CHAPTER IX
RESULTS AND DISCUSSION

To test the performance of the database developed, result of estimation of gas and liquid properties are compared with data from some reference and other computer simulation packages.

9.1 VAPOR PRESSURE

In this work, Antoine equation and Wagner equations are used to predict vapor pressure. The results of estimation are compared with these published data in from some references(Perry,1984 and Sinnott ,1983).

In this work, substance is classified substance into five groups, which are hydrocarbon, inorganic compounds, alcohol, halogenated hydrocarbon and miscellaneous. Table 9.1 is a list of compounds of each group, which are selected randomly for testing the performance vapor pressure prediction of this database system in consideration of vapor pressure.

Table 9.1 Names of compounds in each group for testing vapor pressure

Name of group	Name of compounds
1. Hydrocarbons	ethane, n-butane, 2-methyl pentane, 2-methyl heptane, cyclopentane, cyclohexane, ethylene, 1-hexene, benzene, ethyl benzene
2. Inorganic compounds	argon, chlorine
3. Alcohol	methanol, ethanol
4. Halogenated hydrocarbon	carbontetrachloride, chloroform
5. Miscellaneous	methyl amine, acetone, formaldehyde

9.1.1 Hydrocarbons

There are ten hydrocarbons whose vapor pressure is estimated and compared with the reference data. The results of comparison are shown in figure 9.1 to 9.10. Tmin refers to the minimum temperature used to predict vapor pressure by each equation. Tmax refers to the maximum temperature. Pexp refers to the reference values. Pant refers to vapor pressure estimated by Antoine equation. Pwag refers to vapor pressure estimated by Wagner equation. Percent deviation refers to $\frac{P\exp - Pant}{Pant} * 100$ and $\frac{P\exp - Pwag}{Pwag} * 100$.

Equation	Tmin(K)	Tmax(K)
Antoine	130	199
Wagner	133	305.4

Range of temperature	Percent deviation (%)	
(K)	Antoine	Wagner
130 - 199	-0.63	-
133 - 305.4	-	0.13
130 - 305.4	-4.37	0.24

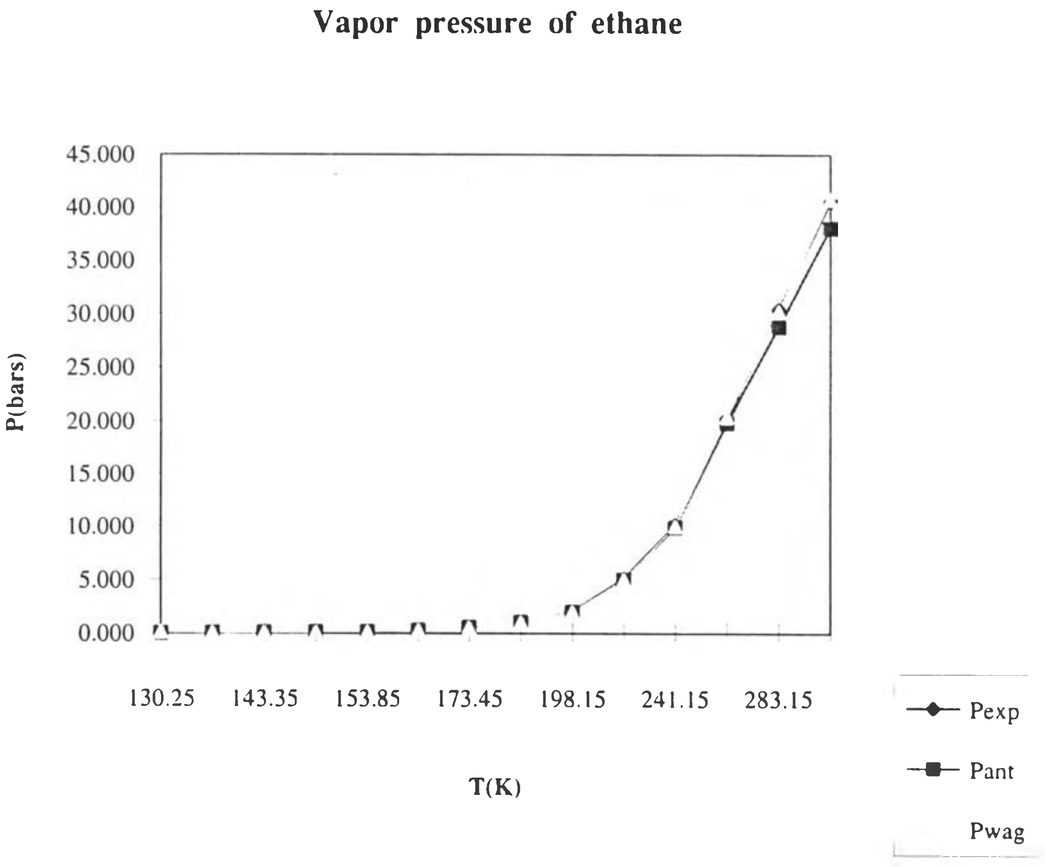

Figure 9.1 Comparison between calculated vapor pressure of ethane and reference data

Equation	Tmin(K)	Tmax(K)
Antoine	195.15	290.15
Wagner	170	425.2

Range of temperature	Percent deviation (%)	
(K)	Antoine	Wagner
195.15 - 290.15	-0.34	-
170 - 425.2	-	1.4
170-425.2	-4.5	1.4

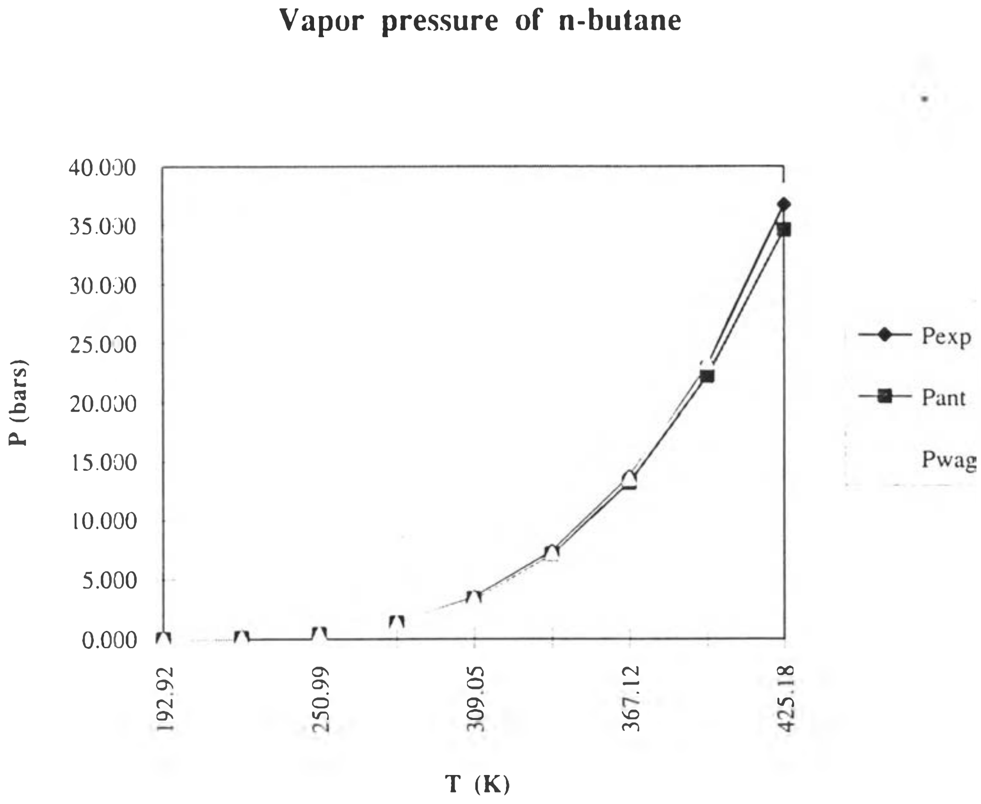

Figure 9.2 Comparison between calculated vapor pressure of n-butane and reference data

Equation	Tmin(K)	Tmax(K)
Antoine	240.15	370.15
Wagner	240	497.5

Range of temperature	Percent deviation (%)	
(K)	Antoine	Wagner
240.15 - 333.45	0.56	-
240 - 333.45	-	2.3
240 - 333.45	0.56	2.3

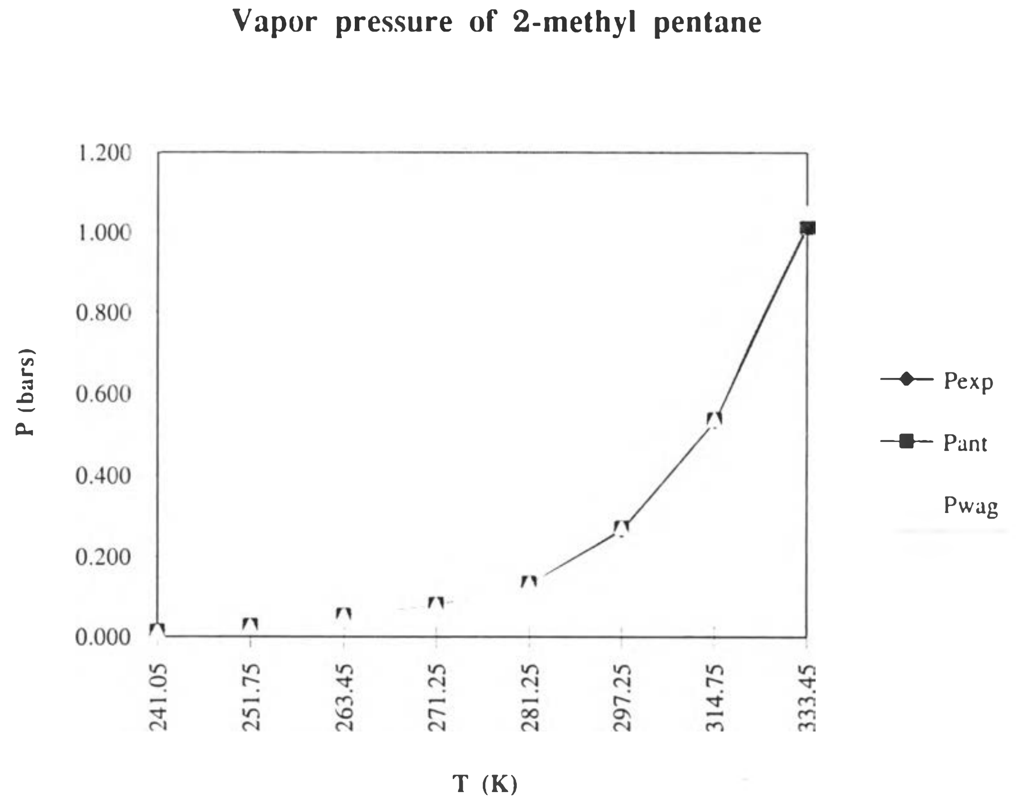

Figure 9.3 Comparison between calculated vapor pressure of 2-methyl pentane and reference data

Equation	Tmin(K)	Tmax(K)
Antoine	285.15	417.15
Wagner	250	559.6

Range of temperature	Percent deviation (%)	
(K)	Antoine	Wagner
285.45 - 390.75	-5.88	-
285.45 - 390.75	-	2.82
285.45 - 390.75	-5.88	2.82

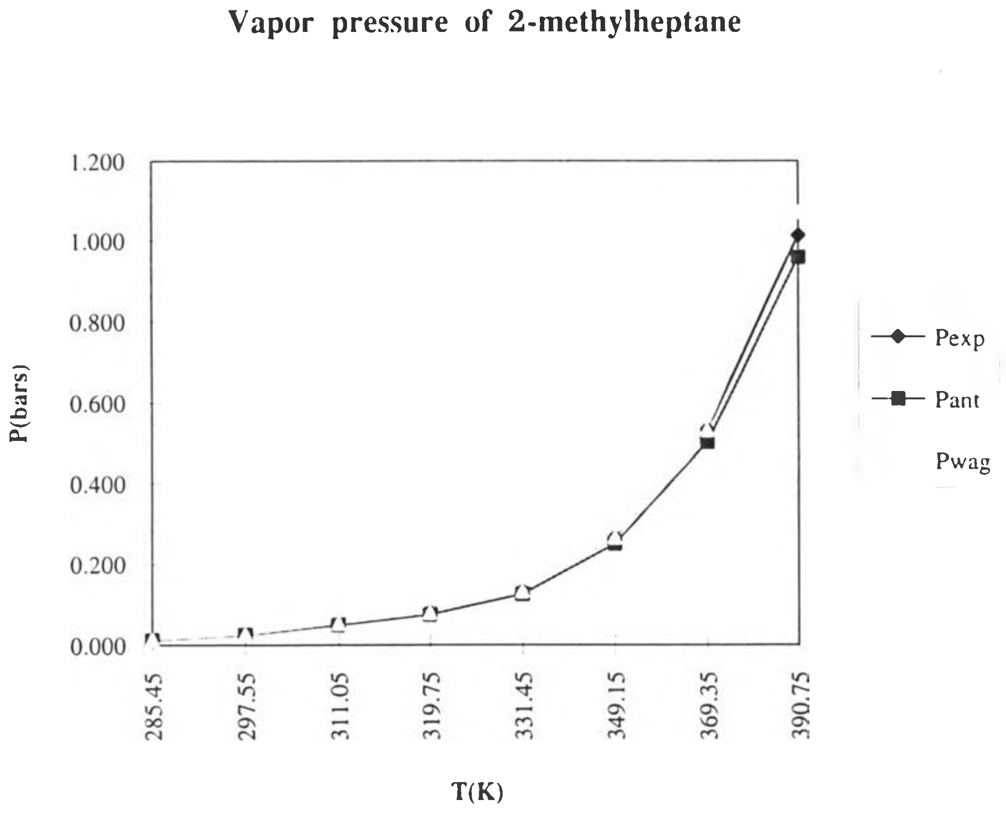

Figure 9.4 Comparison between calculated vapor pressure of 2-methyl heptane and reference data

Equation	Tmin(K)	Tmax(K)
Antoine	230.15	345.15
Wagner	289	511.7

Range of temperature	Percent deviation (%)	
(K)	Antoine	Wagner
230.15-345.15	0.11	-
289-478.51	-	1.07
230.15-478.51	-2.47	1.07

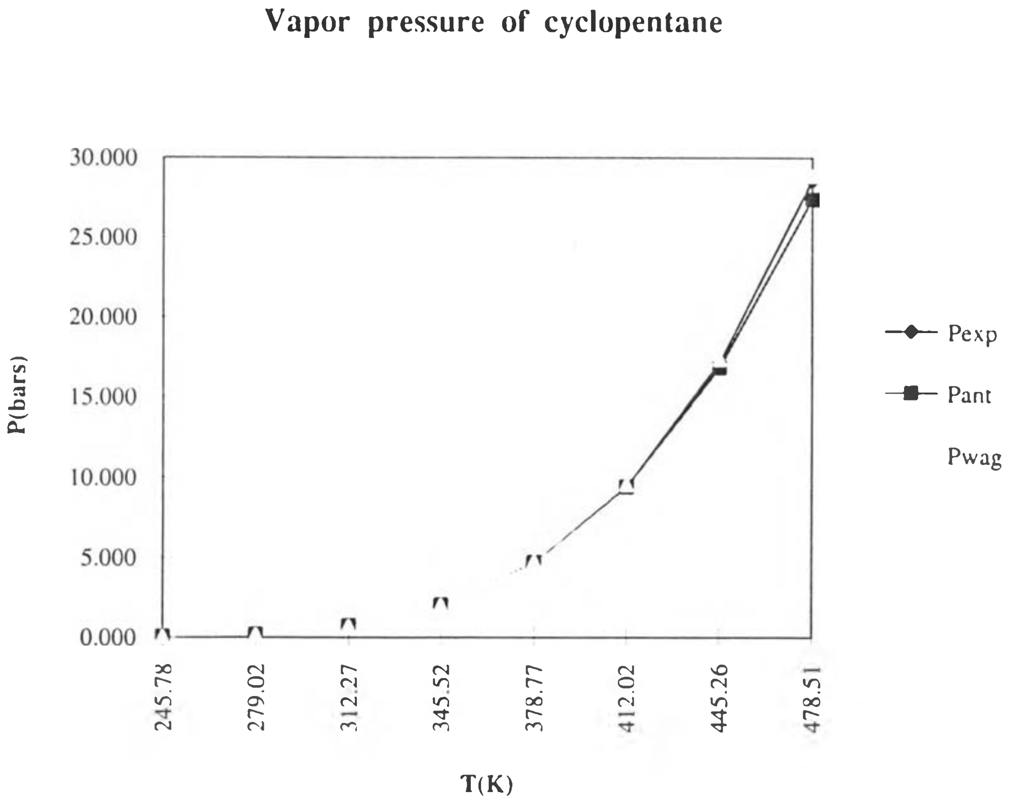

Figure 9.5 Comparison between calculated vapor pressure of cyclopentane and reference data

Equation	Tmin(K)	Tmax(K)
Antoine	280.15	380.15
Wagner	293	533.5

Range of temperature	Percent deviation (%)	
(K)	Antoine	Wagner
307.07-380.15	0.41	-
307.07 - 533.5	-	0.61
307.07 - 533.5	-1.8	0.61

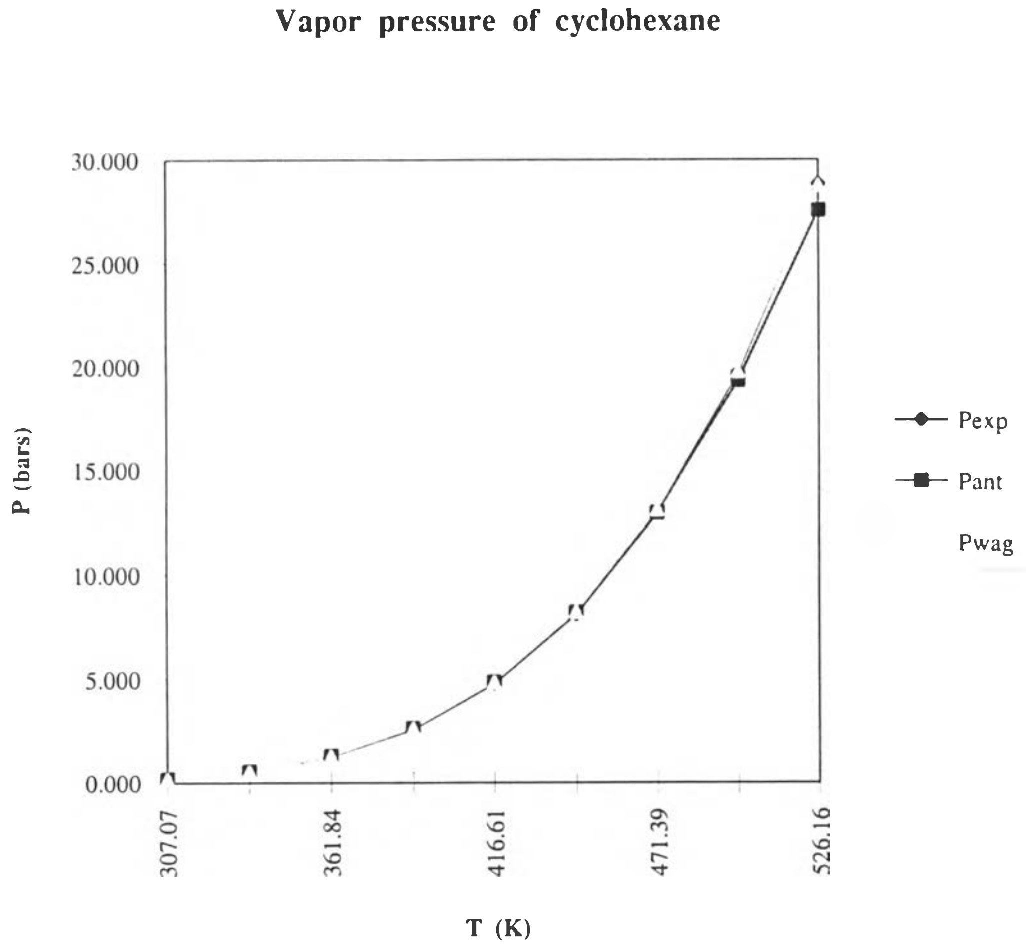

Figure 9.6 Comparison between calculated vapor pressure of cyclohexane and reference data

