

MODIFICATION OF THE PENG-ROBINSON EQUATION OF STATE
(GENERALIZATION)

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ABSTRACT

A modification of Peng-Robinson equation is described wherein in the parameter b is expressed as a linear function of temperature. The modified equation is then applied to a series of light hydrocarbons and refrigerants, and predicted values for vapor pressure, saturated vapor volume, saturated liquid volume and the heat of evaporation are compared with the corresponding experimental data. Considerable improvement is clearly observed.

INTRODUCTION

The Peng-Robinson equation of state (PR EOS) is widely used in simulation and design of chemical processes [5,3]. Its accuracy in predicting vapor phase thermodynamic properties is good enough for practical design applications; however, it gives poor results when used to predict liquid phase densities.

The PR EOS is a cubic equation which has two parameters, a and b . The a parameter is a function of T_c , P_c , ω , and temperature of system, but the b parameter is a function of T_c and P_c only. In order to improve the accuracy

of this EOS in predicting liquid phase densities, the b parameter has been expressed as a linear function of temperature of the system.

Peng-Robinson equation and the modified model

Peng and Robinson proposed their equation of state in 1976 as follows [5,6]:

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

or in dimensionless form as

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

where:

$$A = (aP/R^2 T^2) \quad (3)$$

$$B = (bP/RT) \quad (4)$$

$$Z = (PV/RT) \quad (5)$$

$$a = \alpha a(T_c) \quad (6)$$

$$b = b(T_c) \quad (7)$$

$$\alpha^{1/2} = 1 + \kappa(1 - T_r)^{1/2} \quad (8)$$

$$b(T_c) = 0.0778(RT_c/P_c) \quad (9)$$

$$a(T_c) = 0.42724(R^2T_c^2/P_c) \quad (10)$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (11)$$

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

$$H-H^* = RT(z-1) + \frac{T(da/dT) - a}{2\sqrt{2}B} \ln\left(\frac{z+2.414B}{z+0.414B}\right) \quad (12)$$

The fugacity coefficient can be obtained from

$$\ln(\phi) = z - 1 - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \ln\left(\frac{Z + 2.414B}{Z + 0.414B}\right) \quad (13)$$

In order to improve the predictive power of the PR EOS for liquid densities, the b parameter needs to be modified. For this purpose a modification similar to the one suggested by Soave [9] for the a parameter is proposed as follows.

$$b = \beta b(T_c) \quad (14)$$

$$\text{where: } \beta = 1 + \eta(1 - T_r)$$

Because b is expressed as a function of temperature, the expression for departure of enthalpy from the ideal gas state had to be rederived. The following equation is obtained for enthalpy deviation based on the proposed modification.

$$H-H^* = RT(z-1) + \frac{T(da/dT) - a}{2\sqrt{2}b} \ln\left(\frac{Z+2.414B}{Z+0.414B}\right) +$$

$$PT\left(\frac{db}{dt}\right)\left[\frac{1}{Z-B} - \frac{AZ}{B(Z^2+2BZ-B^2)} + \frac{A}{2\sqrt{2}B^2} \ln\left(\frac{Z+2.414B}{Z+0.414B}\right)\right] \quad (16)$$

In addition the acentric factor for each pure component had to be optimized to maximize the accuracy of this EOS. As a result of this optimization, κ in equation of 11 has a new set of coefficients. However, equations 1 through 6 and 8 through 10 remain unchanged.

Determination of κ and η

In order to determine the best values of κ and η which are needed in equations 8 and 15, the following procedure was followed for each component:

- 1- Initial values for κ and η were guessed.
- 2- At a specified temperature below the critical point, the vapor pressure, saturated vapor volume, saturated liquid density and heat of vaporization were calculated. These calculated values were compared with the experimental data [1] and the absolute value of the relative error was summed up as in equation.

$$S_i = C_1 \left| \frac{C_{vp}}{E_{vp}} - 1 \right| + C_2 \left| \frac{C_{svv}}{E_{svv}} - 1 \right| + C_3 \left| \frac{C_{slv}}{E_{slv}} - 1 \right| + C_4 \left| \frac{C_{hv}}{E_{hv}} - 1 \right| \quad (17)$$

where:

