0.20400	0.8530	6.0670	−404.87	−41.44	1.17
$CHCl_2F$	0.20792	0.21000	0.8454	5.2309	−464.19	−110.10	12.09
$C_2Cl_3F_3$	0.25357	0.25600	1.4009	6.3884	−3344.77	−64.46	8.03
$C_2Cl_2F_4$	0.25389	0.26300	1.1129	8.0915	−403.11	−23.66	0.16
R-503	0.19066	0.19100	0.5905	5.2765	−394.93	−57.88	2.25
H_2	−0.25859	−0.23681	0.2993	1.6832	−51.29	0.03	0.00
NH_3	0.24323	0.25200	0.2792	3.0442	−1001.09	−563.06	99.66
H_2O	0.32432	0.33356	0.2000	2.2000	−2651.30	−2779.30	858.50
Ne	−0.03059	−0.02219	0.2606	0.8395	−31.57	−6.13	0.14
A	−0.00706	0.00100	0.3498	2.0133	−189.80	−33.80	2.20

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.

Table 2

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

Number	Refrigerant		No. of Points	Reduced Temperature Range	
	Formula	Number		From	To
1	CCl_3F	11	40	0.436	0.990
2	CCl_2F_2	12	35	0.447	0.935
3	$CClF_3$	13	28	0.478	0.974
4	$CBrF_3$	13B1	30	0.522	0.996
5	CF_4	14	18	0.561	0.976
6	$CHCl_2F$	21	19	0.442	0.996
7	$CHClF_2$	22	32	0.466	0.977
8	CHF_3	23	21	0.579	0.965
9	CH_3Cl	40	22	0.507	0.827
10	CH_4	50	33	0.524	0.990
11	$C_2Cl_3F_3$	113	37	0.490	0.980
12	$C_2Cl_2F_4$	114	33	0.431	0.982
13	C_2ClF_5	115	28	0.534	0.975
14	$C_2H_2F_4$	134a	33	0.475	0.950
15	$C_2H_3ClF_2$	142b	35	0.501	0.963
16	$C_2H_4F_2$	152a	35	0.459	0.948
17	C_2H_6	170	30	0.436	0.963
18	C_3H_8	290	30	0.540	0.976
19	$cycC_4F_8$	C318	29	0.600	0.993
20	R-500	500	31	0.542	0.983
21	R-502	502	25	0.601	0.985
22	R-503	503	26	0.512	0.987
23	R-504	504	27	0.556	0.981
24	nC_4H_{10}	600	35	0.405	0.980
25	iC_4H_{10}	600a	30	0.598	0.993
26	H_2	702	14	0.417	0.947
27	He	704	20	0.418	0.811
28	NH_3	717	34	0.482	0.986
29	H_2O	718	29	0.423	0.824
30	Ne	720	12	0.553	0.963
31	N_2	728	12	0.500	0.968
32	O_2	732	19	0.352	0.970
33	A	740	24	0.556	0.973
34	C_2H_4	1150	27	0.452	0.983
35	C_3H_6	1270	28	0.456	0.974

For each saturated property, the percent error defined as:

Percent Error = {ASHRAE Value — Calculated Value} (100)/{ASHRAE Value} 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 $C_2H_2F_4$, NH_3 and CHF_3.

Figs. 1, 5 & 9 present the error in calculated vapor pressure of $C_2H_2F_4$, 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 $C_2H_2F_4$, 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 hand-book. The SRK gives poor results for $C_2H_2F_4$ 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 hand-book.
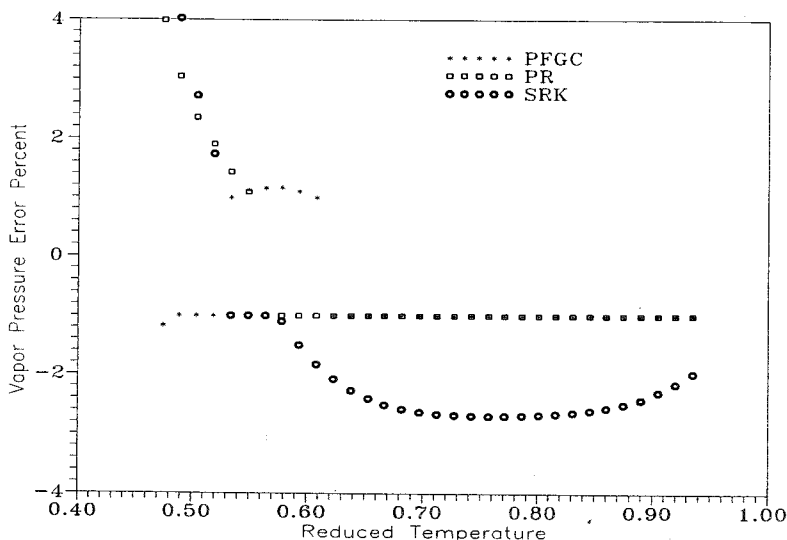

Fig. 1: Error in Liquid Vapor Pressure of $C_2H_2F_4$ Calculated by the SRK, PR and PFMC.