Equation	Tmin(K)	Tmax(K)
Antoine	120.15	182.15
Wagner	105	282.4

Range of temperature	Percent deviation (%)	
(K)	Antoine	Wagner
125.55 - 182.15	0.039	-
125.55 - 282.4	-	-2.47
125.55 - 282.4	-7.41	-2.47

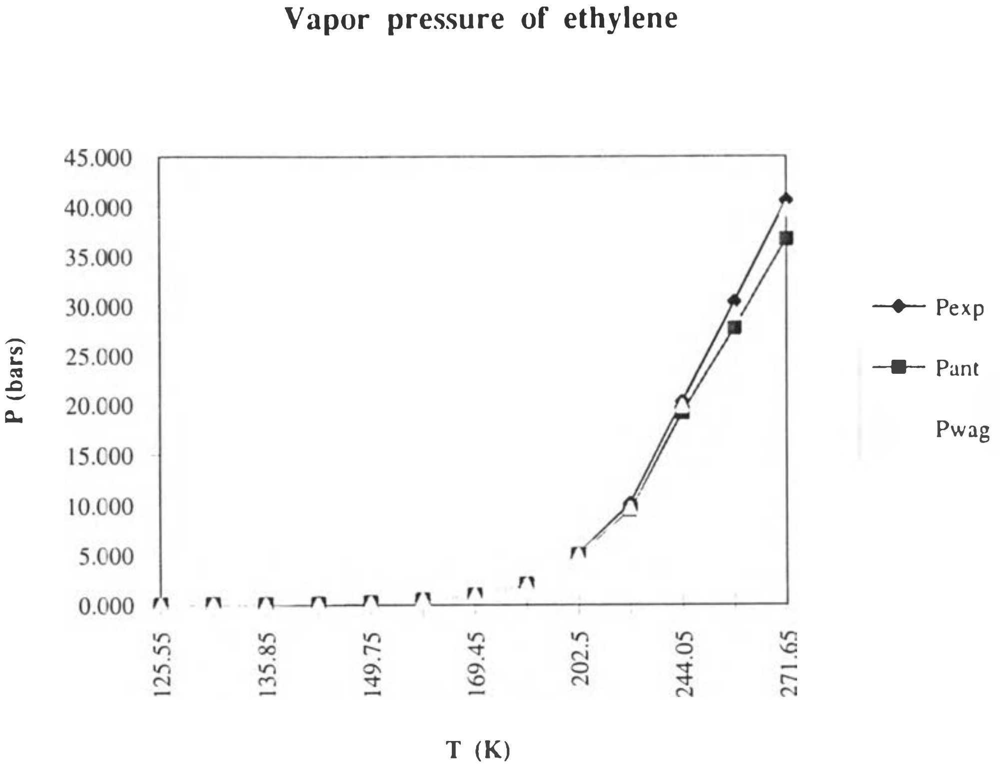

Figure 9.7 Comparison between calculated vapor pressure of ethylene and reference data

Equation	Tmin(K)	Tmax(K)
Antoine	240.15	360.15
Wagner	289	504

Range of temperature	Percent deviation (%)	
(K)	Antoine	Wagner
244.58- 360.15	0	-
289 - 466.97	-	-1.08
244.58 - 466.97	-2.43	-1.08

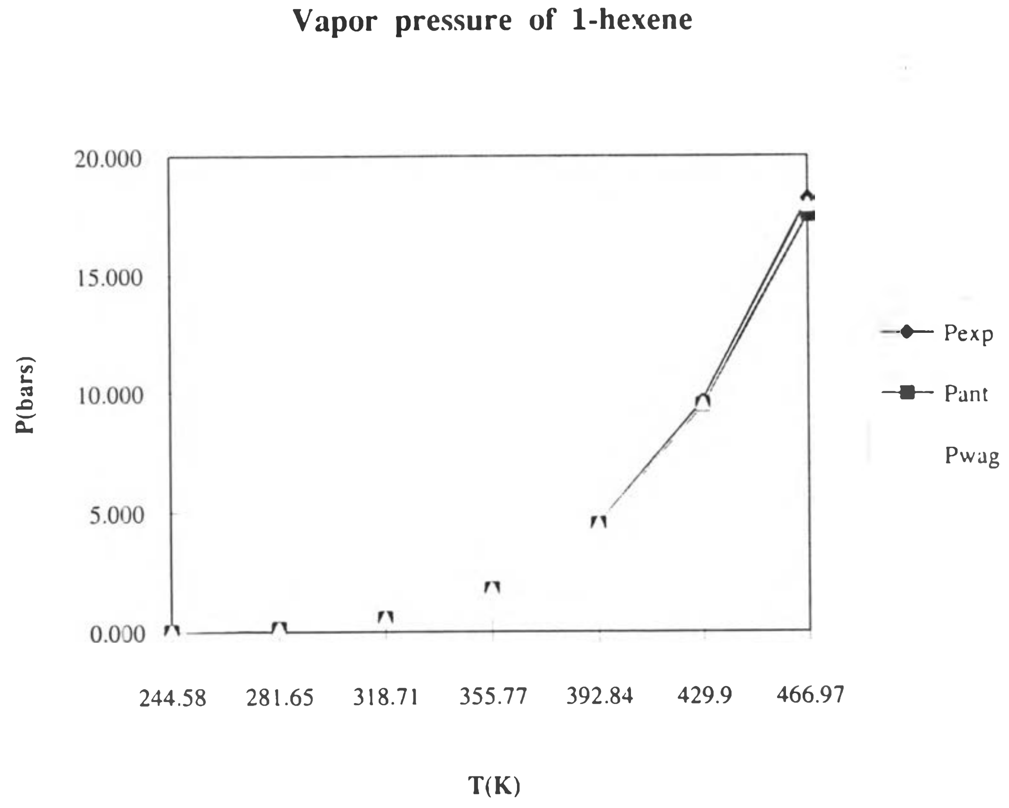

Figure 9.8 Comparison between calculated vapor pressure of 1-hexene and reference data

Equation	Tmin(K)	Tmax(K)
Antoine	280.15	377.15
Wagner	288	562.2

Range of temperature	Percent deviation (%)	
(K)	Antoine	Wagner
280.15 - 377.15	-0.78	-
288 - 545.45	-	-1.94
280.15-545.45	-5.21	-1.94

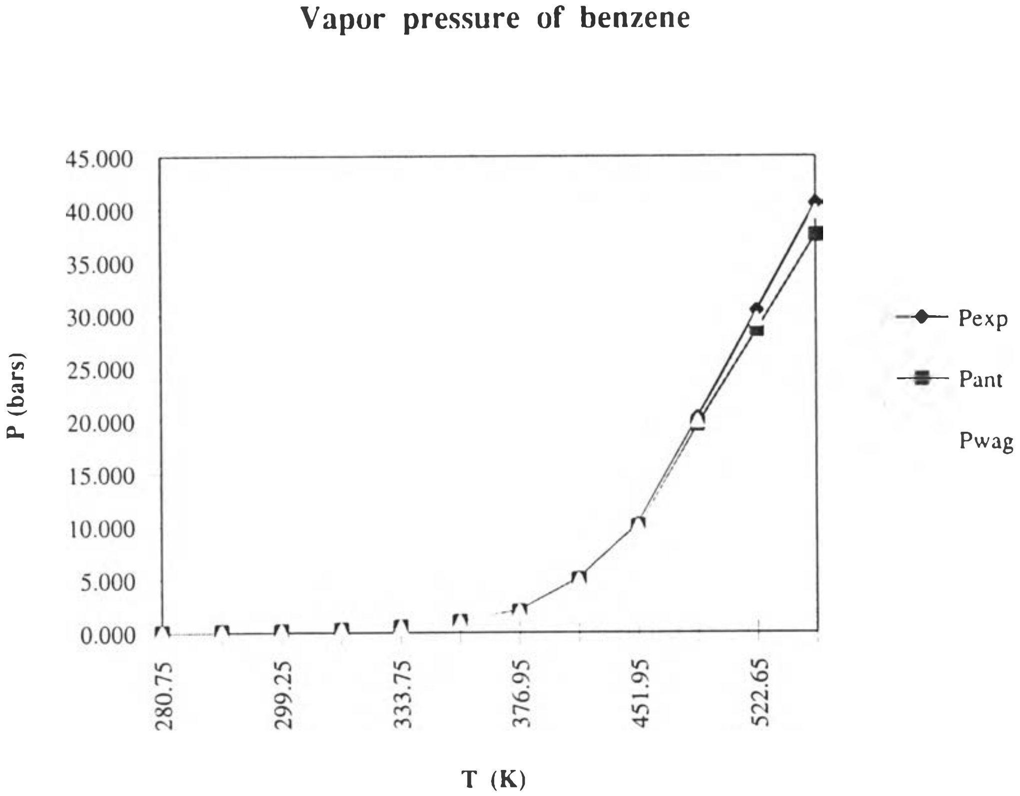

Figure 9.9 Comparison between calculated vapor pressure of benzene and reference data

Equation	Tmin(K)	Tmax(K)
Antoine	300.15	350.15
Wagner	330	617.2

Range of temperature	Percent deviation (%)	
(K)	Antoine	Wagner
309.86 - 350.15	2	-
330 - 573.27	-	-0.2
309.86 - 573.27	-0.33	0.33

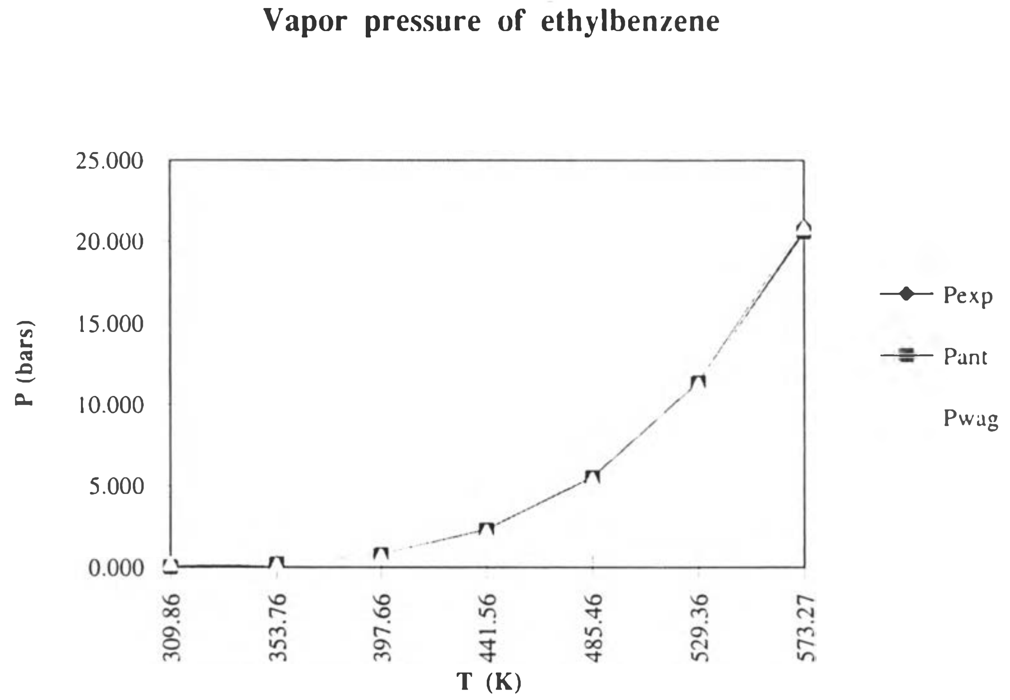

Figure 9.10 Comparison between calculated vapor pressure of ethylbenzene and reference data

9.1.2 Inorganic compounds

Two inorganic compounds are tested by this work. The results of testing are compared with the results derived from reference data.

Equation	Tmin(K)	Tmax(K)
Antoine	81.15	94.15
Wagner	84	150.8

Range of temperature	Percent deviation (%)	
(K)	Antoine	Wagner
83.78 - 94.15	0.033	-
84 - 144.15	-	-0.52
83.78 - 144.15	-4.75	-0.52

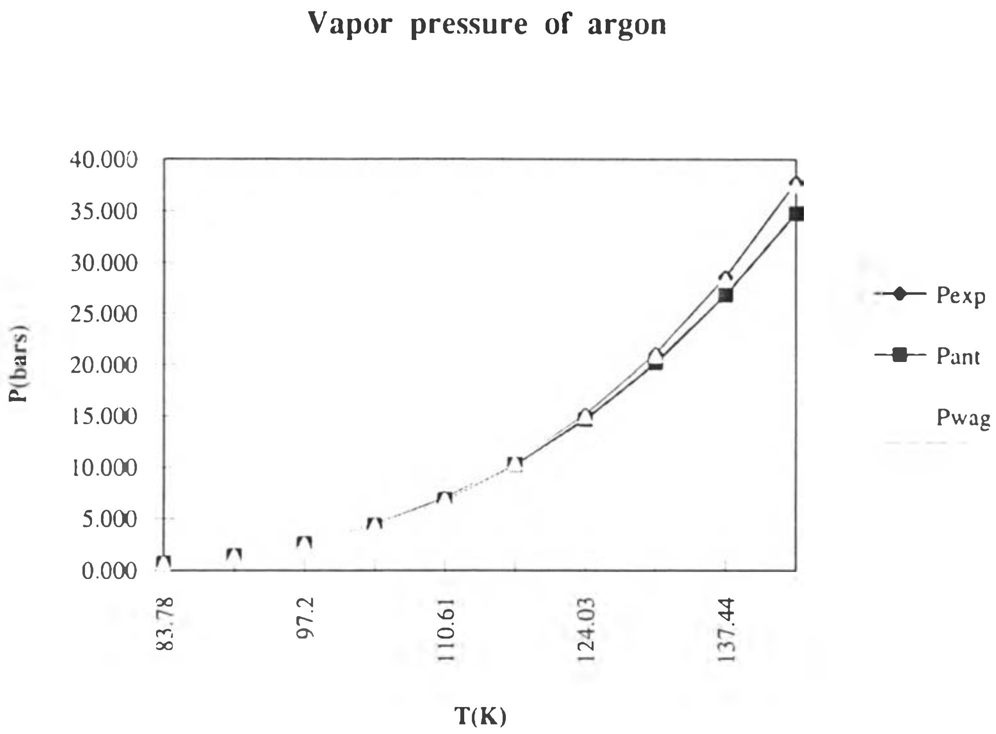

Figure 9.11 Comparison between calculated vapor pressure of argon and reference data

Equation	Tmin(K)	Tmax(K)
Antoine	172.15	264.15
Wagner	206	416.9

Range of temperature	Percent deviation (%)	
(K)	Antoine	Wagner
172.12 - 264.15	0.15	-
206 - 416.9	-	0.69
172.12 - 264.15	-4	0.78

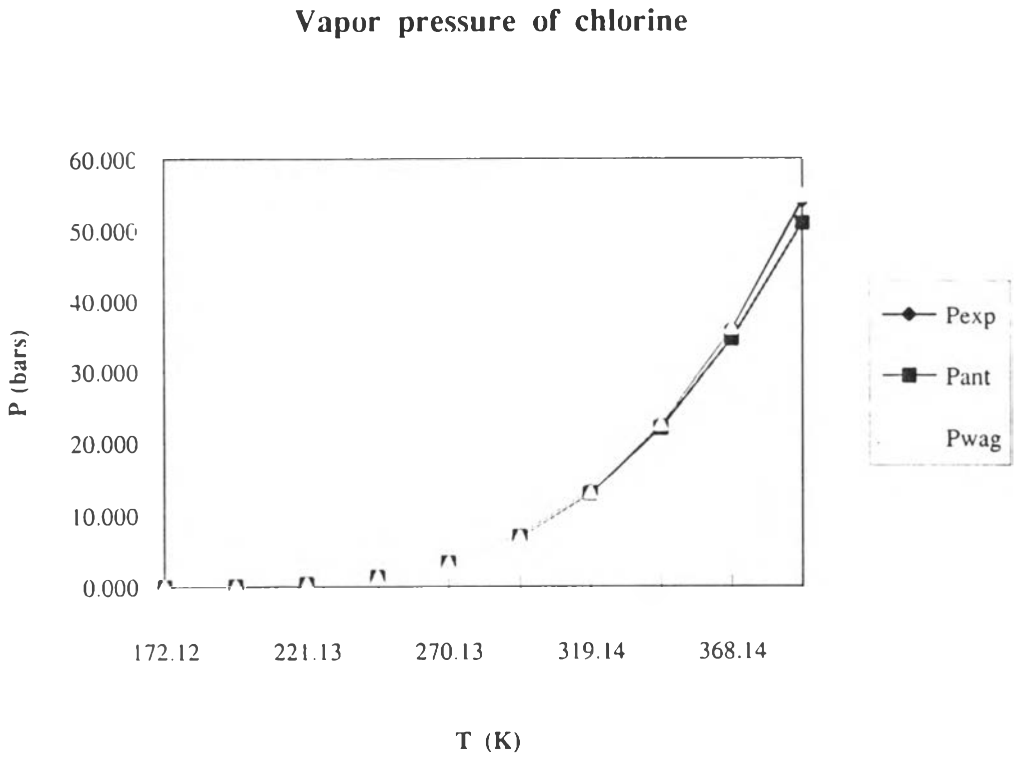

Figure 9.12 Comparison between calculated vapor pressure of chlorine and reference data

Figure 9.13 to Figure 9.14 show the results of estimation vapor pressure of alcohol compared with those from reference data.

Equation	Tmin(K)	Tmax(K)
Antoine	257.15	364.15
Wagner	288	512.6

Range of temperature	Percent deviation (%)	
(K)	Antoine	Wagner
257.15 - 364.15	0.69	-
288 - 478.88	-	0.64
242.99 - 478.88	1.27	0.64

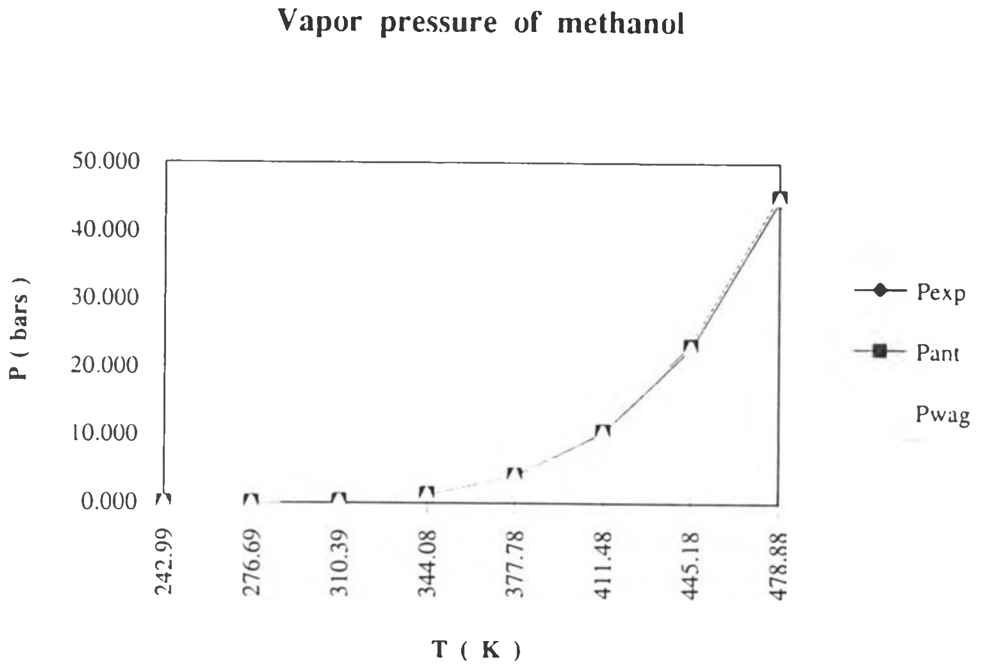

Figure 9.13 Comparison between calculated vapor pressure of methanol and reference data

Equation	Tmin(K)	Tmax(K)
Antoine	270.13	369.15
Wagner	293	513.9

Range of temperature	Percent deviation (%)	
(K)	Antoine	Wagner
270.3 - 369.15	0.24	-
293 - 480.53	-	-0.55
266.21 - 480.53	6.86	-0.55

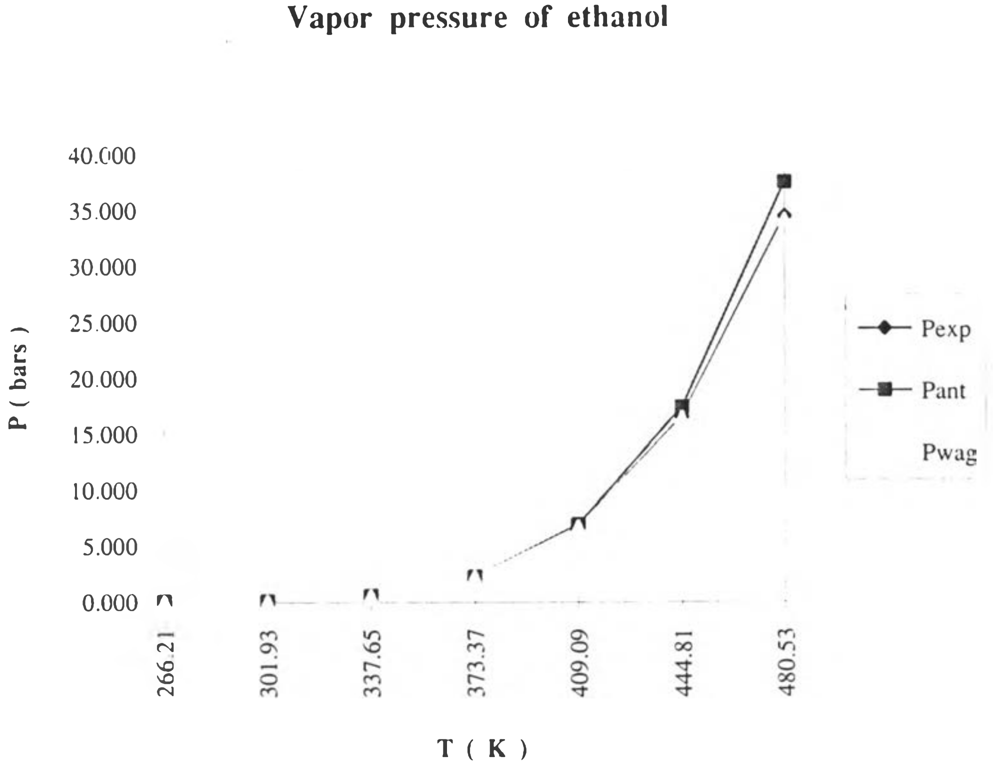

Figure 9.14 Comparison between calculated vapor pressure of ethanol and reference data

9.1.4 Halogenated hydrocarbon

Figure 9.15 to Figure 9.16 show the results of estimation vapor pressure of halogenated hydrocarbon compared with those from reference data.