C_{vp}	calculated vapor pressure
E_{vp}	experimental vapor pressure
C_{svv}	calculated saturated vapor volume
E_{svv}	experimental saturated vapor volume
C_{slv}	calculated saturated liquid volume
E_{slv}	experimental saturated liquid volume
C_{hv}	calculated heat of vaporization
E_{hv}	experimental heat of vaporization
C_1, C_2	weighting factor for each error
C_3, C_4	

3- Step 2 was repeated for several other temperatures below the critical point and the following objective function was defined:

$$\phi = \sum (S_i) \quad (18)$$

4- Values of κ and η were changed and steps 2 and 3 were repeated to find the minimum values of ϕ . A nonlinear regression computer package developed by Chandler [2] was used to find the best values κ and η that minimized the value of ϕ .

Using a similar procedure Moshfeghian et al. [7,8] obtained values for η and κ which improved the results, but η was independent of ω . In other words, for each component they intro-

duced an additional parameter.

In this work, η has been expressed as a linear function of optimized ω and the need for an additional parameter has been eliminated. To obtain the optimized value of ω for each component, the following procedure was used.

- 1- A value for ω was assumed.
- 2- With this assumed value for ω , and using T_c , and P_c the values of vapor pressure, saturated liquid density, vapor volume and heat of vaporization were calculated at several temperature below the critical point using the original PR EOS equation.
- 3- Calculated values in step 2 were compared with experimental data [1] and values of S_i and ϕ as defined by equations 17 and 18 were calculated.
- 4- Value of ω was changed and step 2 and 3 were repeated to find the minimum value of ϕ and the corresponding value of ω .

Tables 1 and 2 present the best values of η , κ and ω which were determined by the above step-by-step procedures. In addition the functional dependency of κ and η on ω are shown in Figures 1 and 2. As a last step, both κ and η has been correlated as a function of optimized ω and the resulting correlations are:

$$\kappa = 0.61544 - 0.1907\omega + 7.0339\omega^2 - 15.489\omega^3 \quad (19)$$

$$\eta = 0.30075 - 2.2485\omega + 9.1977\omega^2 - 18.486\omega^3 \quad (20)$$

RESULTS

The capability and accuracy of this modified PR EOS and the original PR EOS have been tested against experimental data. The thermodynamic properties used to test the accuracy of these equations were vapor pressure, saturated vapor volume, saturated liquid volume and heat of vaporization of several light hydrocarbons and refrigerants. Number of temperature points tested for each component ranged from 10 to 42 covering a reduced temperature range from 0.4 to 1.0. A summary of comparison analysis for refrigerants is presented in Table 3. Similar comparison analysis is also presented for several light hydrocarbons in Table 4. Figures 3 through 6 also show typical improvements obtained in predicting saturated liquid volumes of propane, isobutane, dichlorodifluoromethane and dichlorofluoromethane by using the modified form of PR EOS.

Tables 3 and 4 indicate that not only the accuracy of predicting saturated liquid volumes increases, but the accuracy of other thermodynamic properties increases. Only prediction of heat of vaporization of some hydrocarbons becomes slightly worse.

CONCLUSIONS

By expressing the b parameter of

the PR EOS as a linear function of temperature the quality of thermodynamic properties predicted by this EOS improves considerably. A measure of percent of improvement defined as:

$$\text{Percent of improvement} = \frac{(\text{AVG. ABS. ERROR OF PR}) - (\text{AVG. ABS. ERROR OF MPR})}{(\text{AVG. ABS. ERROR OF PR})}$$

was used. In the above expression PR represents the original and MPR represents the modified PR EOS, respectively.

For the 12 light hydrocarbons tested, the improvements for vapor pressure is 44.2 percent and for the saturated liquid volume is 34.2 percent. Also for the 13 refrigerants studied in this work, improvements of 21.5 percent for the saturated liquid volume and 6.83 percent for vapor pressure were obtained.