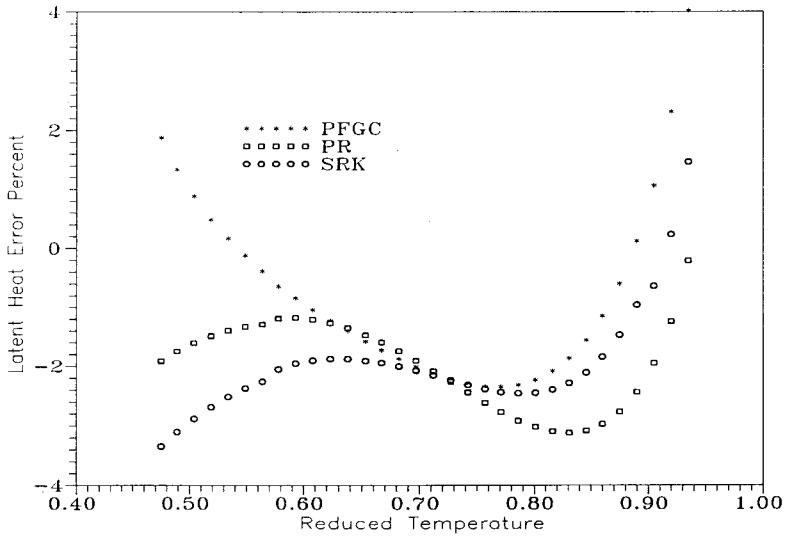Fig. 2: Error in Latent Heat Vaporization of $C_2H_2F_4$ Calculated by the SRK, PR and PFMC.
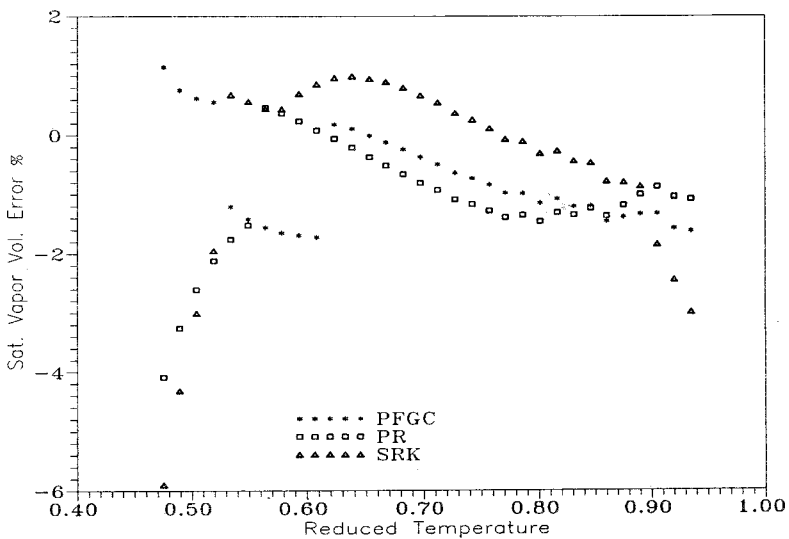

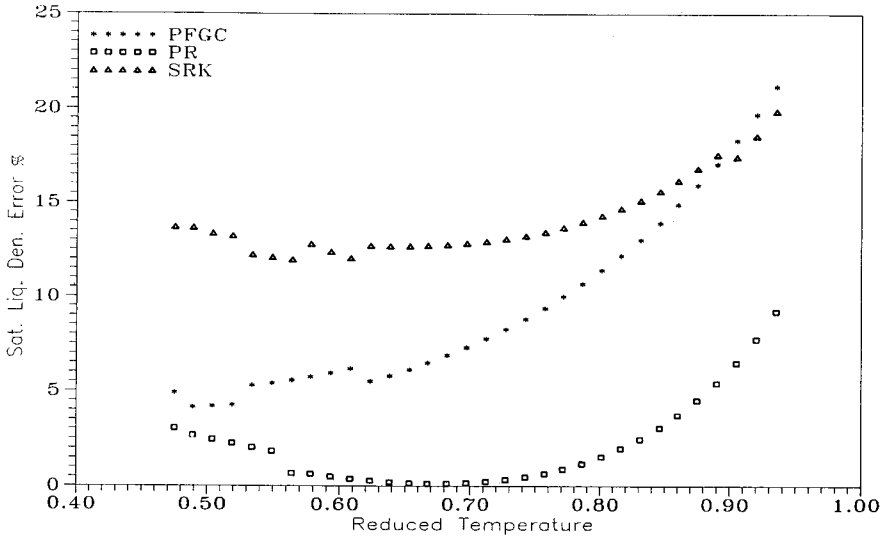Fig. 3: Error in Saturated Vapor Volume of $C_2H_2F_4$ Calculated by the SRK, PR and PFMC.