Equation	Tmin(K)	Tmax(K)
Antoine	253.15	374.15
Wagner	250	556.4

Range of temperature	Percent deviation (%)	
(K)	Antoine	Wagner
253.15 - 374.15	0.134	-
250.33 - 525.75	-	-0.049
250.33 - 525.75	-1.51	-0.049

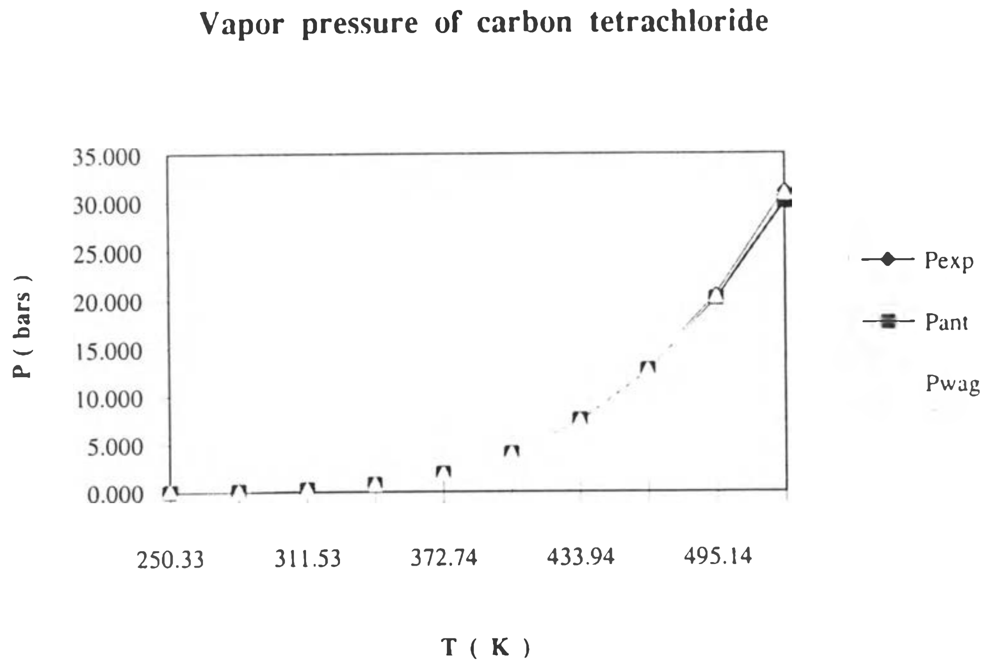

Figure 9.15 Comparison between calculated vapor pressure of carbon tetrachloride and reference data

Equation	Tmin(K)	Tmax(K)
Antoine	260.15	370.15
Wagner	215	536.4

Range of temperature	Percent deviation (%)	
(K)	Antoine	Wagner
260.15 - 370.15	-3.05	-
242.31-503.72	-	-3.23
242.31-503.72	-9.58	-3.23

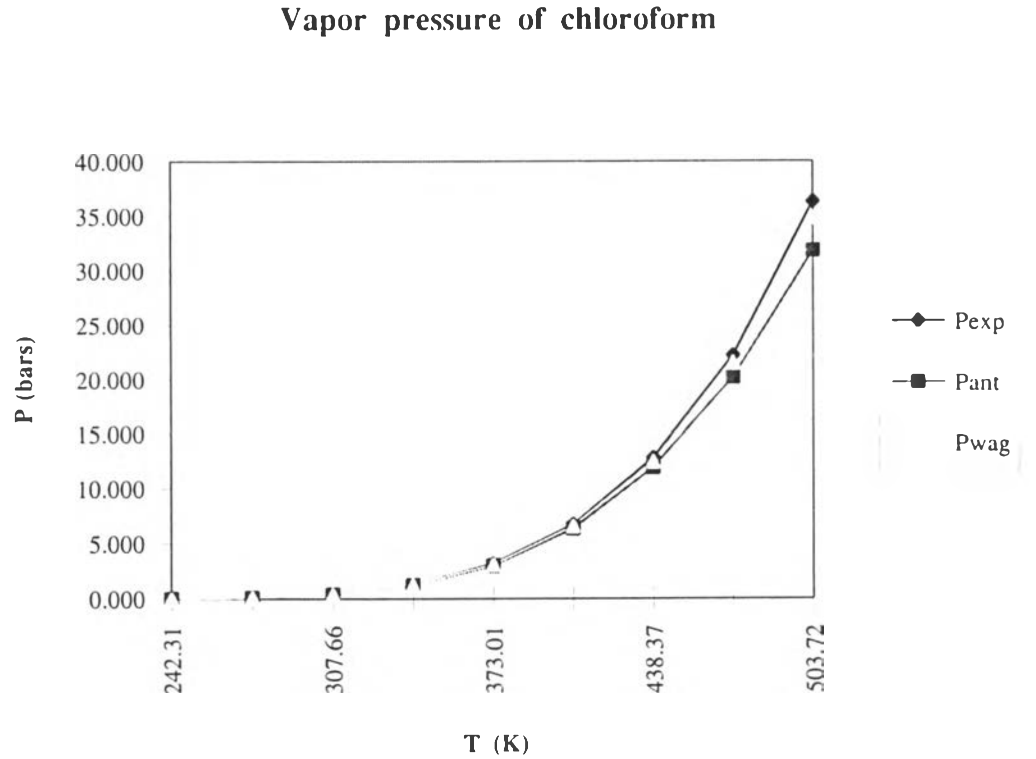

Figure 9.16 Comparison between calculated vapor pressure of chloroform and reference data

9.1.5 Miscellaneous compounds

Figure 9.17 to Figure 9.18 show the results of estimation vapor pressure of miscellaneous compounds compared with those from reference data.

Equation	Tmin(K)	Tmax(K)
Antoine	212.15	311.15
Wagner	200	430

Range of temperature	Percent deviation (%)	
(K)	Antoine	Wagner
212.15 - 311.15	1.18	-
204.73-405.01	-	-2.3
204.73-405.01	5.99	-2.3

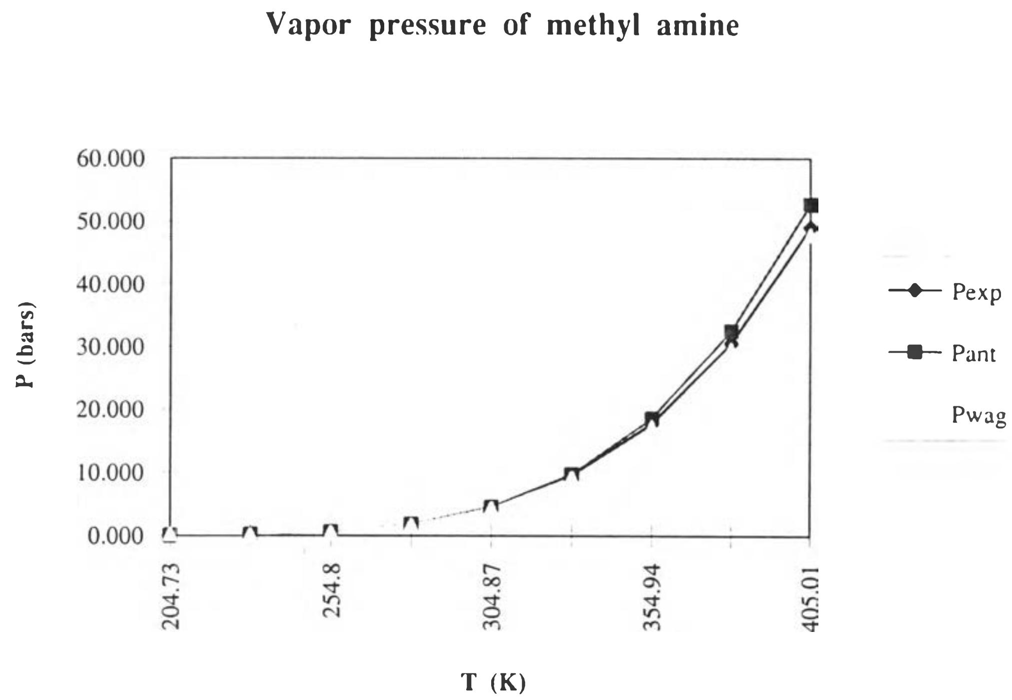

Figure 9.17 Comparison between calculated vapor pressure of methyl amine and reference data

Equation	Tmin(K)	Tmax(K)
Antoine	241.15	350.15
Wagner	259	508.1

Range of temperature	Percent deviation (%)	
(K)	Antoine	Wagner
244.4 - 350.15	-0.35	-
259 - 475.22	-	-0.3
244.4 - 475.22	-1.27	-0.057

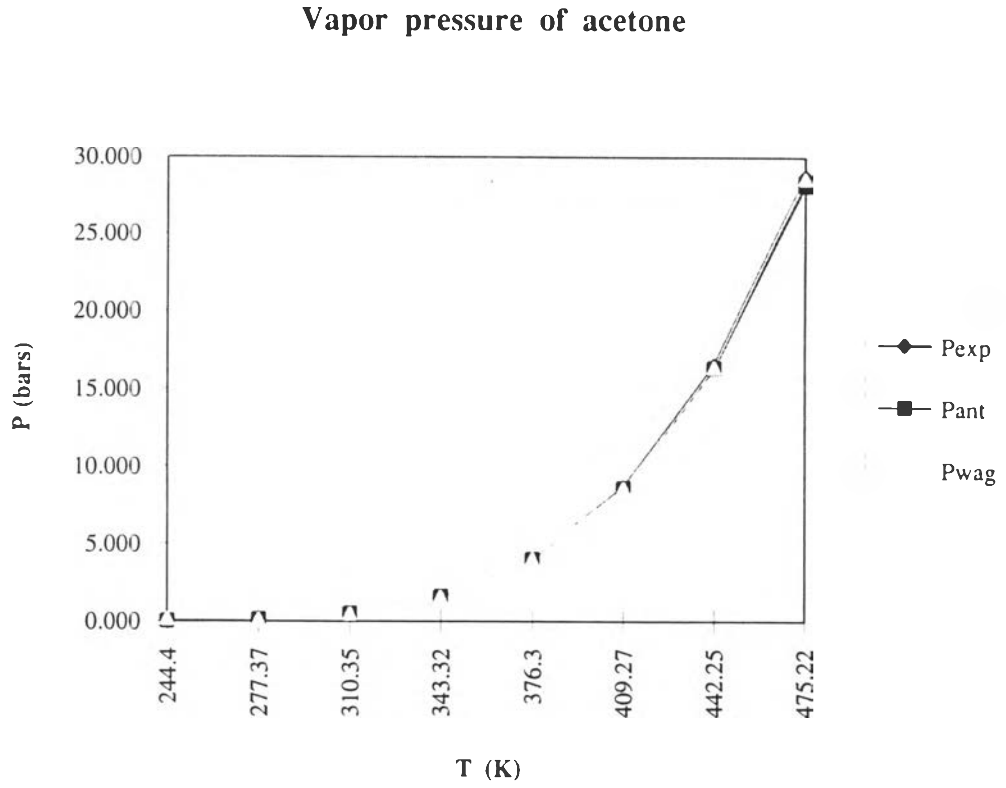

Figure 9.18 Comparison between calculated vapor pressure of acetone and reference data

Equation	Tmin(K)	Tmax(K)
Antoine	185.15	271.15
Wagner	184	408

Range of temperature	Percent deviation (%)	
(K)	Antoine	Wagner
203.83 - 271.15	-0.15	-
203.83-385.31	-	1.25
203.83-385.31	-7.43	1.25

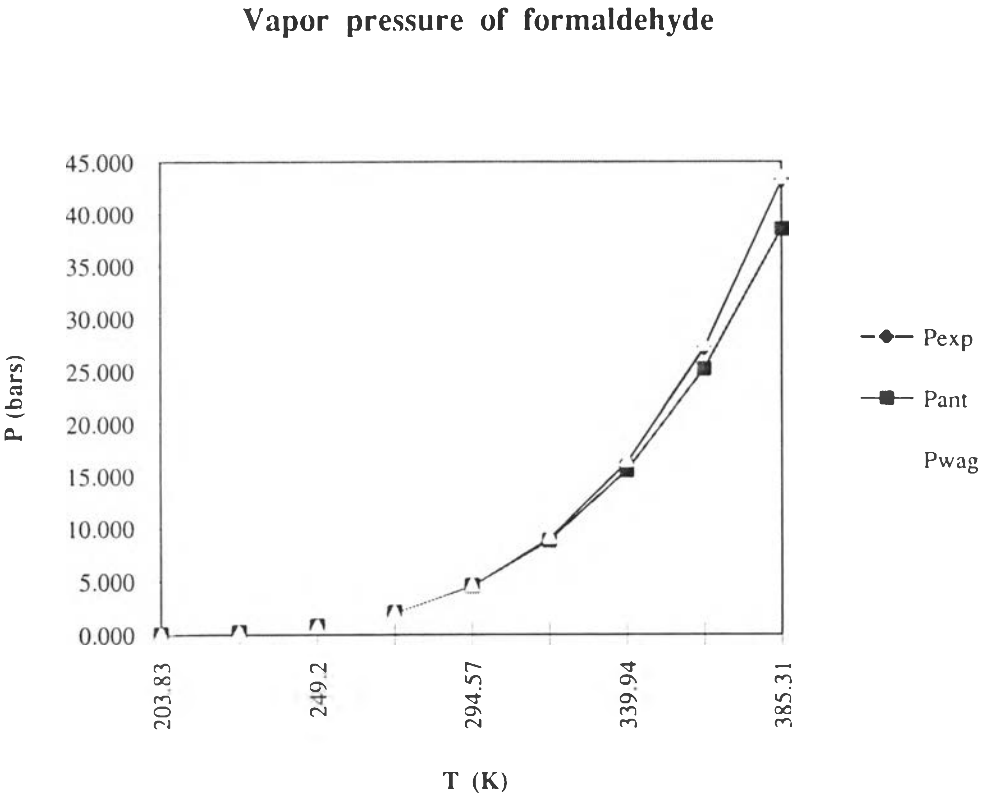

Figure 9.19 Comparison between calculated vapor pressure of formaldehyde and reference data

Table 9.2 to 9.6 show percent deviation of vapor pressure compared with reference data. Δant refers to percent deviation of vapor pressure estimated by Antoine equation between Tmin and Tmax of Antoine equation. Δwag refers to percent deviation of vapor pressure estimated by Wagner equation between Tmin and Tmax of Wagner equation. Δoant refers to percent deviation of vapor pressure all through range of temperature estimated by Antoine equation in an temperature range covering the range of both equations. Δowag refers to percent deviation of vapor pressure estimated by Wagner equation.

Table 9.2 Percent deviation for vapor pressure of hydrocarbons

Components	Δant	Δwag	Δoant	Δowag
1. ethane	-0.63	0.13	-4.37	0.24
2. n-butane	-0.34	1.40	-4.50	1.40
3. 2-methyl pentane	0.56	2.30	0.56	2.30
4. 2-methyl heptane	-5.88	2.82	-5.88	2.82
5. cyclopentane	0.11	1.07	-2.47	1.07
6. cyclohexane	0.41	0.61	-1.80	0.61
7. ethylene	0.04	-2.47	-7.41	-2.47
8. 1-hexene	0.00	-1.08	-2.43	-1.08
9. benzene	-0.78	-1.94	-5.21	-1.94
10. ethyl benzene	2.00	-0.20	-0.33	0.33
Average deviation (%)	-0.45	0.26	-3.38	0.34

Table 9.3 Percent deviation for vapor pressure of inorganic compounds

Components	Δant	Δwag	Δoant	Δowag
1. argon	0.09	-0.52	-4.75	-0.52
2. chlorine	0.15	0.69	-4.00	0.78
Average deviation (%)	0.09	0.08	-4.37	0.13

Table 9.4 Percent deviation for vapor pressure of alcohol

Components	Δant	Δwag	Δoant	Δowag
1. methanol	0.69	0.64	1.27	0.64
2. ethanol	0.24	-0.55	6.86	-0.55
Average deviation (%)	0.46	0.04	4.06	0.04

Table 9.5 Percent deviation for vapor pressure of halogenated hydrocarbon

Components	Δant	Δwag	Δoant	TPwag
1. carbontetrachloride	0.34	-0.05	-1.51	-0.05
2. chloroform	-3.05	-3.23	-9.58	-3.23
Average deviation (%)	-1.35	-1.64	-5.54	-1.64

Table 9.6 Percent deviation for vapor pressure of miscellaneous compounds

Components	Δant	Δwag	Δoant	Δowag
1. methyl amine	1.18	-2.30	5.99	-2.30
2. acetone	-0.35	-0.30	-1.27	-0.06
3. formaldehyde	-0.15	1.25	-7.43	1.25
Average deviation (%)	0.23	-0.45	-0.90	-0.37

Table 9.7 Conclusion of percent deviation of vapor pressure

Components	Δant	Δwag	Δoant	Δowag
1. Hydrocarbon	-0.45	0.26	-3.38	0.33
2. Inorganic compound	0.09	0.08	-4.37	0.13
3. Alcohol	0.46	0.04	4.06	0.04
4. Halogenated hydrocarbon	-1.35	-1.64	-5.54	-1.64
5. Miscellaneous	0.23	-0.45	-0.90	-0.37

From Table 9.7, the results show that both Wagner and Antoine equation are appropriate to predict vapor pressure for hydrocarbon, inorganic compound, and alcohol in a limited range of temperature, because its deviation is less than ±0.5 %. But estimation of vapor pressure by Wagner equation is comparatively better than that of Antoine equation. For halogenated hydrocarbon and miscellaneous compounds both Antoine and Wagner equations are also proper to estimate vapor pressure, even though the deviation is comparatively high (less than ±2%). For overall range of temperature, Wagner equation is appropriate to estimate vapor pressure for hydrocarbon, inorganic compound, and alcohol (the deviation is less than ±0.5%). For halogenated hydrocarbon and miscellaneous compounds, Wagner equation are also recommended to predict vapor pressure although the deviation is much higher (less than ±2%).