Symbols

- A Dimensionless parameter defined by equation 3
- B Dimensionless parameter defined by equation 4
- a Interaction parameter
- b Molecular volume
- f Fugacity
- H Enthalpy
- P Absolute pressure
- T Absolute temperature
- R Universal gas constant
- V Molar volume
- ω Acentric factor
- Z Compressibility factor defined by equation 5
- ϕ Fugacity coefficient = fugacity /

- pressure
- Φ Sum of absolute fractional deviation from experimental data
- Subscript and Superscript
- L Liquid phase property
- V Vapor phase property
- c Critical property
- i Point number i
- r Reduced property
- * Ideal gas state property

Table 1 - Pure component properties of refrigerants

Compound	$T_c, ^\circ F$	$P_c, Psia$	Litratue ω	Calculated ω	κ	η
CF ₄	-50.2	543.0	0.1754	0.1831	0.7213	0.0839
CH ₃ Cl	289.6	968.7	0.1476	0.1589	0.7006	0.1015
CHCl ₂ F	353.9	749.4	0.2044	0.2124	0.7438	0.0609
CCl ₂ F ₂	233.6	596.9	0.1757	0.1843	0.7222	0.0830
CClF ₃	83.9	561.3	0.1727	0.1768	0.7160	0.0865
CHF ₃	78.1	701.4	0.2684	0.2675	0.7713	0.0035
CHClF ₂	204.8	721.9	0.2212	0.2253	0.7524	0.0496
C ₂ Cl ₃ F ₃	417.4	498.9	0.2568	0.2613	0.7695	0.0114
C ₂ ClF ₅	175.9	57.6	0.2520	0.2534	0.7667	0.0207
C ₂ H ₃ ClF ₂	278.8	598.0	0.2367	0.2129	0.7442	0.0605
C ₂ Cl ₂ F ₄	294.3	473.0	0.2544	0.2610	0.7694	0.0117
R-500	221.9	641.0	0.2059	0.2036	0.7375	0.0682
R-502	179.9	591.0	0.1802	0.2206	0.7494	0.0538

Table 2 - Pure component properties of hydrocarbons.

Compound	$T_c, ^\circ F$	$P_c, Psia$	Litratue ω	Calculated ω	κ	η
N ₂	-232.4	492.9	0.0400	0.03228	0.6162	0.2362
CO ₂	87.9	1070.0	0.2250	0.2187	0.7481	0.0556
CH ₄	-116.5	673.1	0.0070	0.0137	0.6141	0.2716
C ₂ H ₆	90.01	709.8	0.0910	0.1015	0.6524	0.1480
C ₃ H ₈	205.6	617.4	0.1450	0.1514	0.6940	0.1070
i-C ₄ H ₁₀	275.0	529.1	0.1764	0.1837	0.7218	0.0835
n-C ₄ H ₁₀	305.6	550.7	0.1930	0.1996	0.7344	0.0714
i-C ₅ H ₁₂	369.0	490.4	0.2270	0.2268	0.7533	0.0482
neo-C ₅ H ₁₂	321.1	463.6	0.1970	0.1934	0.7296	0.0762
n-C ₅ H ₁₂	385.7	488.6	0.2517	0.2511	0.7658	0.0762
n-C ₆ H ₁₄	453.6	430.6	0.2964	0.2977	0.7734	0.0234
C ₆ H ₆	552.1	709.8	0.2095	0.2157	0.7461	-0.0412

Table 3- Comparison between accuracy of Peng-Robinson(PR)and the Modified Peng-Robinson(MPR)EOS for refrigerants.