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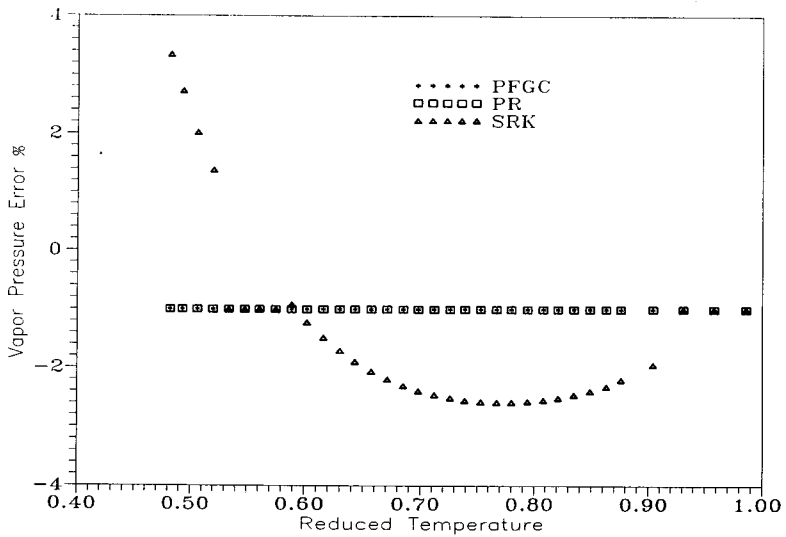

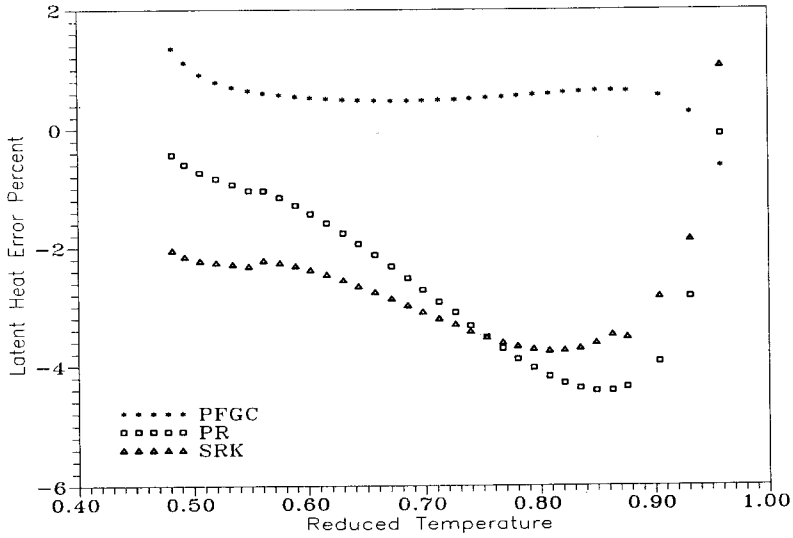Fig. 5: Error in Vapor Pressure of NH_3 Calculated by the SRK, PR and PFMC.