When Antoine equation is used to predict vapor pressure outside limited range of temperature, the values of vapor pressure are smaller than reference data because Antoine equation is modified from Clapeyon equation (equation 7-76). ΔHv and ΔZv of the equation are weak function of temperature near critical point and decrease with an increase in temperature. Wagner equation can predict over a wide range of temperature because the parameters in this equation are derived from experimental data over wide range of temperature. But it can be used at a reduced temperature of 0.5 up to critical point and extrapolations outside these range may lead to unacceptable results. It is also reported that Antoine equation should not be used above 2.0 to 2.7 bars (Robert C. Ried, John M. Prausnitz, and Bruce E. Poling, 1987).

9.2 HEAT OF VAPORIZATION

Heat of vaporization is predicted using Pitzer acentric factor correlation, Riedel, Chen, and Vetere equations. Heat of vaporization is predicted at normal boiling point shown in table 9.3 to 9.8. ΔHexp. (J/mol) refers to heat of vaporization from reference data (Sinnott,1983). HvR, HvV, HvC, HvP refer to heat of vaporization (J/mol) estimated by each method.

9.2.1 Hydrocarbons

Table 9.8 shows the results of estimation of heat of vaporization for hydrocarbons compared with reference data.

Table 9.8 Percent deviation of heat of vaporization of hydrocarbon

Compound	T (K)	ΔHexp.	HvR	HvV	HvC	HvP
1. Ethane	184.45	14717	14820.07	14749.28	14815.51	14755.48
2. N-butane	272.65	22408	22534.68	22476.38	22480.28	22238.64
3. 2-methyl pentane	333.35	27800	27886.85	27803.79	27745.68	27371.35
4. 2-methyl heptane	390.75	33829	33698.4	33436.05	33338.35	32703.69
5. Cyclopentane	322.35	27315	27311.68	27190.63	27244.18	26987.07
6. Cyclohexane	353.85	29977	29773.71	29667.26	29685.18	29418.96
7. Ethylene	169.35	13553	13529.81	13458.24	13527.22	13528.74
8. 1-hexene	336.55	28303	28512.5	28409.7	28349.16	27996.79
9. Benzene	353.25	30781	30596.01	30423.95	30507.14	30220.76
10.Ethylbenzene	409.25	35588	35832.35	35641.6	35571.21	35050.8
Deviation(%)			0.08	-0.38	-0.38	-1.51

9.2.2 Inorganic compounds

Table 9.9 shows the results of estimation of heat of vaporization of inorganic compounds compared with reference data.

Table 9.9 Percent deviation of heat of vaporization of inorganic compounds

Compound	T (K)	ΔHexp	HvR	HvV	HvC	HvP
1. Argon	87.25	6531	6493.01	6450.03	6486	6546.48
2. Chlorine	238.65	20432	20565.47	20331.95	20601.19	20484.18
3. Nitrogen	77.35	5581	5577.69	5576.30	5583.01	5599.33
4. Nitric oxide	121.35	13816	13638.24	13327.26	13301.78	12902.17
5. Ammonia	239.65	23362	23938.92	23551.15	23969.44	23532.46
Deviation(%)			0.70	-0.70	0.31	-0.94

9.2.3 Alcohol

Table 9.10 shows the results of estimation of heat of vaporization of alcohol compared with reference data.

Table 9.10 Percent deviation of heat of vaporization of alcohol

Compound	T (K)	ΔHexp	HvR	HvV	HvC	HvP
1. Methanol	337.75	35278	38244.22	37394.28	37509.32	36506.99
2. Ethanol	351.45	38770	40258.32	39230.55	39064.52	37942.09
3. N-butanol	390.85	43124	41817.99	40898.41	40606.08	39505.99
4. Isobutanol	380.95	42077	40581.43	39691.66	39399.18	38337.49
5. 1-hexanol	430.15	48567	46525.60	45360.93	44953.20	41252.64
Deviation(%)			-0.19	-2.52	-3.02	-6.88

9.2.4 Halogenated hydrocarbon

Table 9.11 shows the results of estimation of heat of vaporization for halogenated hydrocarbon compared with reference data.

Table 9.11 Percent deviation of heat of vaporization of halogenated hydrocarbon

Compound	T (K)	ΔHexp	HvR	HvV	HvC	HvP
1. Carbontetrachloride	349.65	30019	29651.01	29517.13	29580.53	29293.77
2. Chloroform	334.25	29726	29417.77	29219.58	29337.41	29173.2
3. Ethyl chloride	285.35	24702	24719.18	24565.88	24667.38	24395.49
4. Vinyl chloride	259.75	20641	21696.34	21577.45	21676.8	20974.56
5. Chlorobenzene	404.85	36572	35535.92	35336.06	35372.46	34918.01
Deviation (%)			-0.452	-1.019	-0.724	-2.051

9.2.5 Miscellaneous compounds

Table 9.12 shows the results of estimation of heat of vaporization for micellaneous compounds compared with reference data.

Table 9.12 Percent deviation of heat of vaporization of miscellaneous compounds

Compound	T (K)	ΔHexp	HvR	HvV	HvC	HvP
1. Methyl amine	266.75	26000	25812.32	25502.86	25707.76	25314.24
2. Acetone	329.35	29140	30077.14	29847.02	29859.07	29395.33
3. Formaldehyde	253.95	23027	23839.89	23598.25	23747.12	23039.49
4. Phenol	454.95	45636	46727.77	46025.26	46077.98	45055.96
5. Acetonitrile	354.75	31401	33035.26	32747.46	32755.44	32193.16
Deviation (%)			2.76	1.62	1.89	-0.13

Table 9.13 Conclusion of percent deviation of heat of vaporization

Compounds	%Riedel	%Vetere	%Chen	%Pitzer
1. Hydrocarbon	0.08	-0.38	-0.38	-1.51
2. Inorganic compound	0.07	-0.70	0.31	-0.94
3. Alcohol	-0.19	-2.52	-3.02	-6.88
4. Halogenated Hydrocarbon	-0.45	-1.02	-0.72	-2.05
5. Miscellaneous	2.76	1.62	1.89	-0.13

From Table 9.13, the results of prediction heat of vaporization of hydrocarbon, inorganic compound, alcohol and halogenated hydrocarbon is shown and summarized percent deviation of Riedel method is less than ±1%, percent deviation of Vetere method less than -3.1%, percent deviation of Chen method less than -3%, percent deviation of Pitzer acentric factor correlation method less than ±7%. For miscellaneous compounds, percent deviation of Riedel method is less than 3%, percent deviation of Vetere method less than 2%, percent deviation of Chen method less than 2%, percent deviation of Pitzer acentric factor correlation method less than 1%.

The results show that Riedel method is appropriate to estimate heat of vaporization for hydrocarbon, inorganic compound, alcohol, and halogenated hydrocarbon because percent deviation is less than ±1%. But Pitzer acentic factor correlation is proper for miscellaneous compounds (the deviation less than ±1%). Chen and Vetere method yield approximately the same deviation with respect to many types of compounds because both methods are derived from the same equation (equation 6-79). In analytical form, heat of vaporization is approximated by equation (6-80). Thomson and Braun (1964) suggested Pitzer method for predicting heat of heat of vaporization of hydrocarbons.

9.3 COMPRESSIBILITY FACTOR

To test pediction of performance of this program to predict compressibility factor of vapor and liquid phases, the results of prediction are compared with the results calculated by HYSIM package. Saturated condition at bubble point-pressure is selected for testing compressibility factor.

9.3.1 Pure component

Three compounds are randomly selected for testing the prediction of this program (ethane, n-butane, nitrogen). The results of testing are shown in Figure 9.20 to 9.25.

For gas phase

Compressibility factor is tested at bubble point pressure for various temperature. Figure 9.20 to 9.22 show the values of compressibility factor in gas phase which is calculated by Soave-Redlich-Kwong (SRK) equation compared with those from HYSIM.

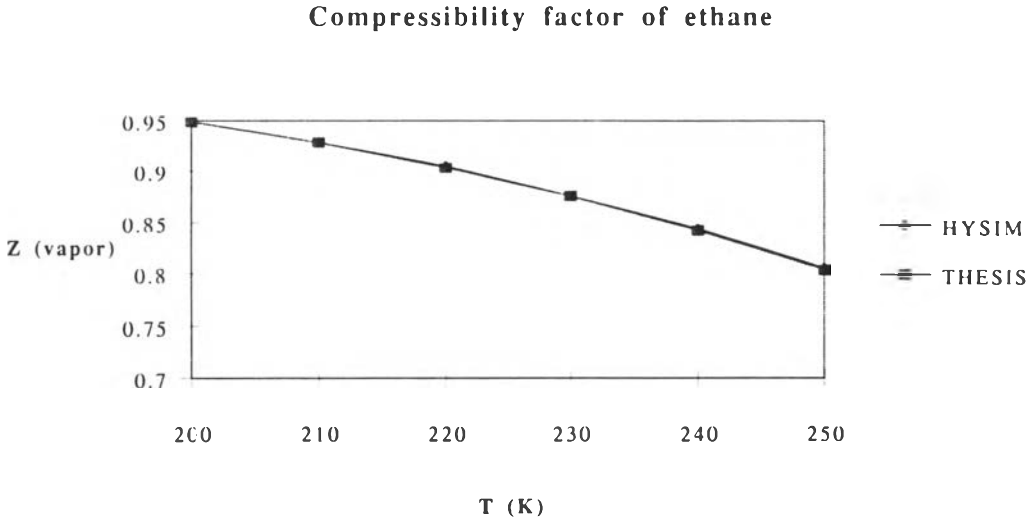

Figure 9.20 Comparison between the calculated values of compressibility factor of pure ethane in gas phase using SRK equation and those from HYSIM (at bubble-point pressure)

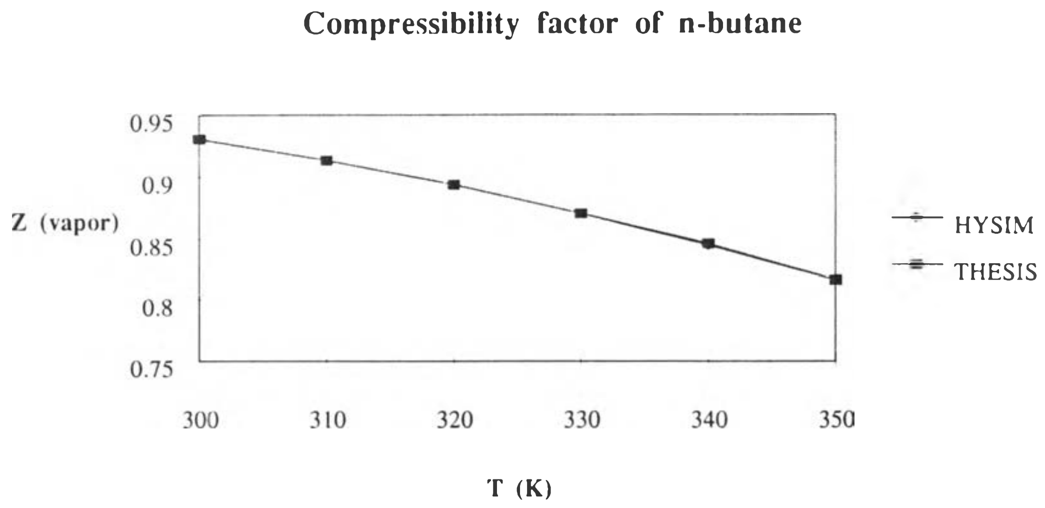

Figure 9.21 Comparison between the calculated values of compressibility factor of pure n-butane in gas phase using SRK equation and those from HYSIM (at bubble-point pressure)

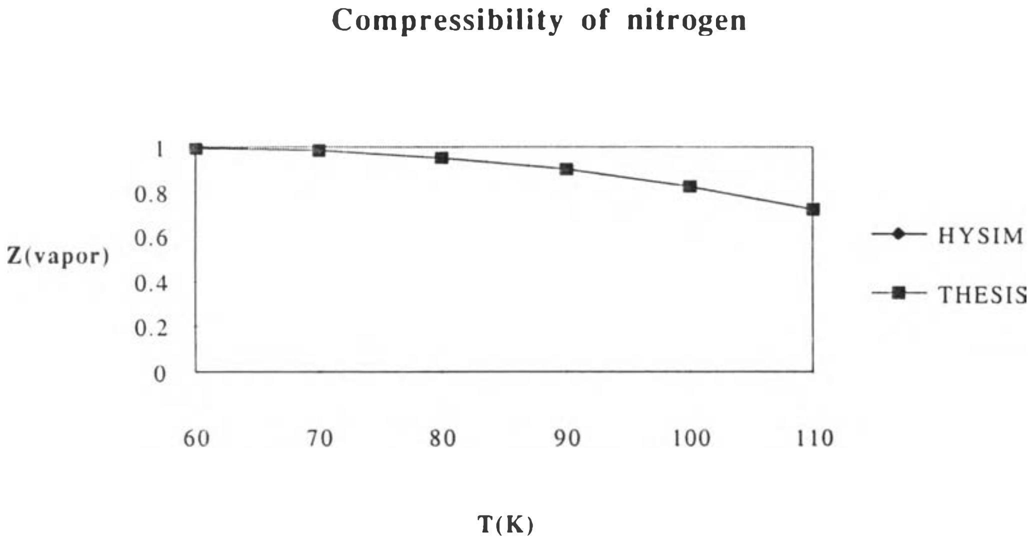

Figure 9.22 Comparison between the calculated values of compressibility factor of pure nitrogen in gas phase using SRK equation and those from HYSIM (at bubble-point pressure)

Figure 9.23 to 9.25 show the compressibility factor in gas phase which is calculated by Peng-Robinson (PR) equation, compared with those from HYSIM

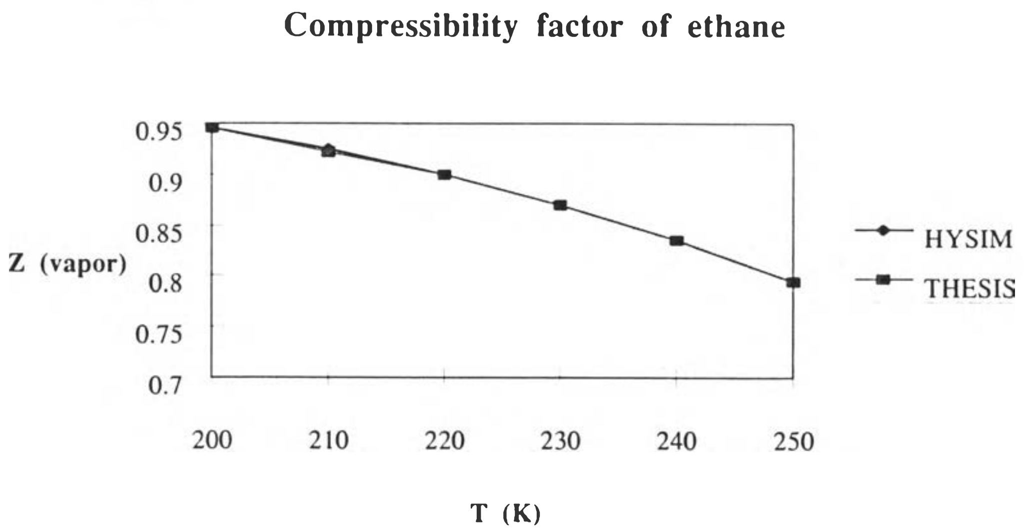

Figure 9.23 Comparison between the calculated values of compressibility factor of pure ethane in gas using PR equation and those from HYSIM (at bubble-point pressure)

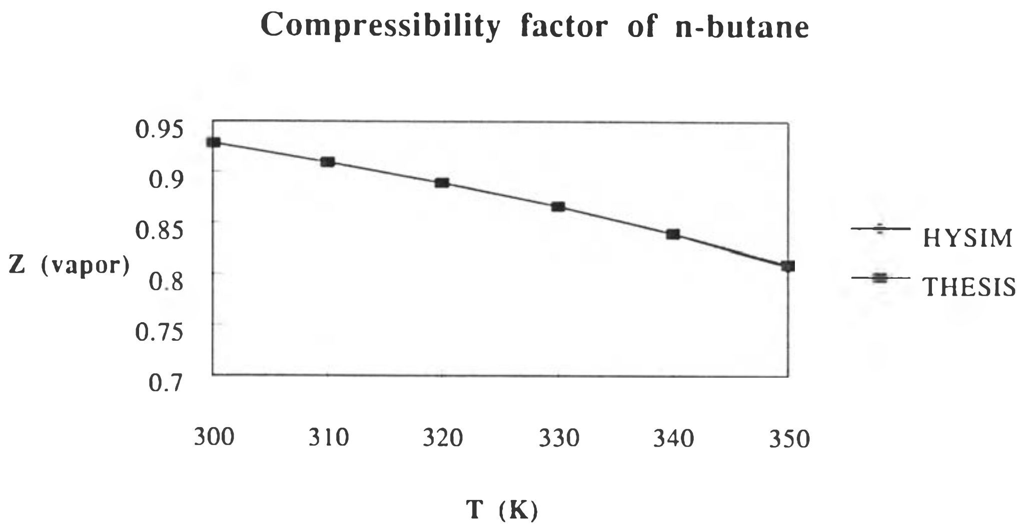

Figure 9.24 Comparison between the calculated values of compressibility factor of pure n-butane in gas phase using PR equation and those from HYSIM (at bubble-point pressure)

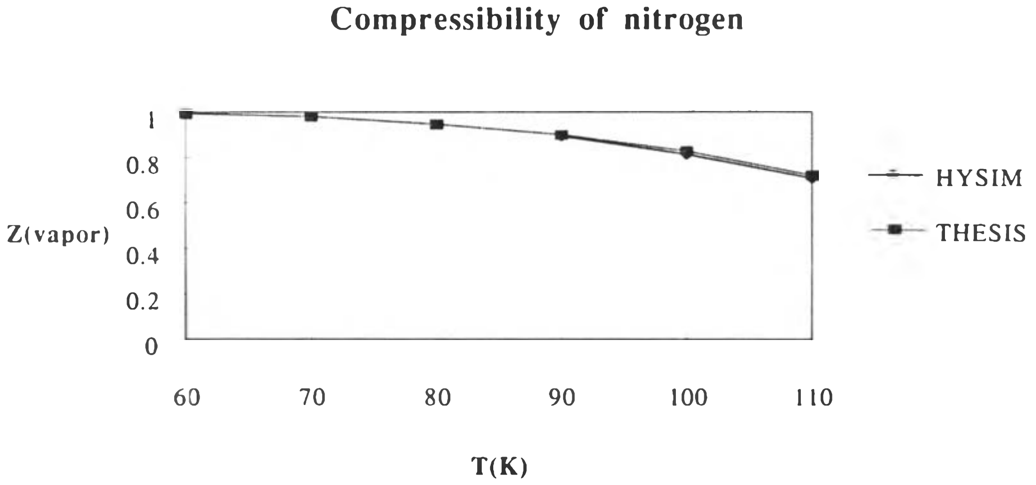

Figure 9.25 Comparison between the calculated values of compressibility factor of pure nitrogen in gas phase using PR equation and those from HYSIM (at bubble-point pressure)

Table 9.14 shows percent deviation of compressibility factor calculated by SRK and PR equations.

Table 9.14 Percent deviation of pure gas compressibility factor calculated by SRK and PR equations in comparison with results of HYSIM using SRK and PR equations

Compounds	Deviation (SRK)	Deviation (PR)
1. ethane	-0.180	-0.056
2. n-butane	0.0197	0.024
3. nitrogen	-0.0514	0.729

$$\text{Deviation} = \left(\frac{Zth - Zhy}{Zhy}\right) * 100$$

Zhy refers to compressibility factor computed by HYSIM.

Zth refers to compressibility factor computed by this work.

Table 9.15 shows percent the deviation of compressibility factor in gas phase which is calculated by Redlich-Kwong (RK) equation.

Table 9.15 Percent deviation of pure gas compressibility factor calculated by RK equation in comparison with results of HYSIM using SRK and PR equations

Compounds	Deviation (SRK)	Deviation (PR)
1. ethane	0.308	0.988
2. n-butane	0.957	1.728
4. nitrogen	-0.08	0.702

$$\text{Deviation} = \left(\frac{Zth - Zhy}{Zhy}\right) * 100$$

Zhy refers to compressibility factor computed by HYSIM with SRK or PR equations

Zth refers to compressibility factor computed by RK in this program.

For liquid phase

Figure 9.26 to 9.28 show the values of compressibility factor in liquid phase which is calculated by SRK equation compared with those values from HYSIM. Compressibility factor is tested at bubble point pressure at various temperature.