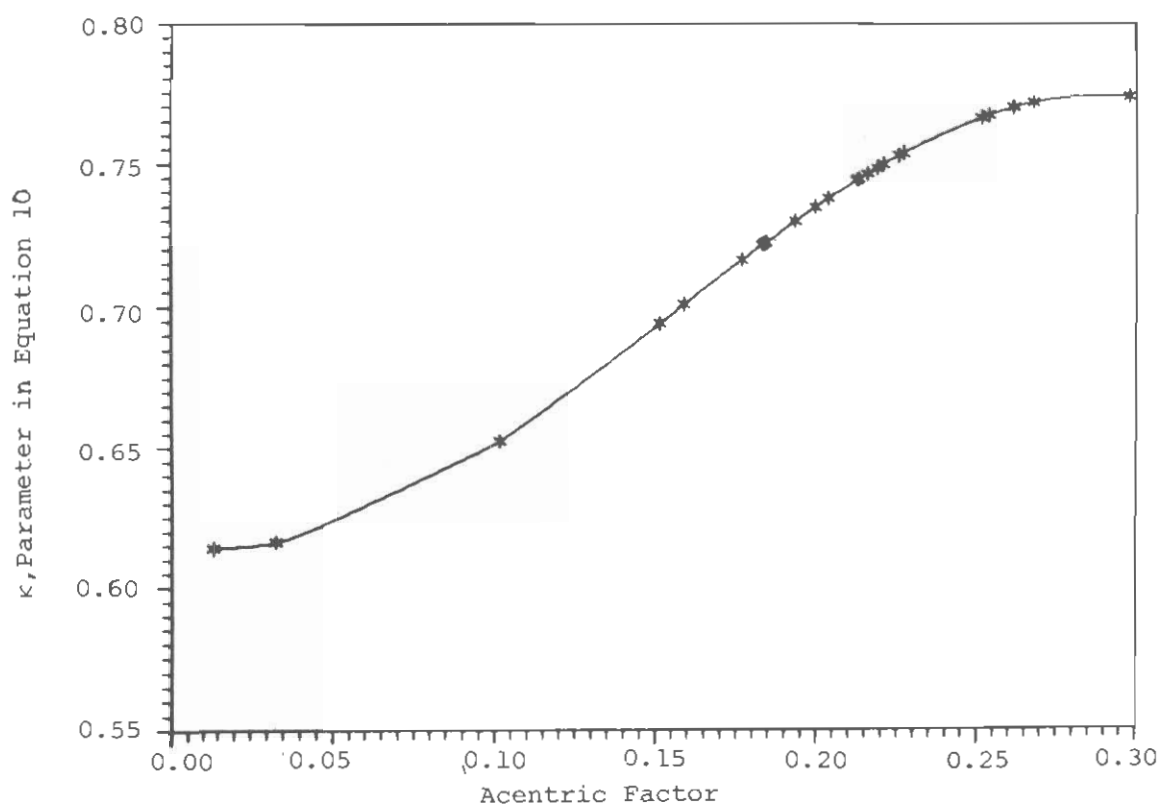
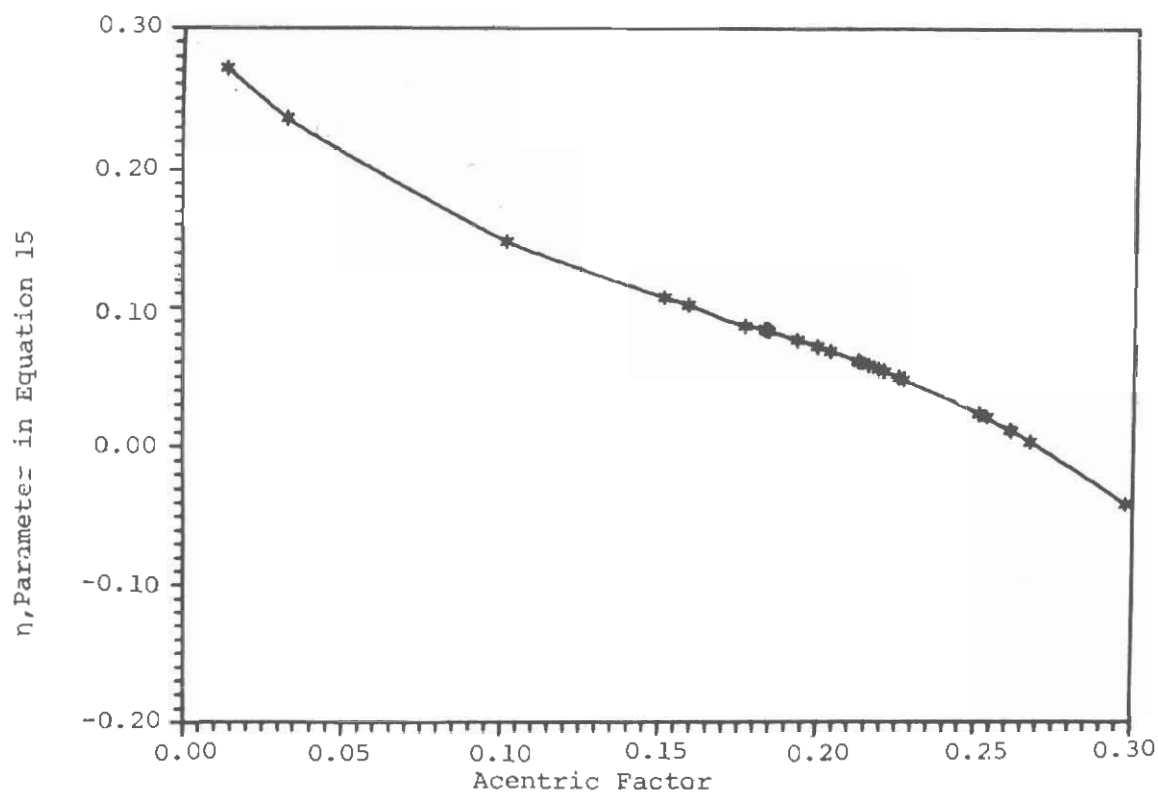
Average absolute percent deviation