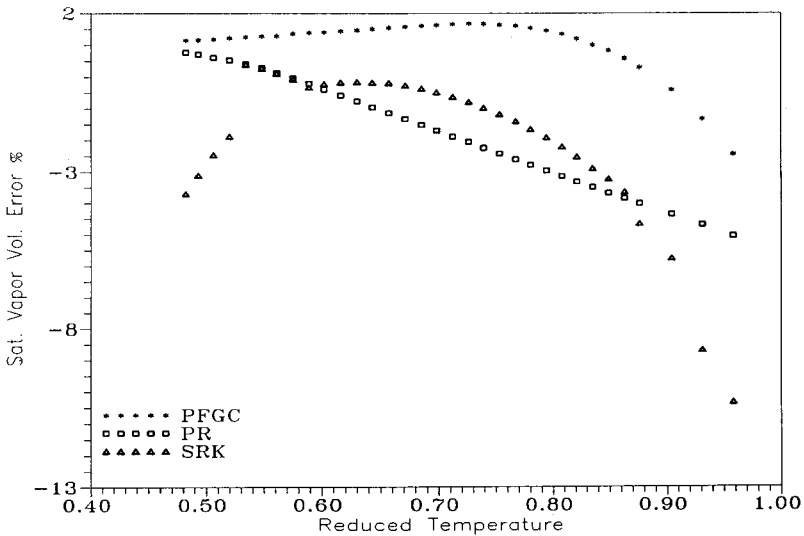Fig. 6: Error in Latent Heat of Vaporization of NH_3 Calculated by the SRK, PR and PFMC.

Fig. 7: Error in Saturated Vapor Volume of NH_3 Calculated by the SRK, PR and PFMC.
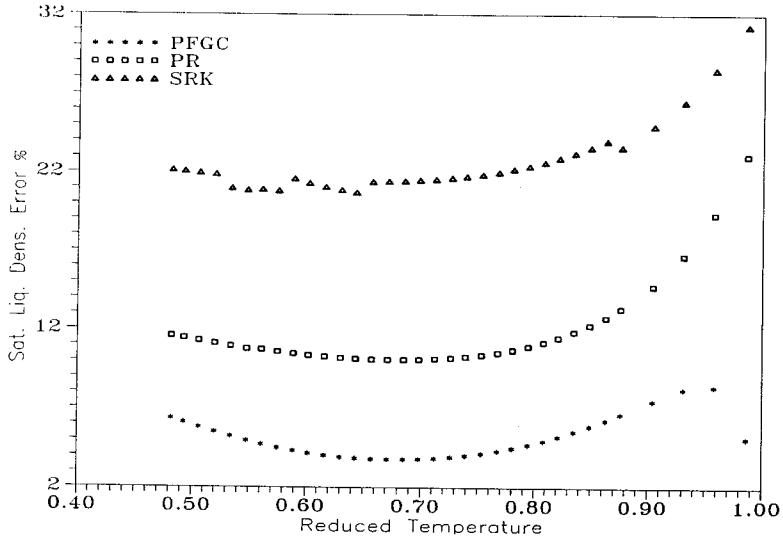
Fig. 8: Error in Saturated Liquid Density of NH_3 Calculated by the SRK, PR and PFMC.
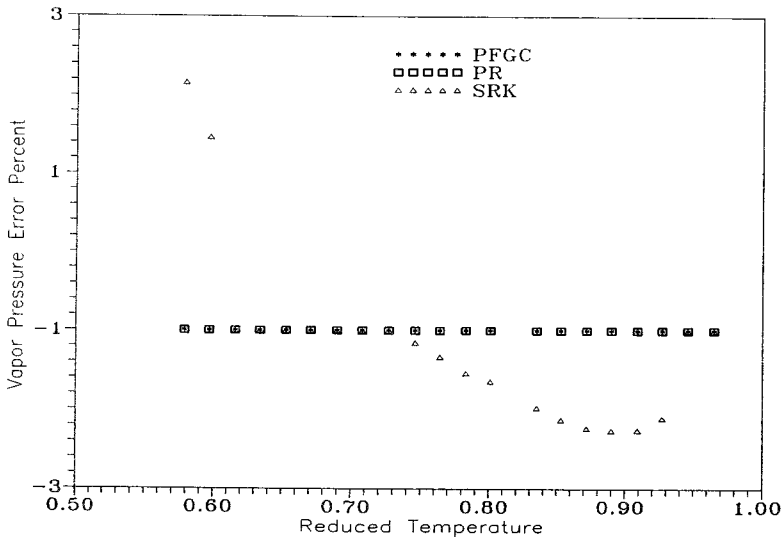