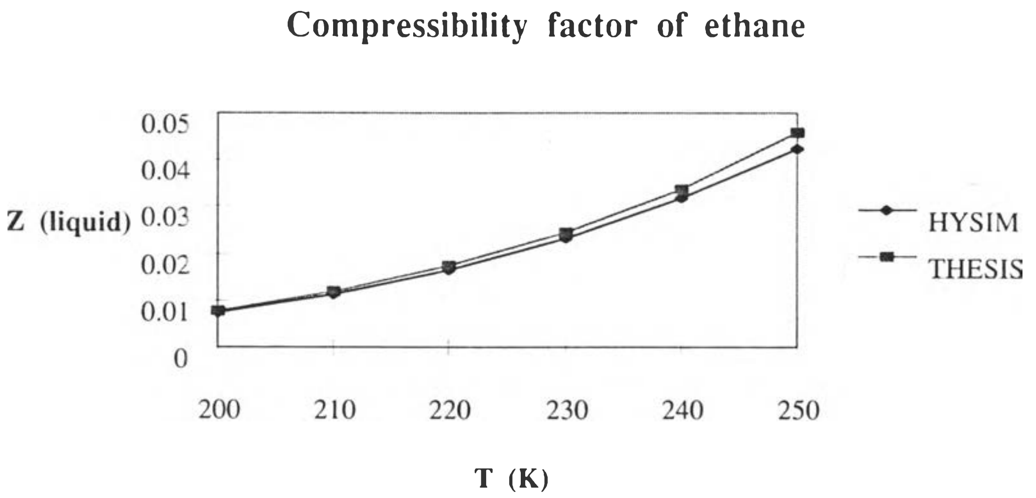

Figure 9.26 Comparison between the calculated values of compressibility factor of pure ethane in liquid phase using SRK equation and those from HYSIM (at bubble-point pressure)

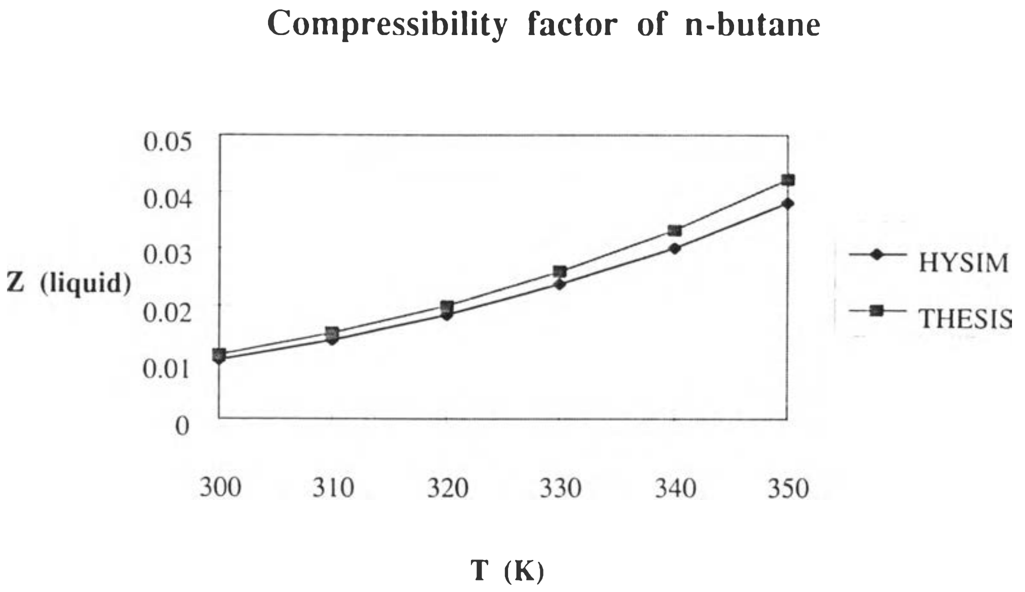

Figure 9.27 Comparison between the calculated values of compressibility factor of pure n-butane in liquid phase using SRK equation and those from HYSIM (at bubble-point pressure)

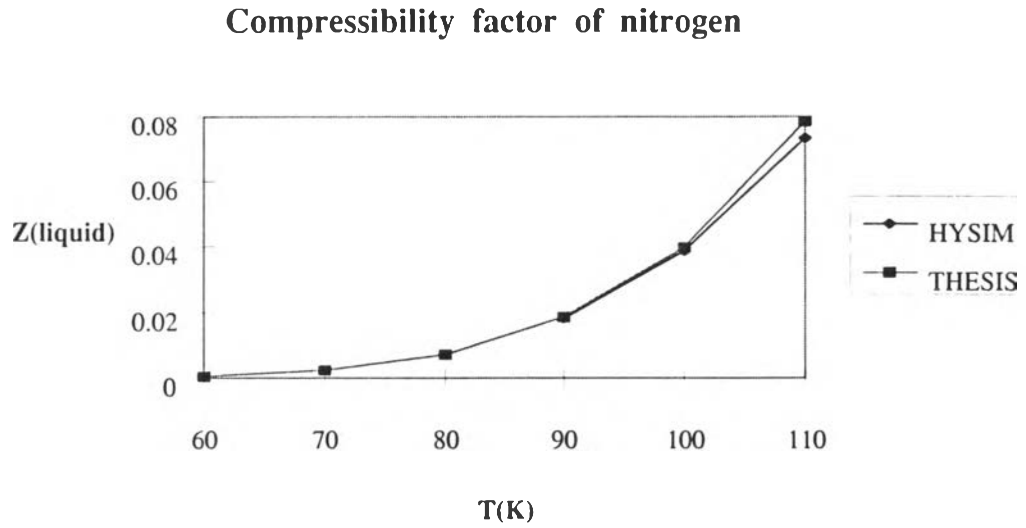

Figure 9.28 Comparison between the calculated values of pure nitrogen in liquid phase using SRK equation and those from HYSIM (at bubble-point pressure)

Figure 9.29 to 9.31 show the compressibility factor of liquid phase which is calculated by Peng-Robinson (PR) equation.

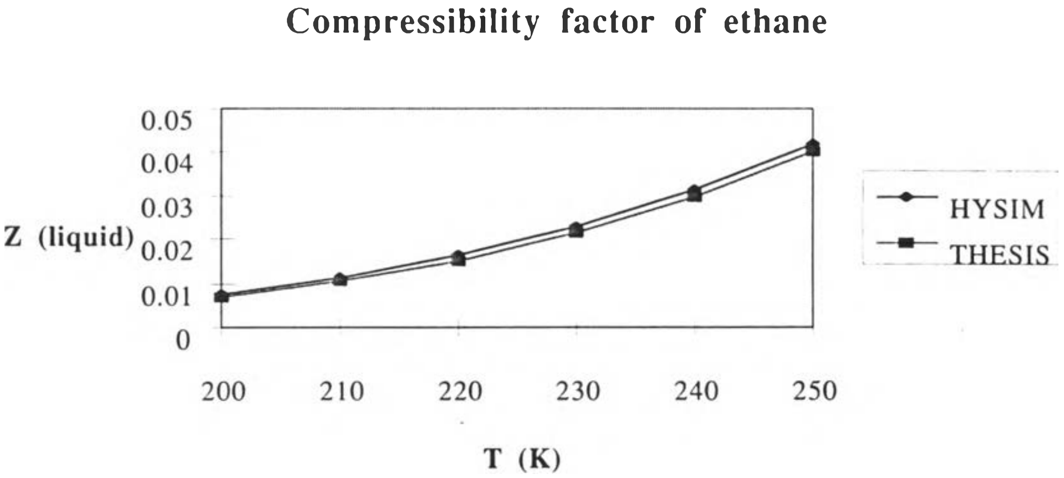

Figure 9.29 Comparison between the calculated values of compressibility factor of pure ethane in liquid phase using PR equation and those from HYSIM (at bubble-point pressure)

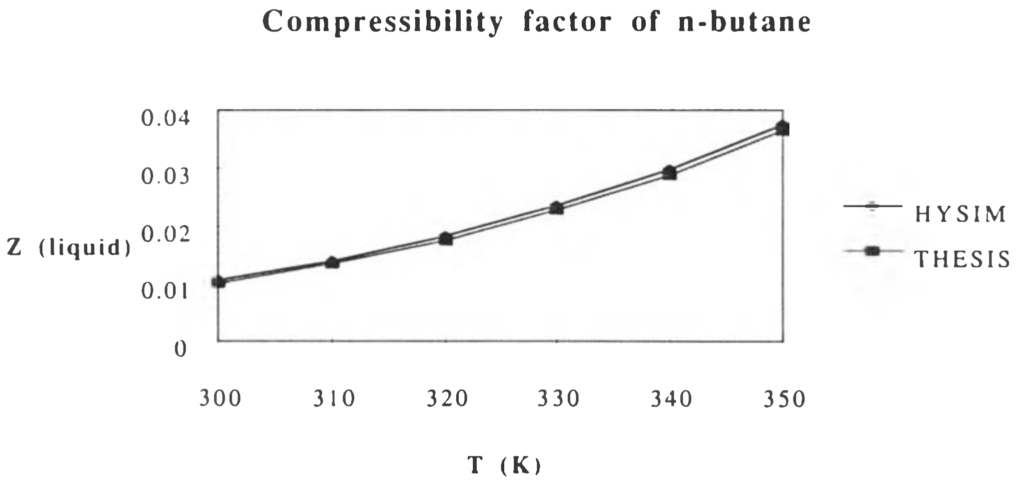

Figure 9.30 Comparison between the calculated values of compressibility factor of pure n-butane in liquid phase using PR equation and those from HYSIM (at bubble-point pressure)

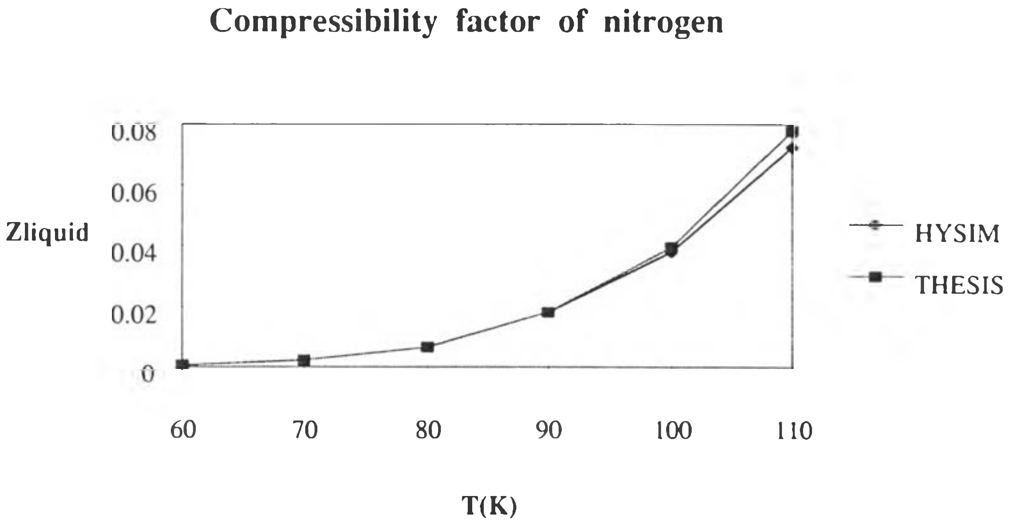

Figure 9.31 Comparison between the calculated values of compressibility factor of pure nitrogen in liquid phase using PR equation and those from HYSIM (at bubble-point pressure)

Table 9.16 shows the conclusion of percent deviation of compressibility factor in liquid phase which is calculated by Soave and Peng-Robinson equations.

Table 9.16 Percent deviation of compressibility of pure component in liquid phase calculated by SRK and PR equations in compaison with results of HYSIM using SRK and PR equations

Compounds	Deviation (SRK)	Deviation (PR)
1. ethane	6.700	-5.600
2. n-butane	9.504	-3.490
4. nitrogen	5.259	5.181

$$\text{Deviation} = \left(\frac{Zth - Zhy}{Zhy} \right) * 100$$

Zhy refers to compressbility factor computed by HYSIM.

Zth refers to compressibility factor computed by this program.

For pure component in gas phase

From Table 9.14, SRK equation can predict compressibility factor fairly well when it is compared with results of HYSIM. The deviation of prediction is less than ± 0.5 %. PR equation can estimate compressibility fairly well when it is compared with results of HYSIM. The deviation is approximate ± 1 %. From Table 9.15, Redlich-Kwong equation has percent deviation less than ± 1 % when it is compared with results using SRK equation of HYSIM. Percent deviation is less than ± 2 % when it is compared with results using PR equation of HYSIM. Therefore SRK and PR equations are more accurate to predict compressibility factor than Redlich-Kwong equation because both SRK and PR equations use third parameter(acentric factor) for calculating compressibility factor.

Acentric factor is an indicator of the nonsphericity of a molecule's force field; for example, a value of acentric factor is equal to zero denoting rare-gas spherical symmetry. Deviations from simple-fluid behavior are evident when acentric factor is greater than zero.

For pure component in liquid phase

From Table 9.16, for hydrocarbon, SRK equation can estimate compressibility factor fairly well when it is compared with those from HYSIM and percent deviation is less than +10%. PR equation can predict compressibility factor fairly well. The percent deviation is less than -6%. For inorganic compounds, SRK and PR equations can predict compressibility factor fairly well and percent deviation is less than 5.5 % when it is compared with those from HYSIM.

The results show that both SRK and PR equations are more accurate to predict compressibility factor of pure component in gas phase than compressibility of pure component in liquid phase because SRK and PR equations are developed from the relation of PVT data in vapor phase.

9.3.2 Multicomponent

Two mixtures are tested at bubble point pressure for various temperature.

For gas phase

Figure 9.32 to 9.33 show the values of compressibility factor which is calculated by SRK and PR equations compared with those values from HYSIM for multicomponent in gas phase

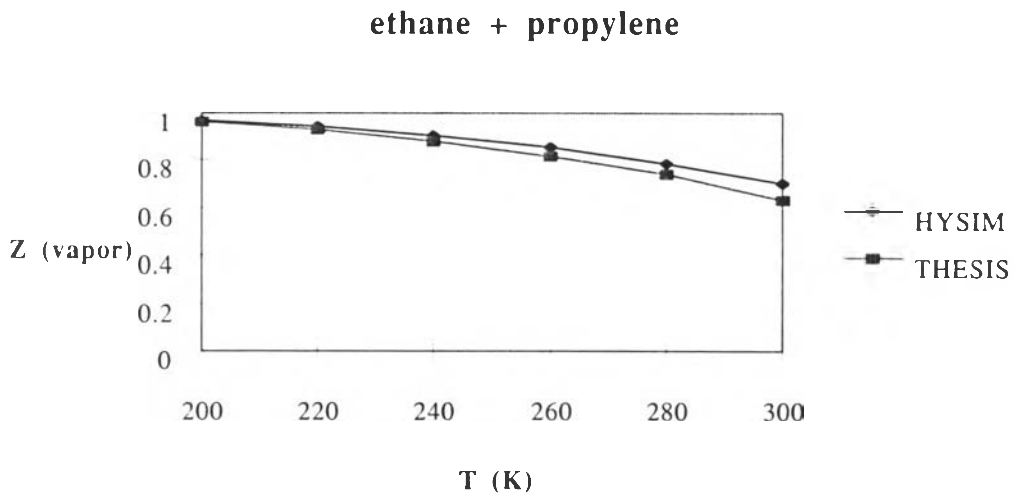

Figure 9.32 Comparison between the calculated values of compressibility factor of ethane and propylene in gas phase using SRK equation and those from HYSIM (at bubble-point pressure)

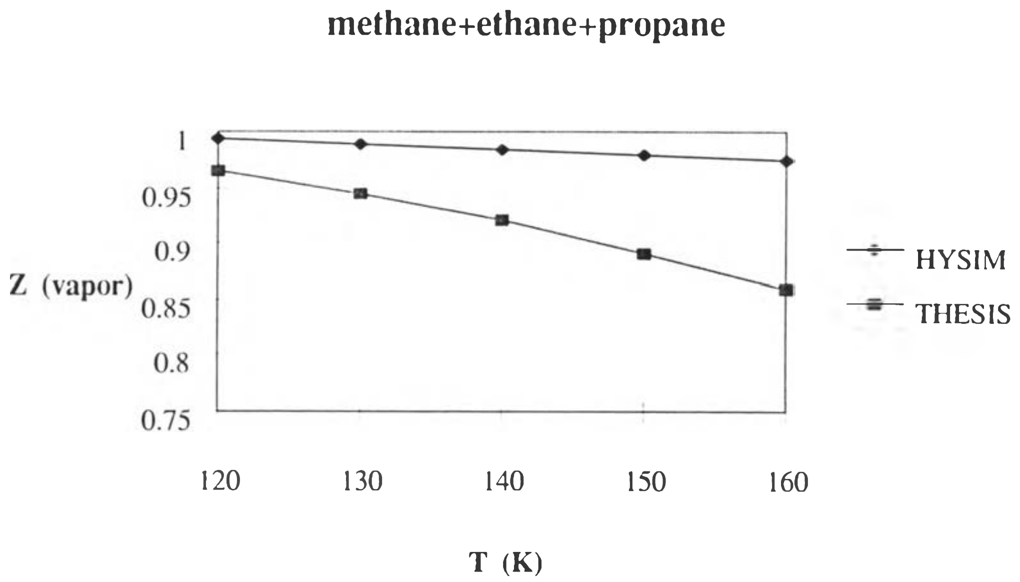

Figure 9.33 Comparison between the calculated values of compressibility factor of methane, ethane, and propane in gas phase using SRK equation and those from HYSIM (at bubble-point pressure)

Figure 9.34 to 9.35 show the compressibility factor in gas phase for multicomponent which is calculated by PR equation.

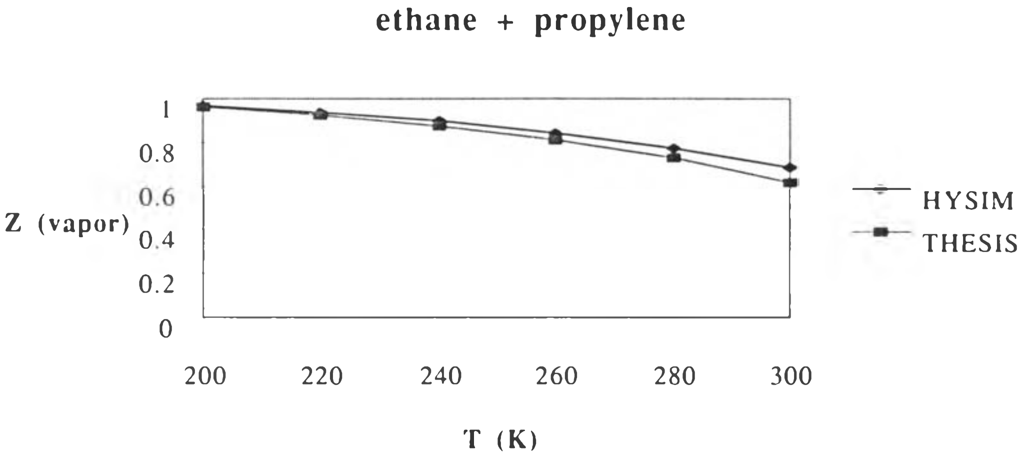

Figure 9.34 Comparison between the calculated values of compressibility factor of ethane and propylene in gas phase using PR equation and those from HYSIM (at bubble-point pressure)

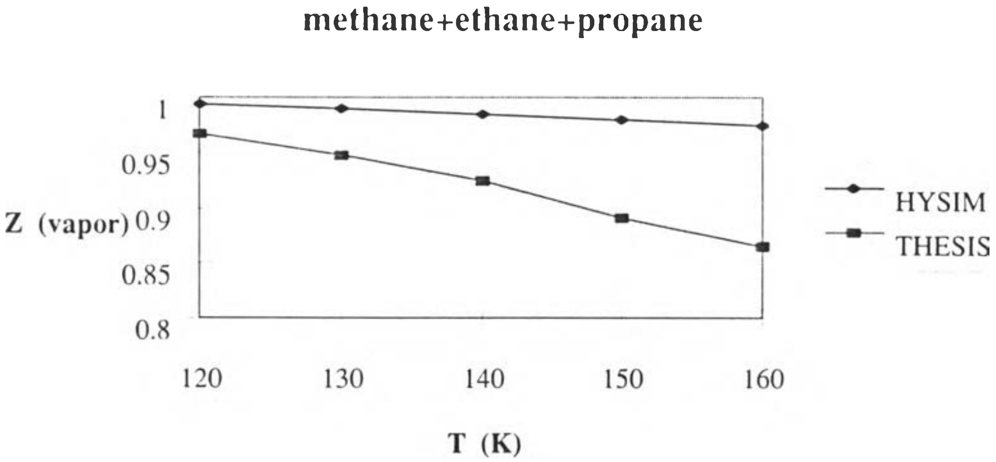

Figure 9.35 Comparison between the calculated values of compressibility factor of methane, ethane, and propane in gas phase using PR equation and those from HYSIM (at bubble-point pressure)

Table 9.17 shows the conclusion of percent deviation of compressibility for multicomponent in gas phase which is calculated by SRK and PR equations.