Compound	No. of vap Pts	Pressure		vap volume		Liq volume		latent heat	
		PR	MPR	PR	MPR	PR	MPR	PR	MPR
CF ₄	18	1.14	1.20	2.98	1.89	5.86	4.24	3.10	3.90
CH ₃ Cl	22	4.36	1.09	2.92	1.94	0.71	3.19	1.28	1.26
CHCl ₂ F	31	2.70	2.98	2.97	3.27	3.35	1.78	1.84	2.00
CCl ₂ F ₂	38	2.21	2.05	2.33	2.54	5.02	2.99	1.65	1.51
CClF ₃	29	1.14	1.45	1.74	2.14	5.95	1.08	2.23	2.73
CHF ₃	27	0.74	0.70	1.41	1.24	6.06	6.18	2.66	2.56
CHClF ₂	35	1.10	0.96	1.48	1.57	3.01	2.53	1.40	1.34
C ₂ Cl ₃ F ₃	37	1.46	1.10	1.95	1.90	5.65	5.39	1.95	1.90
C ₂ ClF ₅	29	0.58	0.52	1.67	1.85	6.55	6.14	2.80	2.64
C ₂ H ₃ ClF ₂	37	3.68	2.90	6.01	2.42	2.75	1.34	4.40	2.00
C ₂ Cl ₂ F ₄	42	1.87	1.12	2.64	1.84	5.06	4.81	1.99	1.72
R-500	31	0.37	0.29	1.50	1.21	5.16	3.60	1.83	0.64
R-502	32	1.13	0.85	1.93	1.39	4.21	3.29	1.45	1.32
Avg abs error		1.42	1.32	2.43	1.94	4.57	3.58	2.20	2.96
% of improvement		6.83		20.01		21.50		10.90	

Table 4- Comparison between accuracy of Peng-Robinson(PR)and the Modified Peng-Robinson(MPR)EOS for hydrocarbons.

Average absolute percent deviation

Compound	No. of vap Pts	Pressure		vap volume		Liq volume		latent heat	
		PR	MPR	PR	MPR	PR	MPR	PR	MPR
N ₂	10	1.92	1.68	1.75	1.33	8.25	3.05	1.75	7.25
CO ₂	46	0.76	0.43	1.79	1.44	3.95	3.28	1.92	2.56
CH ₄	16	2.03	0.90	3.21	3.26	8.03	2.66	2.35	6.42
C ₂ H ₆	31	3.03	1.30	3.22	1.98	6.51	3.11	2.40	3.49
C ₃ H ₈	31	1.57	0.73	1.56	1.68	5.82	3.84	2.39	3.06
i-C ₄ H ₁₀	30	1.43	0.42	2.22	1.61	5.02	3.75	1.92	1.72
n-C ₄ H ₁₀	30	1.22	0.39	1.29	1.38	4.44	3.42	1.75	2.09
i-C ₅ H ₁₂	18	0.46	0.49	0.89	1.01	5.83	5.31	2.52	2.34
neo-C ₅ H ₁₂	16	0.37	0.37	1.61	1.47	5.28	4.17	2.59	2.54
n-C ₅ H ₁₂	18	0.31	0.27	0.83	0.93	5.04	4.83	2.76	2.41
n-C ₆ H ₁₄	23	0.95	0.71	2.53	2.80	4.24	3.67	1.47	1.90
C ₆ H ₆	42	1.18	0.84	2.91	2.81	2.79	1.80	1.67	1.65
Avg abs error		1.28	0.71	1.98	1.81	5.43	3.57	2.12	4.77
% of improvement		44.20		8.77		34.2		-124.	