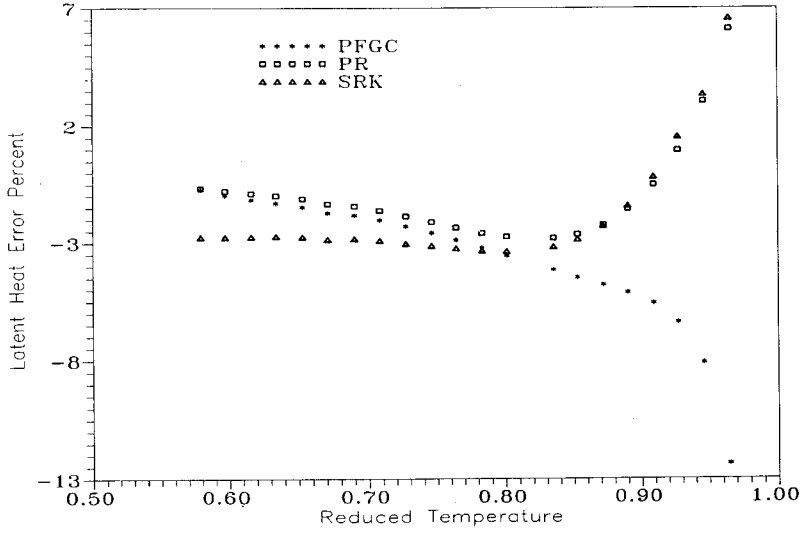Fig. 9: Error in Vapor Pressure of CHF_3 Calculated by the SRK, PR and PFMC.

Fig. 10: Error in Latent Heat of Vaporization of CHF_3 Calculated by the SRK, PR and PFMC.
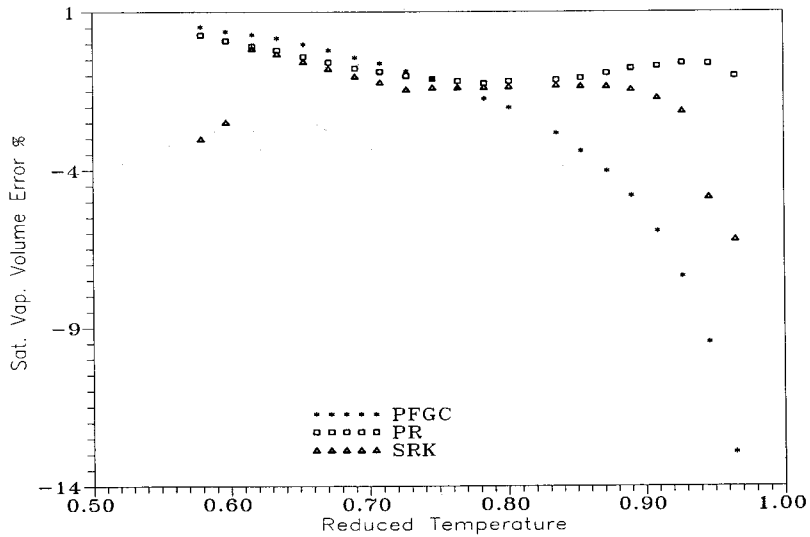

Fig. 11: Error in Saturated Vapor Volume of CHF_3 Calculated by the SRK, PR and PFMC.
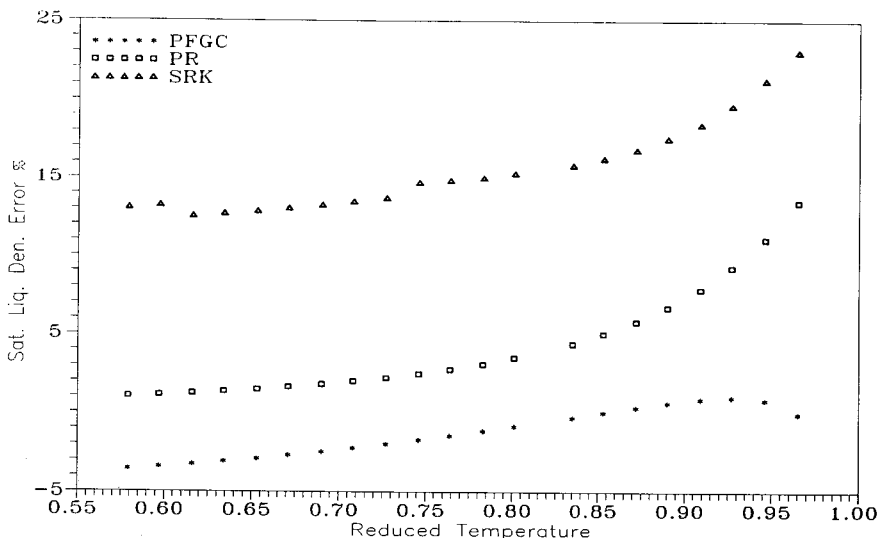
Fig. 12: Percent Error in Saturated Liquid Density of CHF_3 Calculated by the SRK, PR and PFMC.

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 $C_2H_2F_4$. 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 $C_2H_2F_4$, H_2 and H_e, 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.