Table 9.17 Percent deviation of compressibility factor of multicomponent in gas phase calculated by SRK and PR equations in comparison with results of HYSIM using SRK and PR equations

Compounds	Compositions	Deviation (SRK)	Deviation (PR)
1. ethane + propylene	0.5 , 0.5	-3.724	-3.635
2. methane + ethane + propane	0.1 , 0.2 , 0.7	-6.916	-6.636

$$\text{Deviation} = \left(\frac{Zth - Zhy}{Zhy} \right) * 100$$

Zhy refers to compressbility factor computed by HYSIM.

Zth refers to compressibility factor computed by this work.

Table 9.18 shows the conclusion of percent deviation of compressibility factor in gas phase which is calculated by Redlich-Kwong (RK) equation.

Table 9.18 Percent deviation of compressibility factor of multicomponent in gas phase calculated by RK equation. in comparison with results of HYSIM using SRK and PR equations

Compounds	Compositions	Deviation (SRK)	Deviation (PR)
1. ethane + propylene	0.5 , 0.5	-2.924	-1.778
2. methane + ethane + propane	0.1, 0.2, 0.7	-6.914	-6.475

$$\text{Deviation} = \left(\frac{Zth - Zhy}{Zhy}\right) * 100$$

Zhy refers to compressbility factor computed by HYSIM with SRK or PR equations. Zth refers to compressibility factor computed by RK in this program.

For liquid phase

Figure 9.36 to 9.37 show the compressibility factor in liquid phase for multicomponent which is calculated by SRK equation

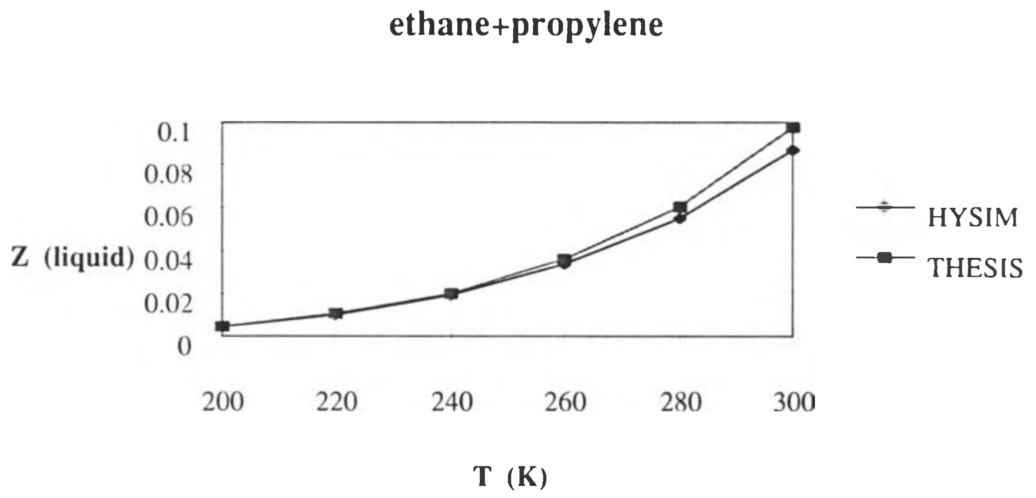

Figure 9.36 Comparison between the calculated values of compressibility factor of ethane and propylene in liquid phase using SRK equation and those from HYSIM (at bubble-point pressure)

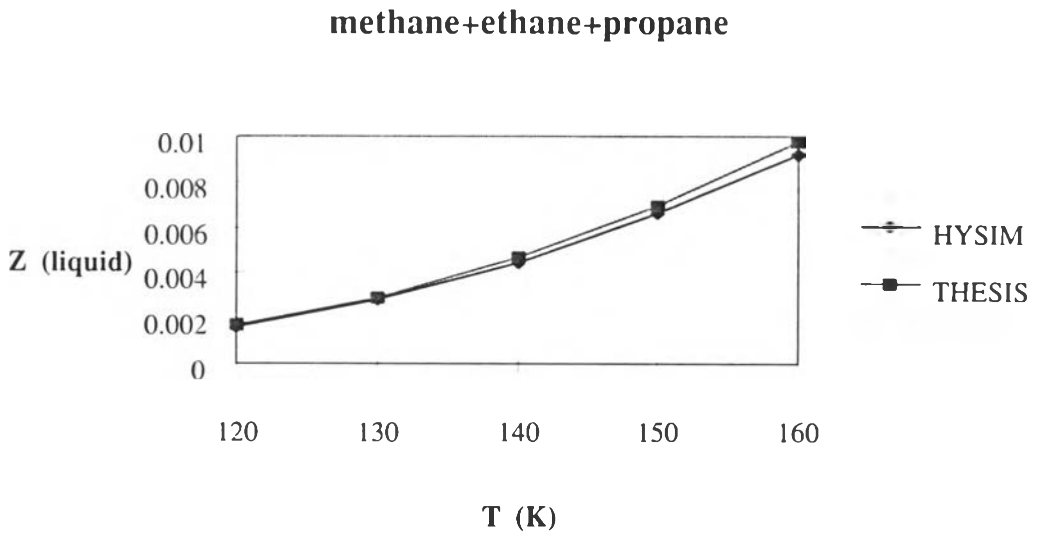

Figure 9.37 Comparison between the calculated values of compressibility factor of methane, ethane, and propane in liquid phase using SRK equation and those from HYSIM (at bubble-point pressure)

Figure 9.38 to 9.39 show the compressibility factor in liquid phase for multicomponent, which is calculated by Peng-Robinson (PR) equation.

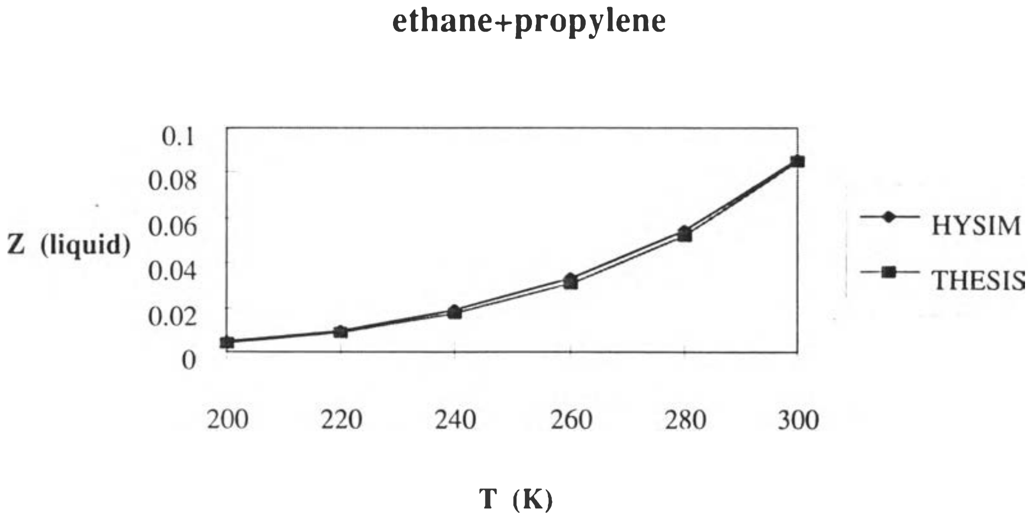

Figure 9.38 Comparison between the calculated values of compressibility factor of ethane and propylene in liquid phase using PR equation and those from HYSIM (at bubble-point pressure)

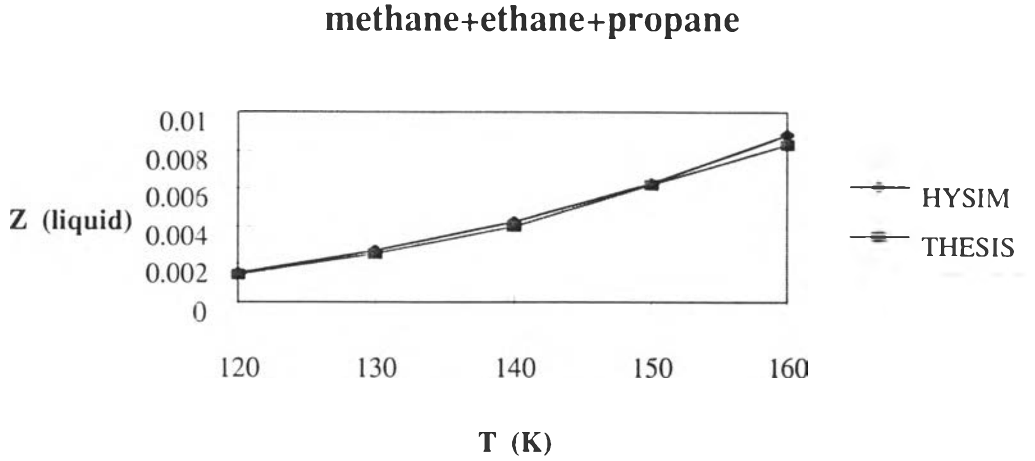

Figure 9.39 Comparison between the calculated values of compressibility factor of methane, ethane, and propane in liquid phase using PR equation and those from HYSIM (at bubble-point pressure)

Table 9.19 shows the conclusion of percent deviation of compressibility for multicomponent in liquid phase, which is calculated by SRK and PR equations.

Table 9.19 Percent deviation of compressibility for multicomponent in liquid phase calculated by SRK and PR equations

Compounds	Compositions	Deviation (SRK)	Deviation (PR)
1. ethane + propylene	0.5 , 0.5	9.611	-3.110
2. methane + ethane + propane	0.1 , 0.2 , 0.7	5.646	-4.600

$$\text{Deviation} = \left(\frac{\text{Zth} - \text{Zhy}}{\text{Zhy}}\right) * 100$$

Zhy refers to compressbility factor computed by HYSIM.

Zth refers to compressibility factor computed by this work.

Multicomponent in gas phase

From Table 9.17, SRK equation can predict compressibility factor fairly well when it is compared with results of HYSIM. The deviation of prediction is less than -7 %. PR equation can estimate compressibility fairly well when it is compared with results of HYSIM. Percent deviation is less than -7 %. From Table 9.18, percent deviation of compressibility factor using RK equation compared with HYSIM using SRK equation is less than -7 % and percent deviation from Peng-Robinson is less than -7 %. Therefore RK, SRK and PR equations do not provide difference in estimating compressibility factor.

Multicomponent in liquid phase

From Table 9.19, SRK equation can estimate compressibility factor fairly well when it is compared with results of HYSIM and the deviation is less than +10%. PR equation can predict compressibility factor fairly well. The deviation is less than -5%. Therefore, PR equation can predict compressibility factor more accurately than does SRK equation.

The results show that SRK and PR equation have no difference to estimate compressibility factor in gas phase. But for liquid phase, PR equation is able to predict compressibility factor more accurately that does the SRK equation. To calculate compressibility factor, equation (5-3) is solved by numerical method. It have three positive real roots, the larged one is vapor, the smallest one is liquid and the intermediate one has no physical significancy. The larged and the smallest root of SRK and PR equations are compressibility factor in vapor phase and liquid phase respectively.

9.4 MOLAR VOLUME

9.4.1 Pure component

For both gas and liquid phase, molar volume is tested at saturated condition. Molar volume for pure component is compared with some reference data (Perry, 1984 and Wark, 1989). Percent deviation is calculated by $\left(\frac{\mathrm{Vth}-\mathrm{Vrh}}{\mathrm{Vrh}}\right)*100$. Vrh refers to the values derive from reference data. Vth refers to the values calculated by this work.

For gas phase

Figure 9.40 to 9.41 show molar volume which is calculated by RK, SRK, and PR equations compared with reference data at various temperature.

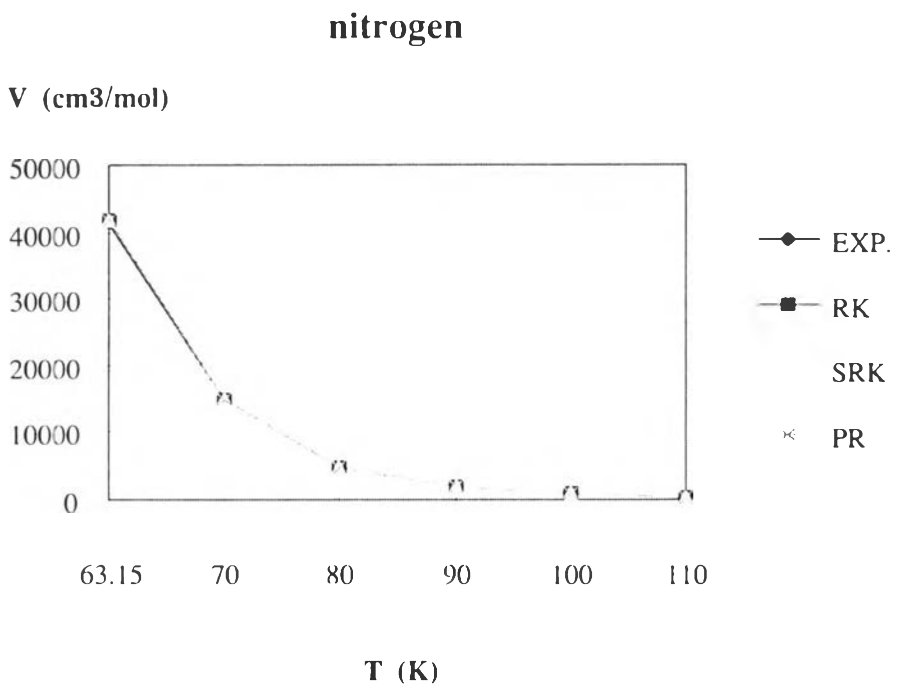

Figure 9.40 Comparison between calculated values of molar volume and reference data for pure nitrogen in gas phase (at saturated condition)

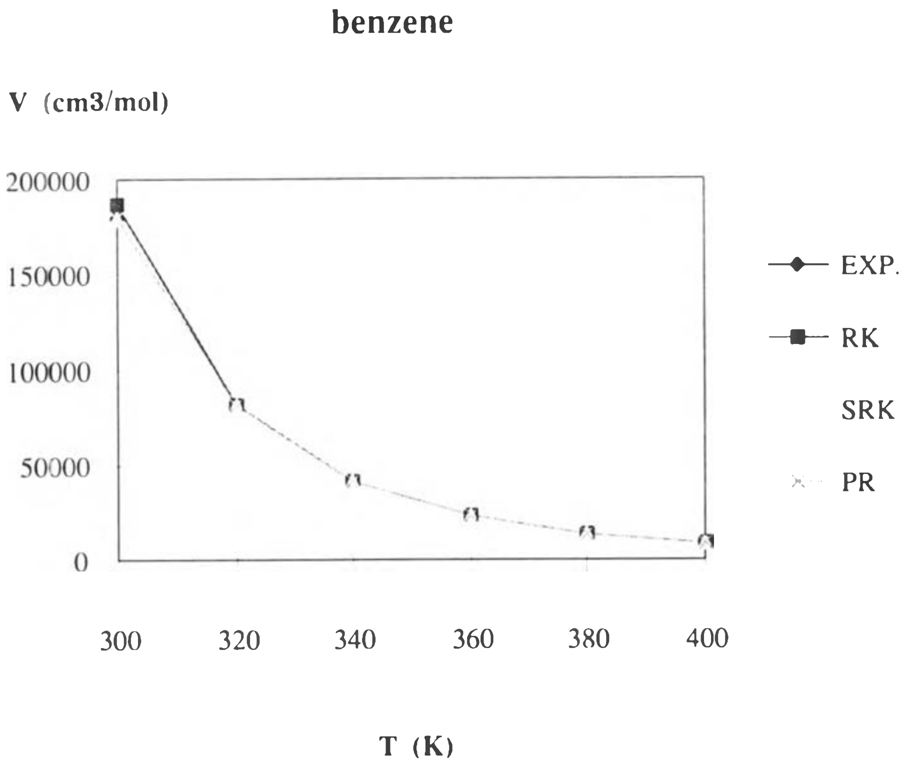

Figure 9.41 Comparison between calculated values of molar volume and reference data for pure benzene in gas phase (at saturated condition)

For liquid phase

Figure 9.42 to 9.43 show molar volume which is calculated by SRK and PR equations compared with reference data.

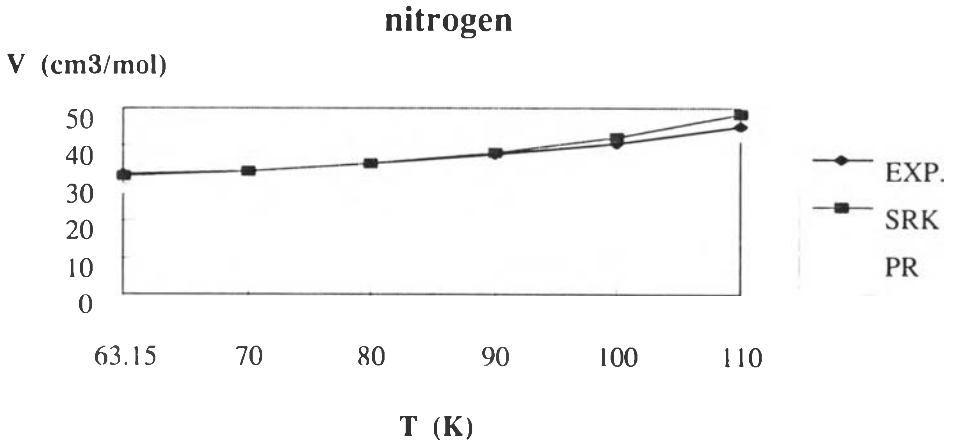

Figure 9.42 Comparison between calculated values of molar volume and reference data for pure nitrogen in liquid phase (at saturated condition)

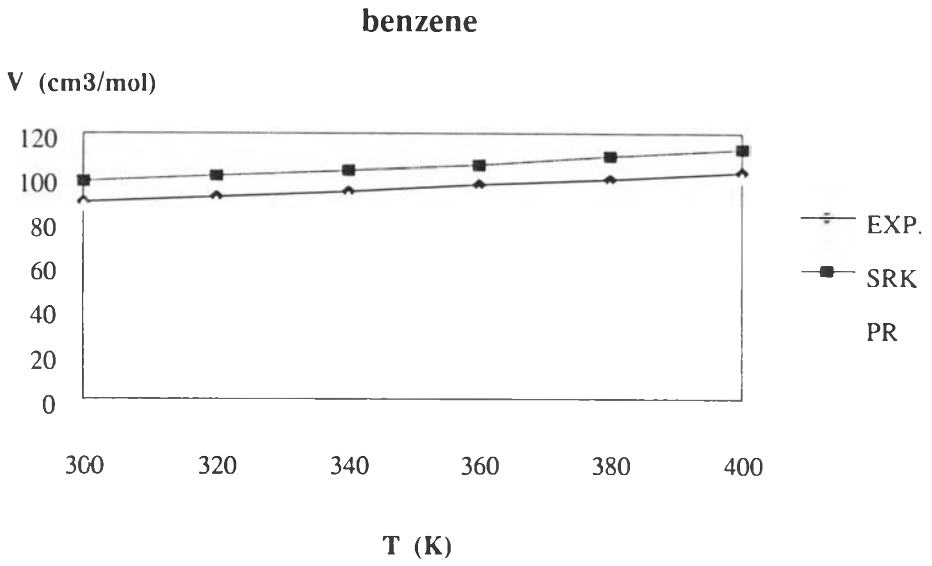

Figure 9.43 Comparison between calculated molar volume and reference data for pure benzene in liquid phase (at saturated condition)

Table 9.20 shows the conclusion of percent deviation for molar volume of pure component in gas phase when it is compared with reference data.