Fig 1 . Variation of κ with respect to optimized acentric factorFig 2 . Variation of η with respect to optimized acentric factor

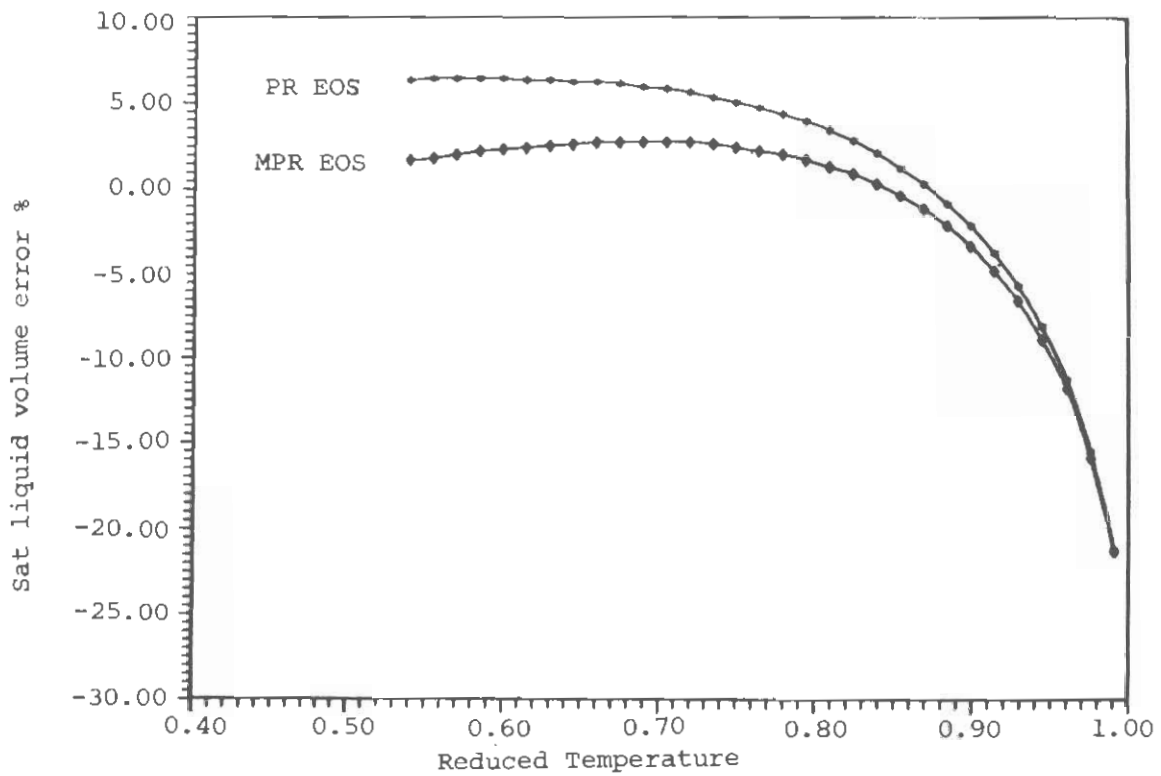