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Table 3

Comparison of Saturated Properties Calculated by Three Equations of State

No.	Average Absolute Percent Error											
	Vapor Pressure			Vapor Volume			Liquid Density			Latent Heat		
	SRK	PR	PFMC	SRK	PR	PFMC	SRK	PR	PFMC	SRK	PR	PFMC
1	1.11	1.92	1.03	1.10	2.06	0.90	7.28	6.20	5.04	1.40	1.26	1.64
2	1.10	1.67	1.04	0.83	2.24	0.83	6.45	5.85	5.88	1.43	1.60	1.35
3	1.09	1.39	1.09	0.40	1.79	1.63	7.23	6.30	2.62	1.77	1.63	2.28
4	1.00	1.05	1.00	0.76	2.34	0.99	8.50	6.03	5.40	2.91	2.83	1.08
5	1.00	1.13	1.00	1.33	2.32	1.60	6.88	6.69	4.14	1.70	2.27	1.03
6	1.10	2.12	1.01	2.63	2.12	2.17	11.28	6.91	4.10	6.54	6.64	2.92
7	1.03	1.22	1.08	0.98	0.88	1.87	11.86	3.12	4.48	1.80	1.38	2.44
8	1.49	1.00	1.00	1.76	0.76	2.89	15.54	4.29	1.66	2.84	1.92	3.65
9	1.71	1.18	1.00	1.49	1.52	1.11	10.46	1.63	1.01	2.18	1.49	0.95
10	1.28	1.00	1.60	0.94	2.12	3.05	5.58	9.23	4.89	3.92	3.09	3.75
11	1.07	1.47	1.00	0.53	2.15	1.53	7.95	5.38	5.36	2.06	1.87	2.25
12	2.18	1.23	0.99	2.33	1.55	0.85	6.67	7.33	6.39	1.51	1.19	0.98
13	2.29	1.29	1.09	1.20	1.39	2.41	5.28	8.79	5.05	3.23	2.70	2.83
14	2.51	1.35	1.11	1.30	1.24	1.01	14.28	2.40	9.84	2.10	1.94	1.66
15	7.32	5.72	1.07	5.89	4.64	2.58	5.01	7.41	4.25	6.59	5.47	3.43
16	7.11	5.79	1.27	9.09	6.93	2.64	20.62	9.83	4.16	4.94	3.96	3.06
17	1.17	1.18	1.03	0.34	1.21	0.50	7.07	6.95	3.68	1.58	1.52	0.78
18	1.22	1.00	1.06	1.05	0.83	2.32	8.08	6.07	2.91	2.60	1.99	2.72
19	1.00	1.30	1.00	0.61	1.90	0.68	8.70	5.74	7.72	2.45	2.17	1.79
20	1.65	1.00	1.00	1.20	0.53	1.37	7.68	6.27	4.32	2.70	2.07	1.46
21	1.00	1.00	1.00	0.84	1.02	0.55	9.50	5.29	5.79	2.34	1.90	1.34
22	2.04	4.41	1.00	5.77	6.93	0.84	11.39	4.08	6.64	1.59	1.84	0.85
23	1.01	1.19	1.00	1.98	2.17	3.36	14.26	3.32	3.62	2.00	1.49	4.78
24	1.55	2.38	1.33	0.94	1.94	2.88	8.79	4.86	1.62	1.57	1.22	2.18
25	1.81	1.37	1.12	0.75	1.71	2.47	9.40	5.61	2.79	3.16	2.71	6.87
26	3.99	2.94	1.34	4.25	4.53	4.07	8.19	21.88	16.84	4.85	4.16	2.12
27	6.19	5.38	1.04	5.87	5.85	1.55	16.31	31.75	11.36	7.12	6.28	1.77
28	1.97	1.00	1.00	2.38	2.10	1.30	22.57	11.75	5.04	3.10	2.71	0.66
29	4.91	3.33	1.91	5.41	2.90	2.01	25.42	15.84	4.53	4.18	2.79	1.79
30	3.32	2.54	1.11	2.94	3.28	4.10	7.40	19.50	3.40	4.05	3.14	3.25
31	1.05	1.21	2.67	0.71	2.18	2.81	3.62	10.61	1.59	2.07	1.70	2.83
32	2.78	2.96	1.05	2.24	2.90	2.34	3.34	11.10	2.14	1.90	1.37	1.96
33	1.00	1.00	1.00	0.46	2.01	2.60	3.83	10.44	8.86	1.86	1.37	2.20
34	1.03	1.93	4.25	0.68	2.24	6.11	6.25	7.35	2.63	1.67	1.87	4.51
35	1.09	1.80	3.03	0.57	1.56	4.86	6.61	6.55	2.71	1.29	1.31	4.15
AA	2.12	1.98	1.30	2.04	2.40	2.14	9.69	8.35	4.93	2.83	2.42	2.35

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 H_2O and NH_3.