Table 9.20 Percent deviation of molar volume for pure component in gas phase calculated by RK, SRK, and PR equations compared with reference data

Compounds	Deviation (RK)	Deviation (SRK)	Deviation (PR)
1. nitrogen	0.564	0.624	0.534
2. benzene	2.583	0.352	0.300

Deviation (RK) = Percent deviation of RK equation
Deviation (SRK) = Percent deviation of SRK equation
Deviation (PR) = Percent deviation of PR equation

The conclusion of percent deviation for molar volume of pure component in liquid phase is shown in Table 9.21.

Table 9.21 Percent deviation of molar volume for pure component in liquid phase calculated by SRK and PR equations compared with reference data

Compounds	Deviation (SRK)	Deviation (PR)
1. nitrogen	2.396	-9.440
2. benzene	9.712	-2.839

Deviation (SRK) = Percent deviation of SRK equation
Deviation (PR) = Percent deviation of PR equation

9.4.2 Multicomponent

For gas phase

Estimation of molar volume for multicomponent in gas phase is shown in Figure 9.44 to 9.45.

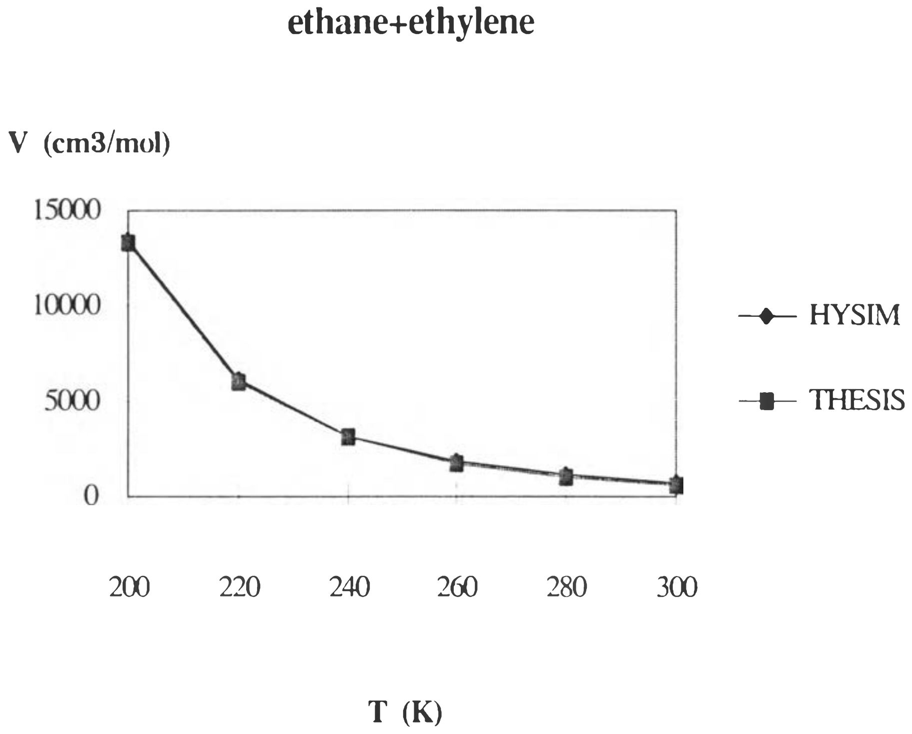

Figure 9.44 Comparison between the calculated values of molar volume of ethane and propylene in gas phase using SRK equation and those from HYSIM (at bubble-point pressure)

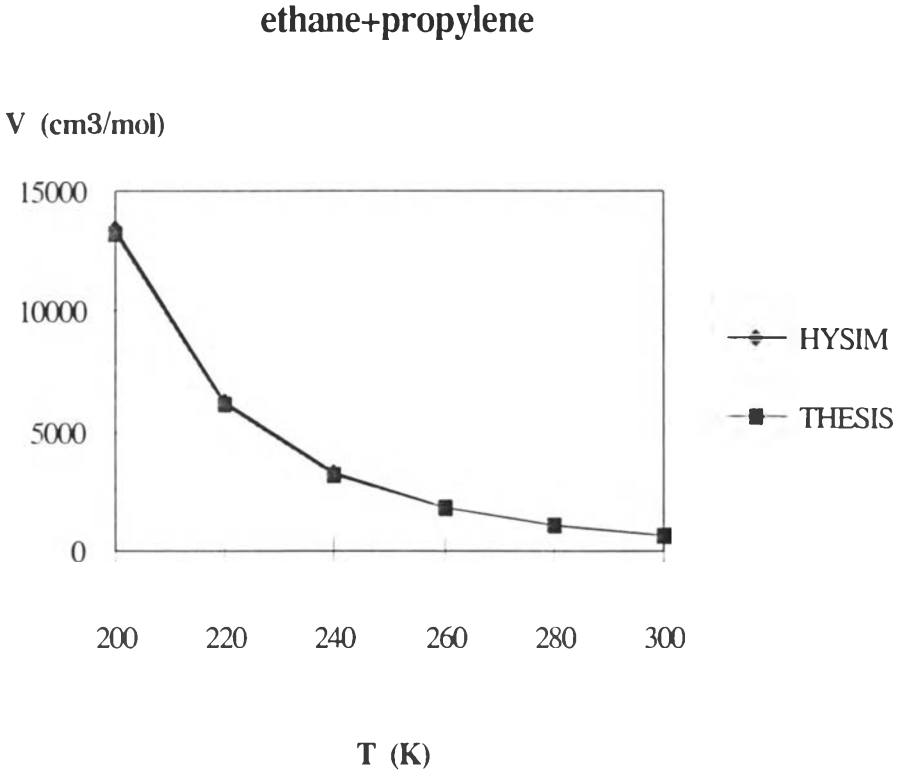

Figure 9.45 Comparison between the calculated values of molar volume of ethane and propylene in gas phase using PR equation and those from HYSIM (at bubble-point pressure)

Table 9.22 shows the percent deviation of molar volume for multicomponent in gas phase which is calculated by SRK, PR equations.

Table 9.22 Percent deviation of molar volume for multicomponent in gas phase calculated by SRK and PR equations in comparison with results of HYSIM using SRK and PR equations

Compounds	Compositions	Deviation(SRK)	Deviation(PR)
1.ethane+ propylene	0.5 , 0.5	-1.842	-1.865

$$\text{Deviation} = \left(\frac{\text{Zth} - \text{Zhy}}{\text{Zhy}}\right) * 100$$

Zhy refers to molar volume computed by HYSIM.

Zth refers to molar volume computed by this work.

Table 9.23 shows percent the deviation of molar volume in gas phase which is calculated by Redlich-Kwong (RK) equation compared with HYSIM.

Table 9.23 Percent deviation of molar volume for multicomponent in gas phase calculated by RK equation in comparison with results of HYSIM using SRK and PR equations

Compounds	Compositions	Deviation (SRK)	Deviation (PR)
1. ethane + propylene	0.5 , 0.5	-1.727	-1.686

$$\text{Deviation} = \left(\frac{\text{Zth} - \text{Zhy}}{\text{Zhy}}\right) * 100$$

Zhy refers to molar volume computed by HYSIM with SRK or PR equations

Zth refers to molar volume computed by this work.

For liquid phase

Estimation of molar volume for multicomponent in liquid phase is shown in Figure 9.46 and 9.47.

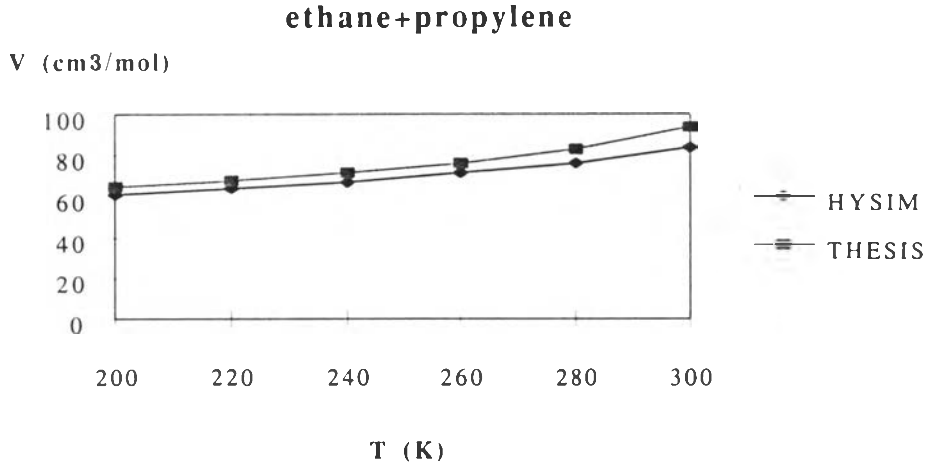

Figure 9.46 Comparison between the calculated values of molar volume of ethane and propylene in liquid phase using SRK equation and those from HYSIM (at bubble-point pressure)

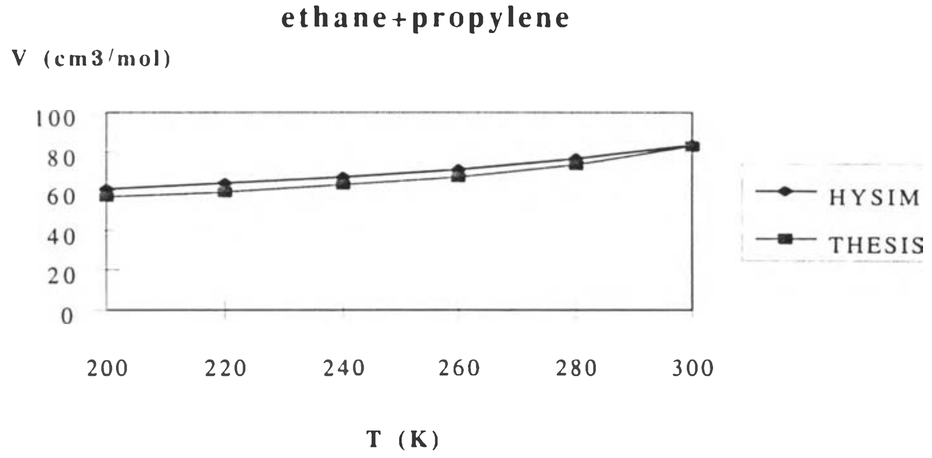

Figure 9.47 Comparison between the calculated values of molar volume of ethane and propylene in liquid phase using PR equation and those from HYSIM (at bubble-point pressure)

The conclusion of molar volume in liquid phase for multicomponent is shown in table 9.24.

Table 9.24 Percent deviation of molar volume for multicomponent in liquid phase calculated by SRK and PR equations in comparison with results of HYSIM using SRK and PR equations

Compounds	Compositions	Deviation(SRK)	Deviation(PR)
1.ethane+ ropylene	0.5 , 0.5	7.905	-4.631

$$\text{Deviation} = \left(\frac{\text{Zth} - \text{Zhy}}{\text{Zhy}}\right) * 100$$

Zhy refers to molar volume computed by HYSIM.

Zth refers to molar volume computed by this work.

Pure component in gas phase

From Table 9.20 , It can seen that RK, SRK and PR equations predict molar volume with an error less than 2%. Therefore, it can be concluded that these equations are suitable for predicting molar volume of pure gas.

Pure component in liquid phase

From Table 9.21 , SRK equation can predict molar volume of pure liquid fairly well when it is compared with reference data. Percent deviation of estimation using SRK equation is less than 10%. PR equation can predict molar volume with lower accuracy compared with those of other equations. Its deviation is less than -10%.

Multicomponent in gas phase

From Table 9.22, SRK and PR equations can estimate molar volume fairly well when it is compared with HYSIM. The percent deviation is less than -2%.

But from Table 9-23, Redlich-Kwong equation can predict molar volume with lower confidence when its prediction results are compared with those of HYSIM.

Multicomponent in liquid phase

From Table 9.24, SRK equation can estimate molar volume fairly well when it is compared with HYSIM. The percent deviation is less than 8%. Peng-Robinson can estimate molar volume with an error less than -5%.

The results show that this program is appropriate to predict molar volume in vapor phase. The percent deviation is less than ±2% when it is compared with reference data. For liquid phase, percent deviation is higher than those of gas phase. Estimation of molar volume in gas phase is more accurate than those of liquid phase because SRK and PR equations are developed from vapor phase and then applied to liquid phase. Therefore, SRK and PR equations have high accuracy to estimate molar volume in vapor phase. For liquid phase, Robert C. Ried recommend Hankinson-Brobst-Thomson technique(1979) and Bhirud's method(1978) for estimating molar volume. Both methods have high accuracy to predict molar volume of liquid.

9.5 ENTHALPY AND ENTROPY

9.5.1 Pure component

Both gas and liquid phase, the values of molar enthalpy changes and molar entropy changes which is calculated by this work are compared with those from HYSIM. Molar enthapy and molar entropy changes are tested at saturated conditions (at bubble-point pressure).

For gas phase

Figure 9.48 to 9.51 show enthalpy changes of pure component which is estimated by SRK and PR equations at saturated conditions(at bubble-point pressure). Figure 9.48 shows the values of enthalpy changes which is calculated by SRK equation at various temperature (T1=300K, T2=310K, T3=320K, T4=330K, T5=340, T6=350K) for pure n-butane.

N-Butane

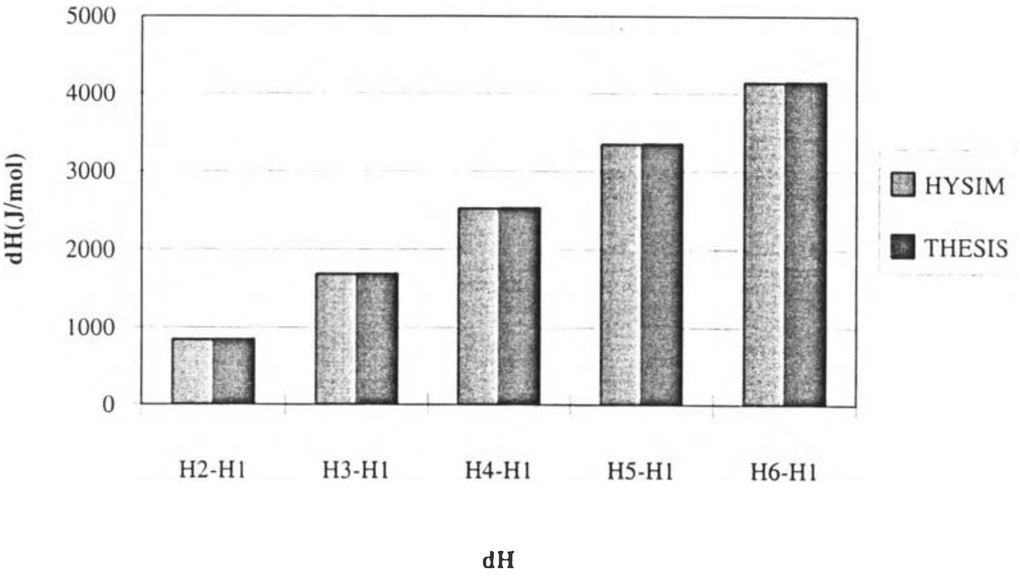

Figure 9.48 Comparison between the calculated values of enthalpy changes of pure n-butane in gas phase using SRK equation and those from HYSIM (at bubble-point pressure)

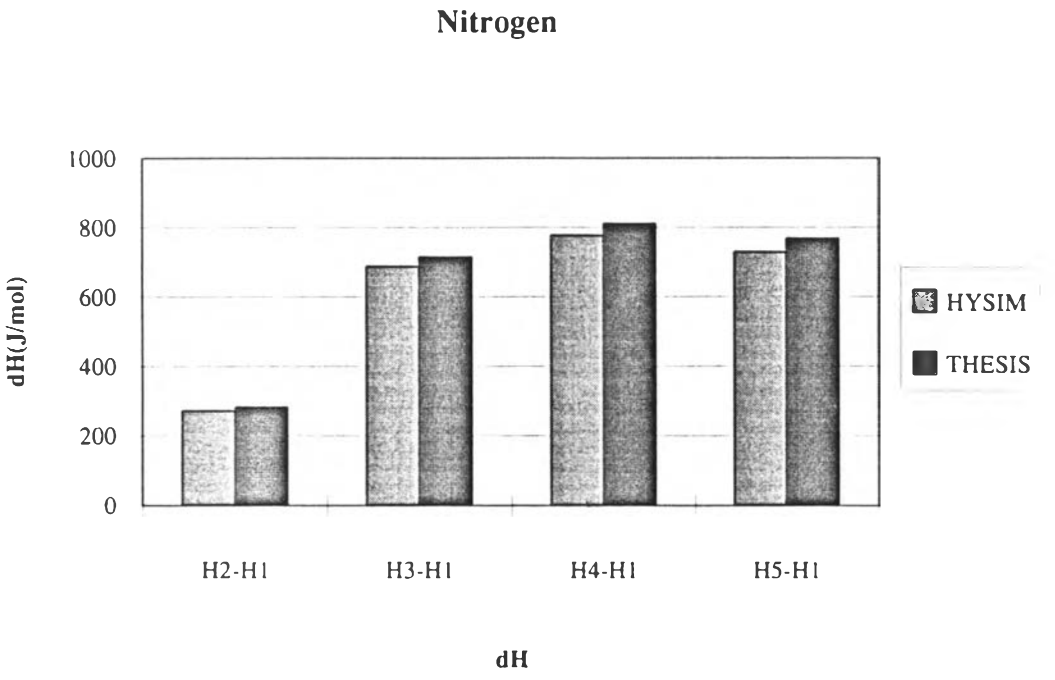

Figure 9.49 Comparison between the calculated values of enthalpy changes of pure nitrogen in gas phase using SRK equation and those from HYSIM (at bubble-point pressure)

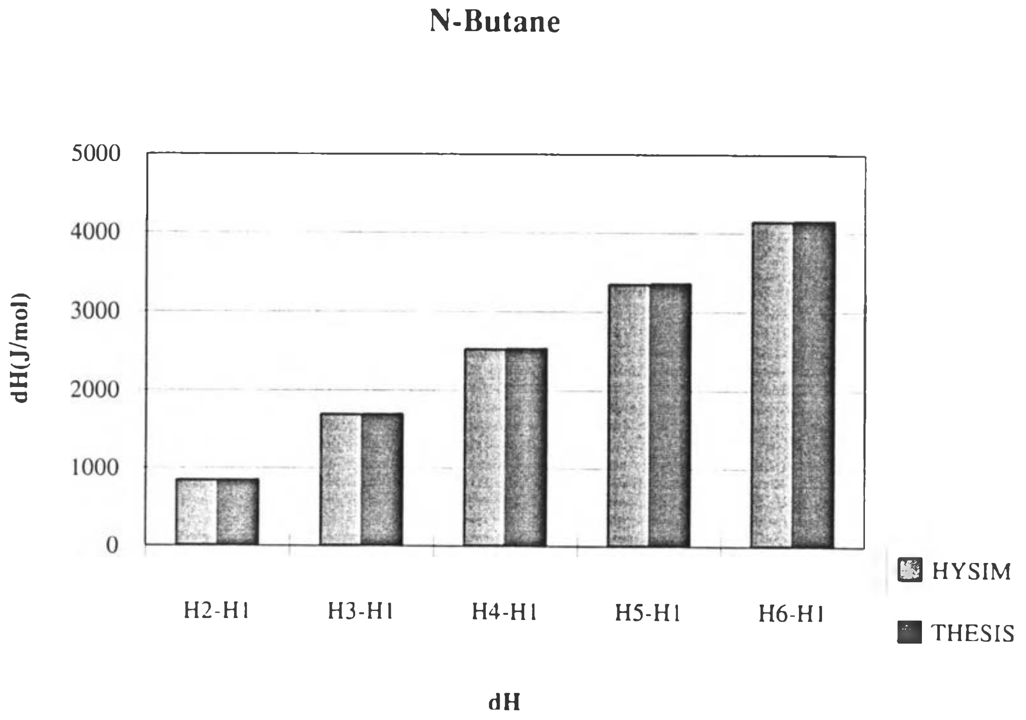

Figure 9.50 Comparison between the calculated values of enthalpy changes of pure n-butane in gas phase using PR equation and those from HYSIM (at bubble-point pressure)

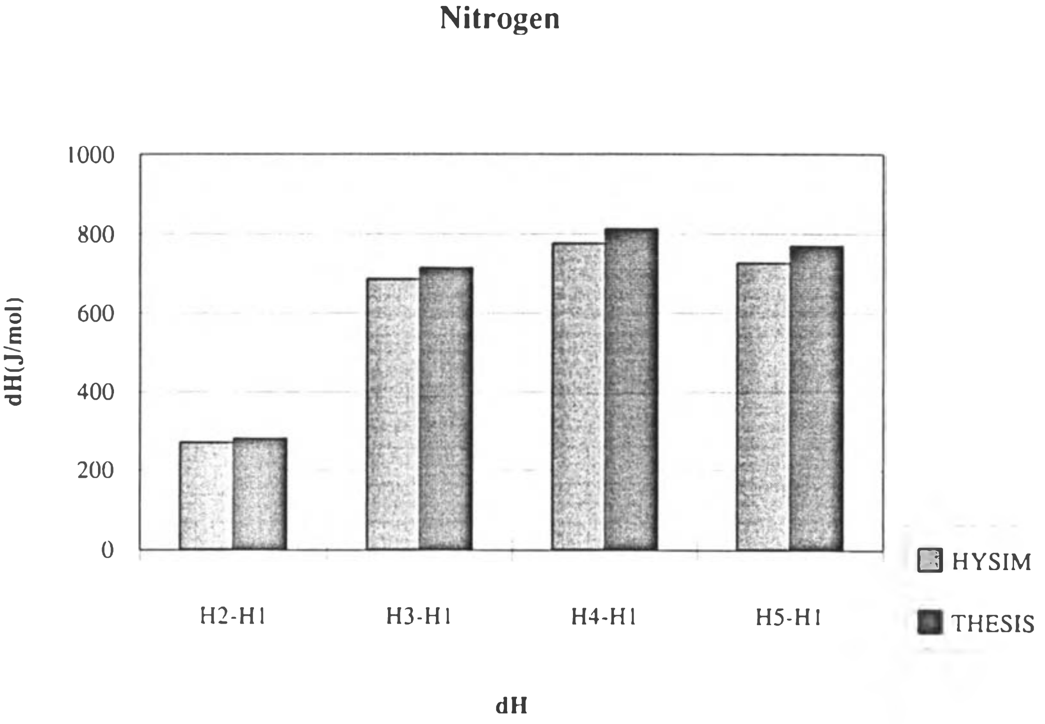

Figure 9.51 Comparison between the calculated values of enthalpy changes of pure nitrogen in gas phase using PR equation and those from HYSIM (at bubble-point pressure)

Percent Deviation of enthalpy changes for pure component in gas phase, which are estimated and compared with reference data are shown in Table 9.25.