Fig 3 . Comparisson of the PR and MPR for C_3H_8 liquid volume error percent

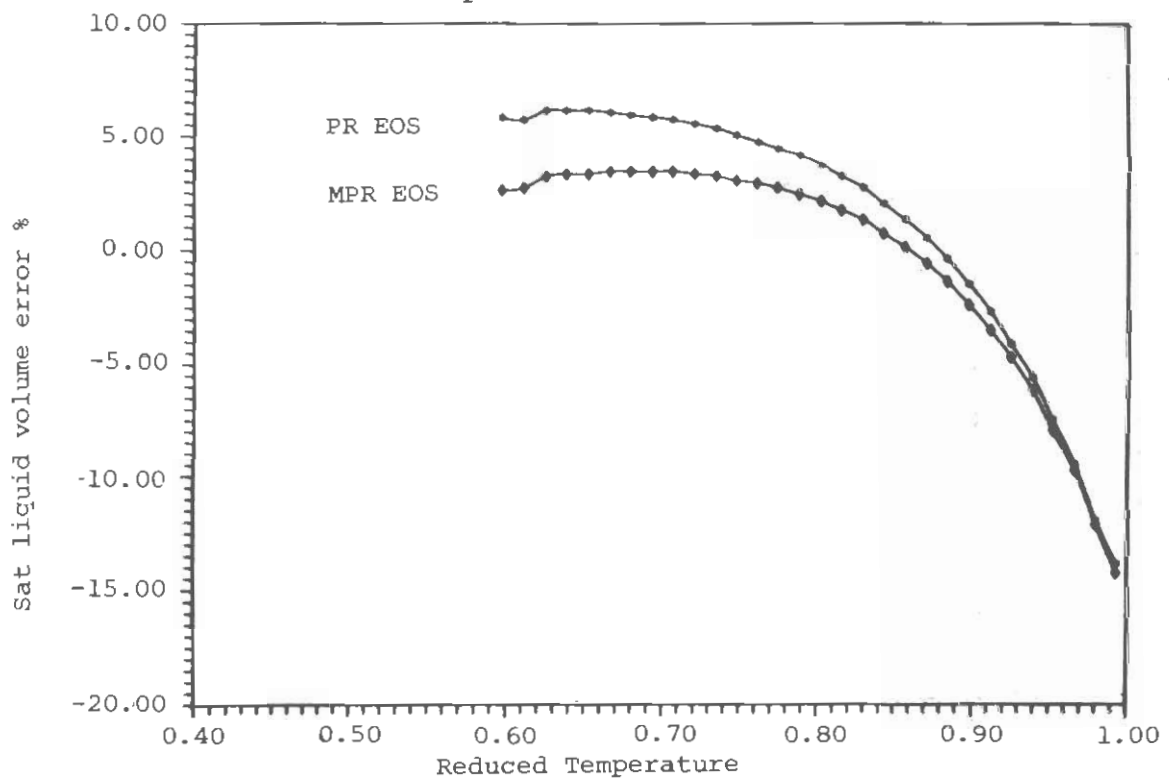


Fig 4 . Comparisson of the PR and MPR for $i-C_4H_{10}$ liquid volume error percent