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

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APPENDIX A

Peng-Robinson EOS

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

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b) + b(V - b)} \tag{1}$$

or in dimensionless form as

$$Z^3 - (1 - B) Z^2 + (A - 3B^2 - 2B) Z - (AB - B^2 - B^3) = 0 \tag{2}$$

where

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

$$b = \sum_i^n y_i \, b_i \tag{12}$$

$$a = \sum_i^n \sum_j^n y_i \, y_j \, (a_i \, a_j)^{1/2} \, (1 - k_{i\,j}) \; i \; j \tag{13}$$

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

$$(H - H°)/RT = 1 - Z - \frac{A}{2\sqrt{2} \, B} \, (1 + D/a) \, 1_n \left(\frac{Z + 2.414B}{Z - 0.414B} \right) \tag{14}$$

where

$$D = \sum_i^n \sum_j^n m_j \, y_i \, y_j \, (a_i \, ac_j \, Tr_j)^{1/2} \, (1 - k_{i\,j}) \tag{15}$$

The fugacity coefficient can be obtained from

$$\ln (\varnothing_i) = (b_i \, / \, b) \, (Z-1) - \ln (Z - B) - \frac{A}{(2 + 2\sqrt{2})B} \, (b_i \, / \, b - 2A_i \, / \, a)$$

$$\ln \left(\frac{Z + 2.414B}{Z - 0.414B} \right) \tag{17}$$

where

$$A_i = \sum_{j}^{n} y_i (a_i a_j)^{1/2} (1 - k_{ij}) \qquad (18)$$

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):

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b)} \qquad (1)$$

or in dimensionless form as

$$Z^3 - Z^2 + (A - B - B^2) Z - AB = 0 \qquad (2)$$

where

$$A = (aP/R^2T^2) \tag{3}$$
$$B = (bP/RT) \tag{4}$$
$$Z = (PV/RT) \tag{5}$$
$$a_i = \alpha_i \, a_{c\,i} \tag{6}$$
$$b_i = b_{c\,i} \tag{7}$$
$$\alpha_i^{1/2} = 1 + m_i \, (1 - T_{r\,i}^{1/2}) \tag{8}$$
$$b_{c\,i} = 0.08667 RT_{c\,i}/P_{c\,i} \tag{9}$$
$$a_{c\,i} = 0.42747 \, (R^2T_{c\,i}^2 \, / \, P_{c\,i}) \tag{10}$$
$$m_i = 0.37464 + 1.54226w_i - 0.26992w_i^2 \tag{11}$$

$$b = \sum_i^n \, y_i \, b_i \tag{12}$$

$$a = \sum_i^n \sum_j^n \, y_i \, y_j \, (a_i \, a_j)^{1/2} \, (1 - k_{i\,j}) \tag{13}$$

$$A_i = \sum_j^n \, y_i \, (a_i \, a_j)^{1/2}(1 - k_{i\,j}) \tag{14}$$

$$\beta = \sum_i^n \sum_j^n \, y_i \, y_j \, (p_{i\,j} + q_{i\,j}) \, (1 - k_{i\,j}) \tag{15}$$

$$p_{i\,j} = (a_{c\,i} \, a_j)^{1/2} \, m_i \, / \, (2T_{c\,i} \, T_{r\,i}) \tag{16}$$
$$q_{i\,j} = (a_{c\,j} \, a_i)^{1/2} \, m_i \, / \, (2T_{c\,j} \, T_{r\,j}) \tag{17}$$

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

$$(H - H^\circ) \, / \, RT = Z - 1 - [A \, / \, B - \beta \, / \, (Rb)] \ln (1 + B/Z) \tag{18}$$

The fugacity coefficient can be obtained from

$$\ln (\varnothing_i) = (b_i/b) \, (Z - 1) - \ln(Z - B) - (A/B) \, [2A_i \, / \, a - b_i \, / \, b] \ln(1 + B/Z) \tag{19}$$

The expression for departure of entropy from ideal gas state is

$$(S - S^\circ) \, / \, R = \sum_i^n y_i \, \ln(\varnothing_i) - (H - H^\circ) \, / \, RT + \sum_i^n y_i \, \ln y_i + \ln(p/p^\circ) \tag{20}$$

The vapor liquid equilibria is defined by

$$K_i = \varnothing_i^L \, / \, \varnothing_i^V \tag{21}$$

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)
$\varnothing$	:	fugacity coefficient

SUBSCRIPTS & SUPERSCRIPTS

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

APPENDIX C

PFMC EOS (11)

The dimensionless form compressibility factor is

$$Z = 1 - (s/x) \ln (1 - x) - s + 12bx \sum_{n}^{g} \Gamma_n \left[\frac{1 - \Sigma_j \Gamma_j \theta_{n\,j}}{1 - x + x\Sigma_j \Gamma_j \theta_{n\,j}} \right] \tag{1}$$

$$b = \sum_{j}^{c} \sum_{i}^{c} y_i y_i (b_i b_j)^{0.5} k_{i\,j} \tag{2}$$

$$s = \sum_{j}^{c} \sum_{i}^{c} y_i y_j (s_i s_j)^{0.5} l_{i\,j} \tag{3}$$

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, Γ_j, is

$$\Gamma_j = (\sum_i^c y_i m_{i\,j}\, b_j)/b \tag{4}$$

The interaction energy function between groups j and n is

$$\theta_{j\,n} = \exp(-E_{j\,n}\,/\,RT) \tag{5}$$

$E_{j\,n}$, the interaction energy parameter between groups j and n is given by

$$E_{j\,n} = a_{j\,n}\,(E_j + E_n)\,/\,2 \tag{6}$$

The binary interaction coefficient, a_{jn}, in equation (6) is defined as a linear function of temperature.

$$a_{j\,n} = p_{j\,n} + q_{j\,n}T/1000 \tag{7}$$

The energy term, E_j, is calculated by

$$E_j\,E_j = E^0_j + E^1_j\,[283.2\,/\,T - 1] + E^2_j\,[(283.2\,/\,T)^2 - 1] \tag{8}$$

In the above equations, b_j, s_j, E^0_j, E^1_j and E^2_j 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, μ_i is derived to be

$$\mu/RT = S_i\,(1 - 1/x)\,\ln\,(1 - x) - B_i\,[1 - s - (s/x)\ln(1 - x)] - \ln(Z)$$

$$12\{ \sum_n^g m_{in}\,b_n\,\ln\,[\,\frac{1 - x + x\sum_j \Gamma_j\,\theta\,n_j}{\theta_{nn}}\,] + x\sum_n^g \Gamma_n\,[\,\frac{b_i - \sum_j m_{i\,j}\,b_j\,\theta_{n\,j}}{1 - x + x\sum_j \Gamma_j\,\theta_{n\,i}}\,]\} \tag{9}$$

where B_i and S_i are defined as:

$$B_i = (b - \sum_j y_j\,(b_i\,b_j)^{0.5}\,k_{i\,j})/b \tag{10}$$

$$S_i = s - \sum_j y_j\,(s_i\,s_j)^{0.5}\,l_{i\,j} \tag{11}$$

The chemical potenial is related to the fugacity coefficient by:

$$\mu_i - \mu_i^\circ = RT\,\ln(\varnothing_i) \tag{12}$$

The expression for departure of entropy from ideal gas state is

$$(S - S^\circ)/R = \sum_i^n y_i\,\ln\,(\varnothing_i) - [(H - H^\circ)/RT + \sum_i^n y_i\,\ln\,y_i + \ln\,(p/p^\circ)] \tag{13}$$

The vapor liquid equilibria is defined by

$$K_i = \varnothing_i^L / \varnothing_i^v \tag{14}$$

NOMENCLATURE

$a_{j\,n}$	:	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_j	:	energy term of group j
$E_{j\,n}$	:	interaction energy term between groups j and n
E^0_j	:	energy parameter in (Equation 8)
E^1_j	:	energy parameter in (Equation 8)
E^2_j	:	energy parameter in (Equation 8)
g	:	number of groups in system
H	:	enthalpy
$m_{i\,j}$	:	number of group j in molecule i
$k_{i\,j}$	:	binary interaction coefficient between molecules i and j for b
$l_{i\,j}$	:	binary interaction coefficient between molecules i and j
$p_{j\,n}$	:	binary parameter between groups j and n
$q_{j\,n}$	:	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 freaction of component i
Z	:	compressibility factor
Γ_j	:	fraction of volume of group j
$\theta_{j\,n}$	:	energy parameter between groups j and n
$\varnothing_i$	:	fugacity coefficient of component i
μ_i	:	chemical potential for component i