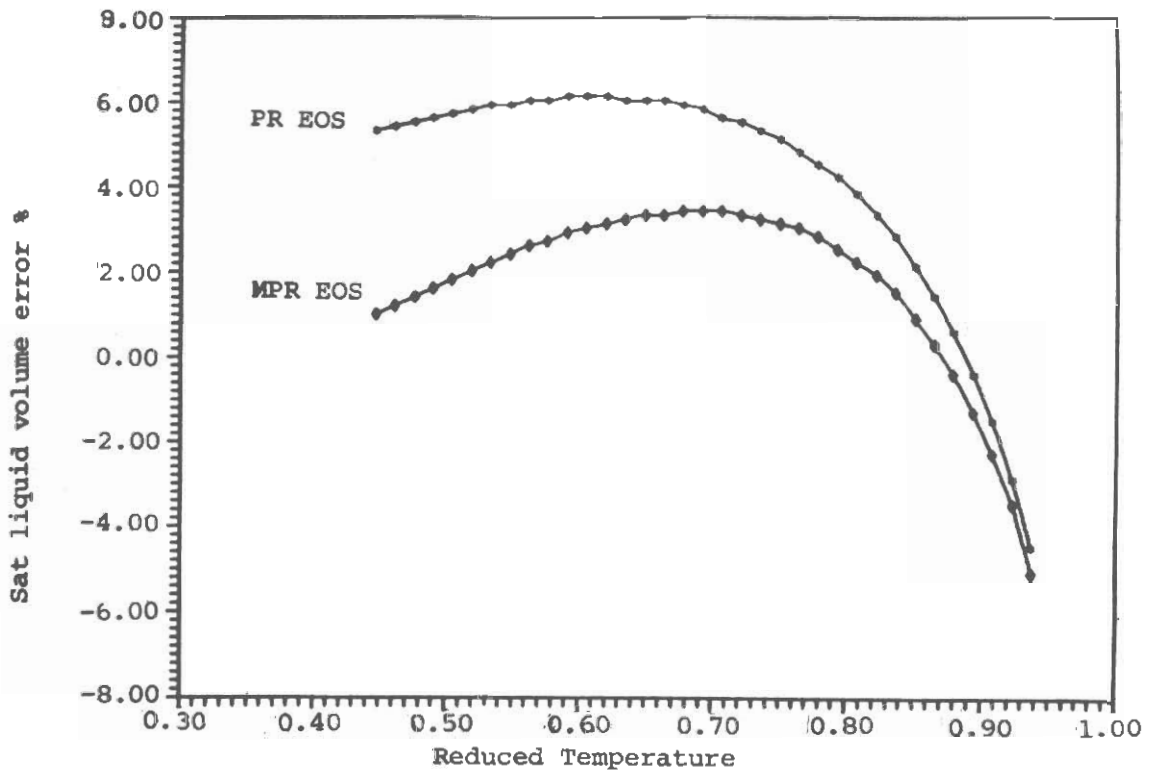


Fig 5 . Comparisson of the PR and MPR for Cl₂F₂C liquid volume error percent

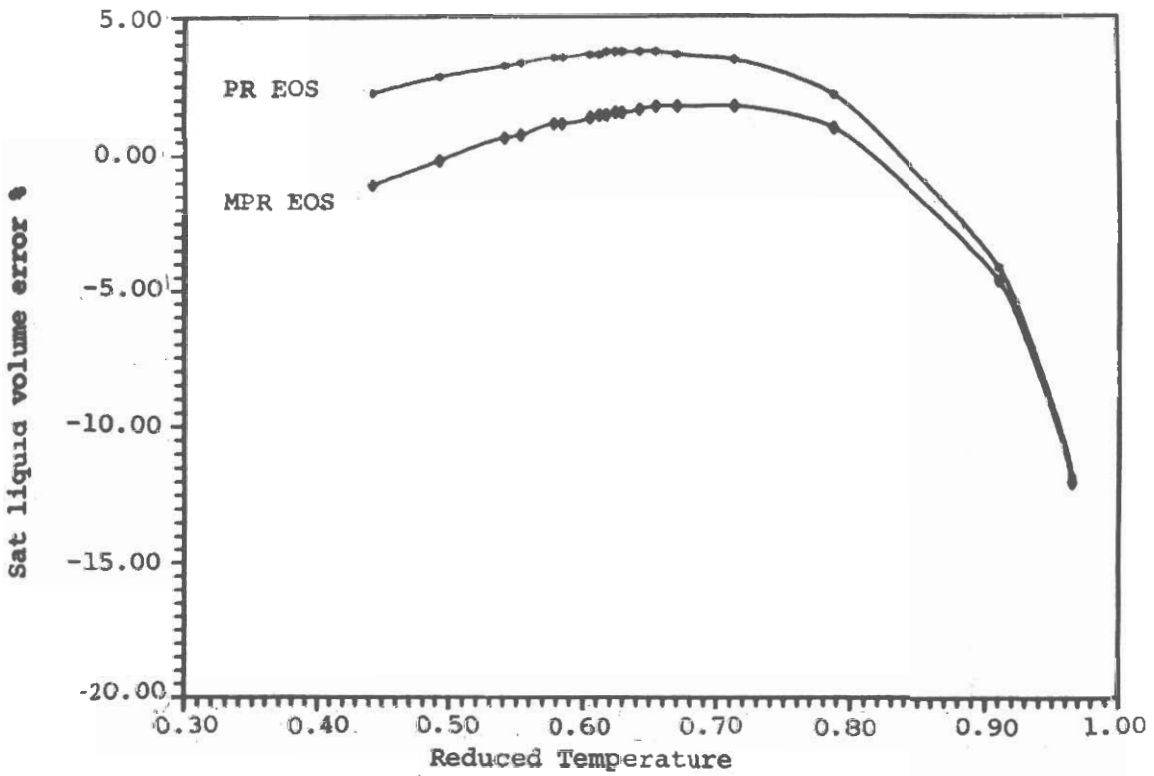


Fig 6 . Comparisson of the PR and MPR for Cl₂FHC liquid volume error percent

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