Table 9.25 Percent deviation of molar enthalpy changes for pure component in gas phase

Compounds	Deviation (SRK)	Deviation (PR)
1. n-butane	0.266	0.276
2. nitrogen	4.434	4.671

Deviation (SRK) = Percent deviation of SRK equation
Deviation (PR) = Percent deviation of PR equation

Molar entropy changes of pure component in gas phase are tested at the same conditions as molar enthalpy changes. Table 9-26 is shows the conclusion of molar entropy changes for pure component in gas phase.

Table 9.26 Percent deviation of molar entropy changes for pure component in gas phase

Compounds	Deviation (SRK)	Deviation (PR)
1. n-butane	0.028	1.136
2. nitrogen	-1.618	-1.681

Deviation (SRK) = Percent deviation of SRK equation
Deviation (PR) = Percent deviation of PR equation

For liquid phase

Figure 9.52 shows enthalpy changes which is calculated by SRK equation at saturated conditions(at bubble-point pressure) and various temperature (T1=300K, T2=310K, T3=320K, T4=330K, T5=340, T6=350K) for pure n-butane.

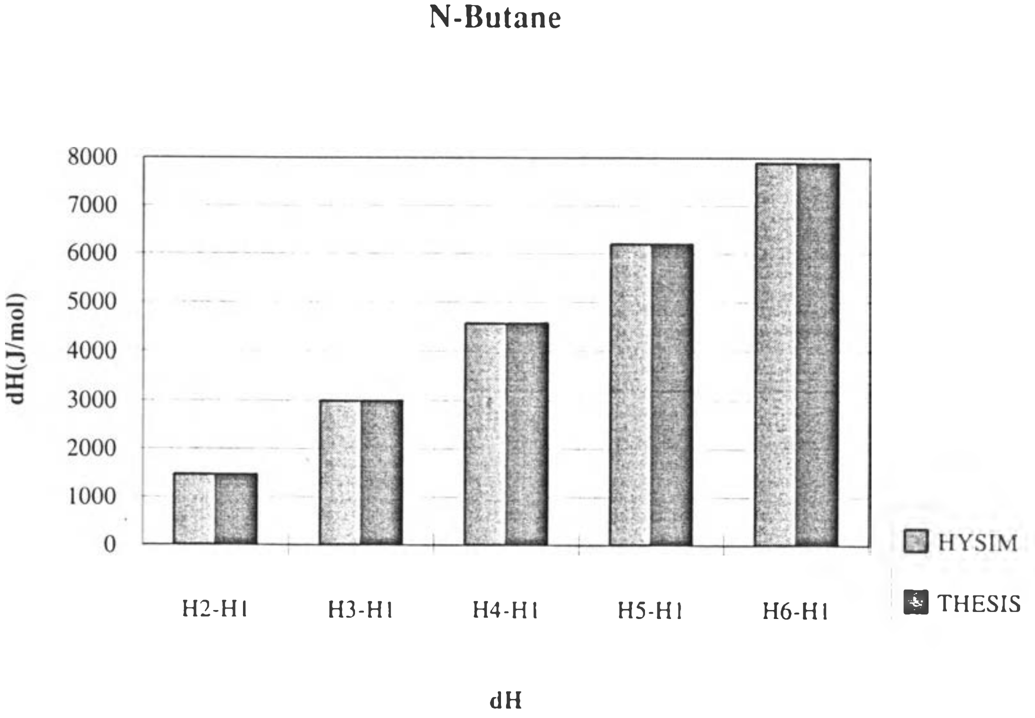

Figure 9.52 Comparison between the calculated values of enthalpy changes of pure n-butane in liquid phase using SRK equation and those from HYSIM (at bubble-point pressure)

Figure 9.53 shows enthalpy changes which are calculated by SRK equation at various temperature (T1=60K, T2=70K, T3=90K, T4=100K, T5=110K) for pure nitrogen in liquid phase.

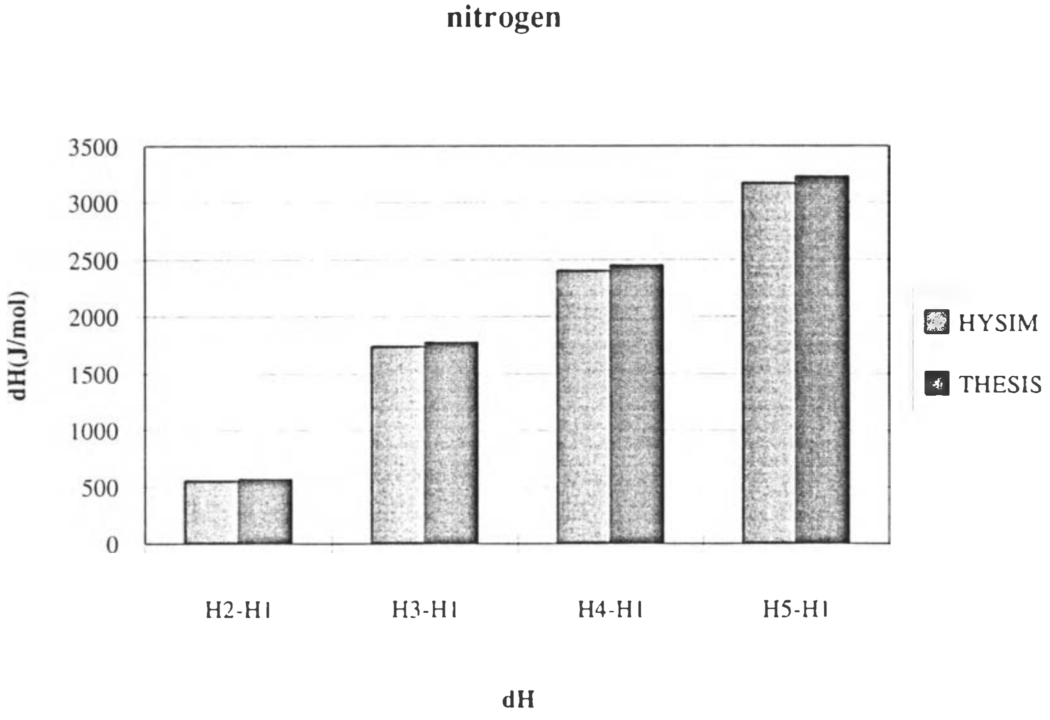

Figure 9.53 Comparison between the calculated values of enthalpy changes of pure nitrogen in liquid phase using SRK equation and those from HYSIM (at bubble-point pressure)

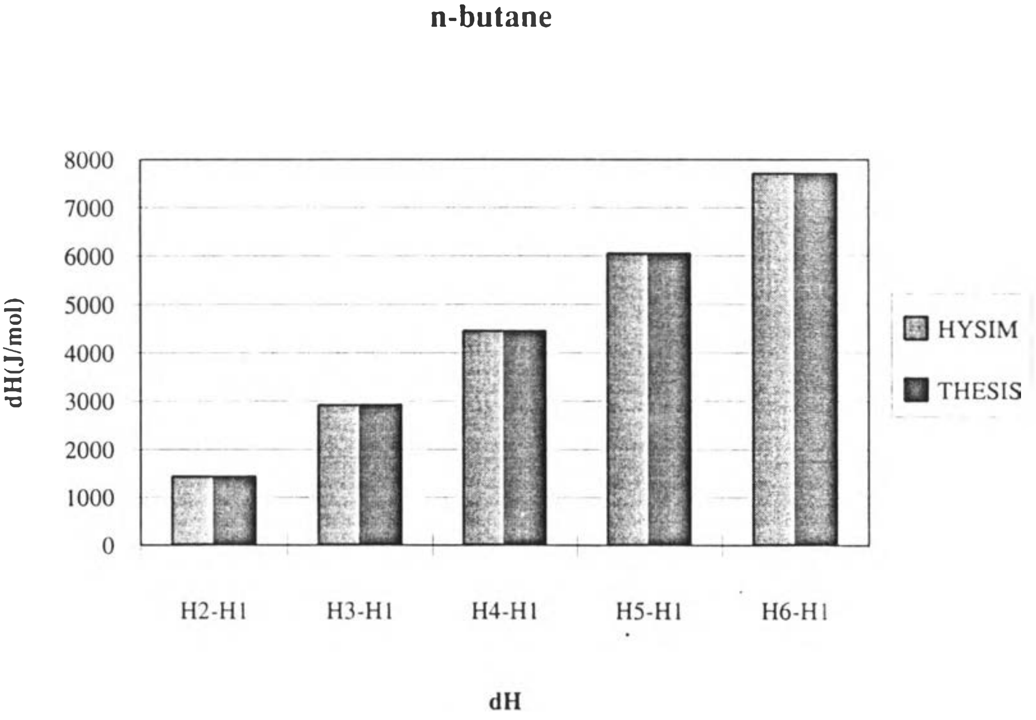

Figure 9.54 Comparison between the calculated values of enthalpy changes of pure n-butane in liquid phase using PR equation and those from HYSIM (at bubble-point pressure)

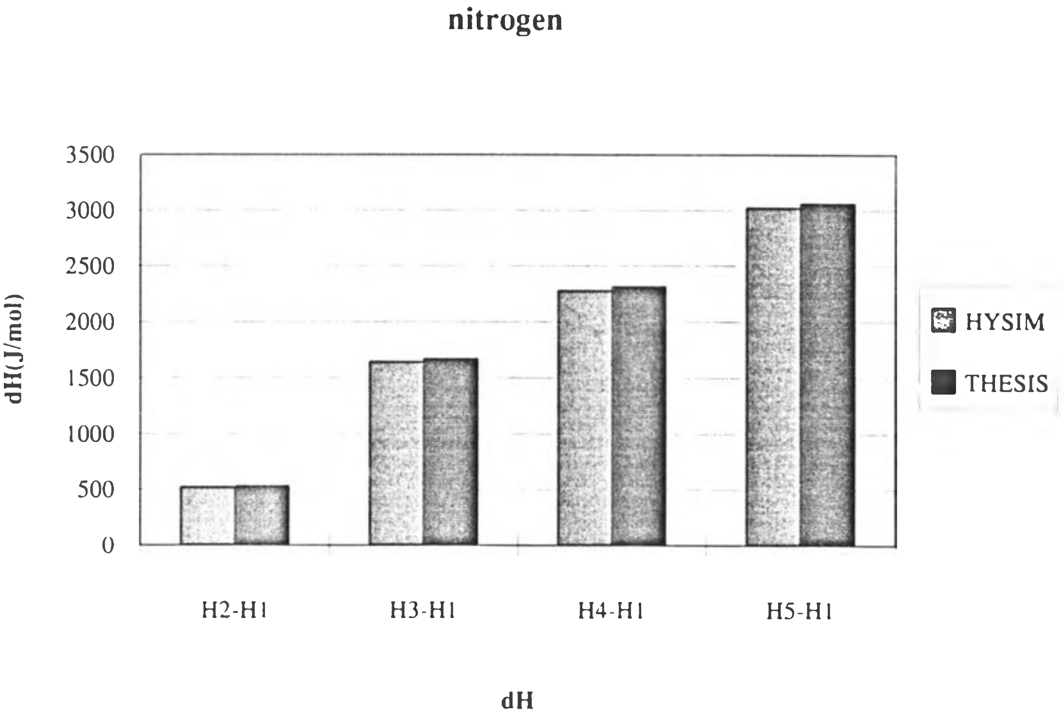

Figure 9.55 Comparison between the calculated values of enthalpy changes of pure nitrogen in liquid phase using PR equation and those from HYSIM (at bubble-point pressure)

Percent Deviation of enthalpy changes and entropy changes for pure component in liquid phase, which are estimated and compared with reference data are shown in Table 9.27 and Table 9.28.

Table 9.27 Percent deviation of molar enthalpy changes for pure component in liquid phase

Compounds	Deviation (SRK)	Deviation (PR)
1. n-butane	0.0346	0.008
2. nitrogen	1.898	1.425

Deviation (SRK) = Percent deviation of SRK equation

Deviation (PR) = Percent deviation of PR equation

Table 9.28 Percent deviation of molar entropy changes for pure component in liquid phase

Compounds	Deviation (SRK)	Deviation (PR)
1. n-butane	0.041	0.014
2. nitrogen	1.967	1.489

Deviation (SRK) = Percent deviation of SRK equation

Deviation (PR) = Percent deviation of PR equation

9.5.2 Multicomponent

The values of molar enthalpy changes of a mixture of ethane and propylene is calculated by SRK and PR equations and the results are compared with the results calculated by HYSIM. A mixture is tested at various temperature (T1=200, T2=220, T3=240, T4=260, T5=280, T6=300) at saturated conditions (at bubble-point pressure).

For gas phase

Figure 9.56 and 9.57 show the results of estimation of molar enthalpy changes for pure component in gas phase which is calculated by SRK and PR equations. The conclusion of molar enthalpy changes are shown in Table 9.29.

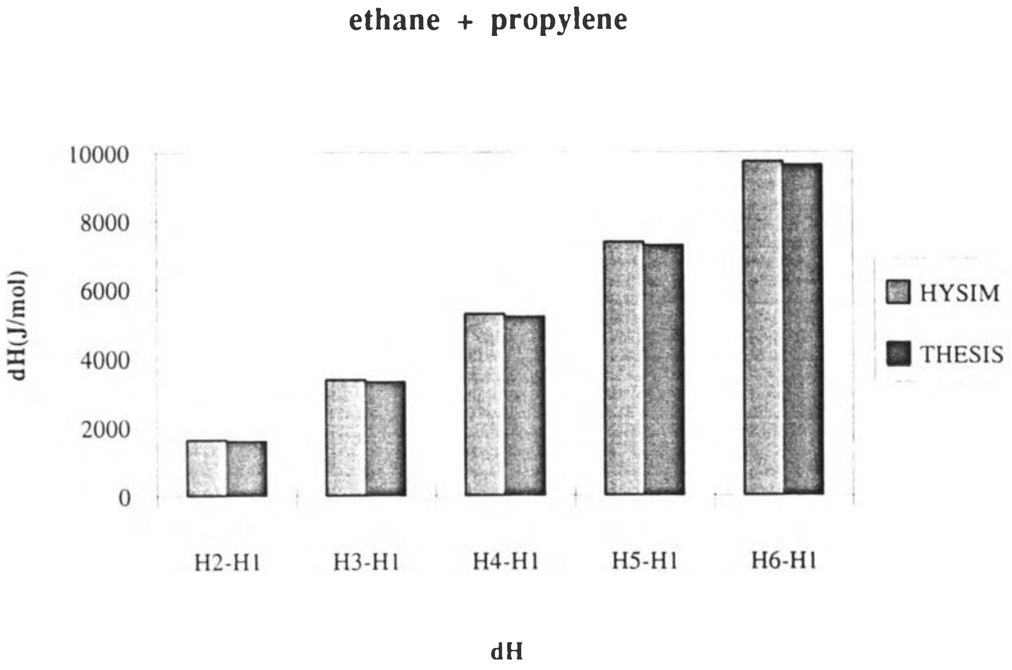

Figure 9.56 Comparison between the calculated values of enthalpy changes of ethane and propylene in gas phase using SRK equation and those from HYSIM (at bubble-point pressure)

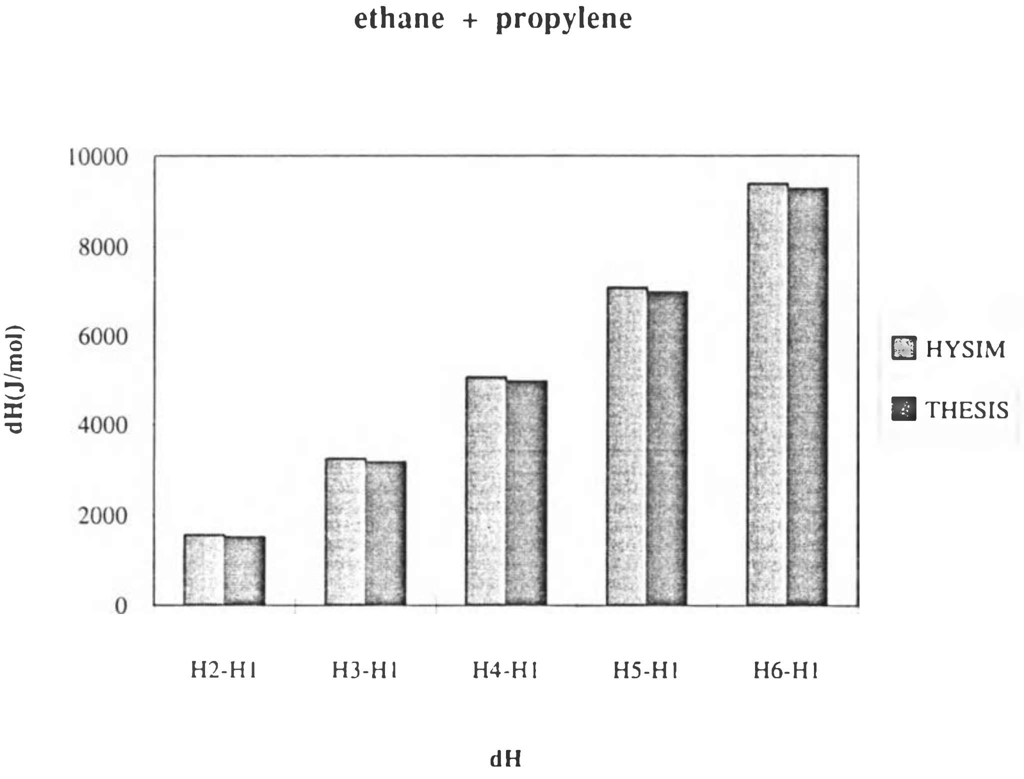

Figure 9.57 Comparison between the calculated values of enthalpy changes of ethane and propylene in gas phase using PR equation and those from HYSIM (at bubble-point pressure)

The conclusion of enthalpy changes for multicomponent in vapor phase is shown in Table 9.29.

Table 9.29 Percent deviation of molar enthalpy changes for multicomponent in gas phase

Compounds	Compositions	Deviation(SRK)	Deviation(PR)
1.ethane+ propylene	0.5 , 0.5	3.687	4.212

Deviation (SRK) = Percent deviation of SRK equation
Deviation (PR) = Percent deviation of PR equation

For liquid phase

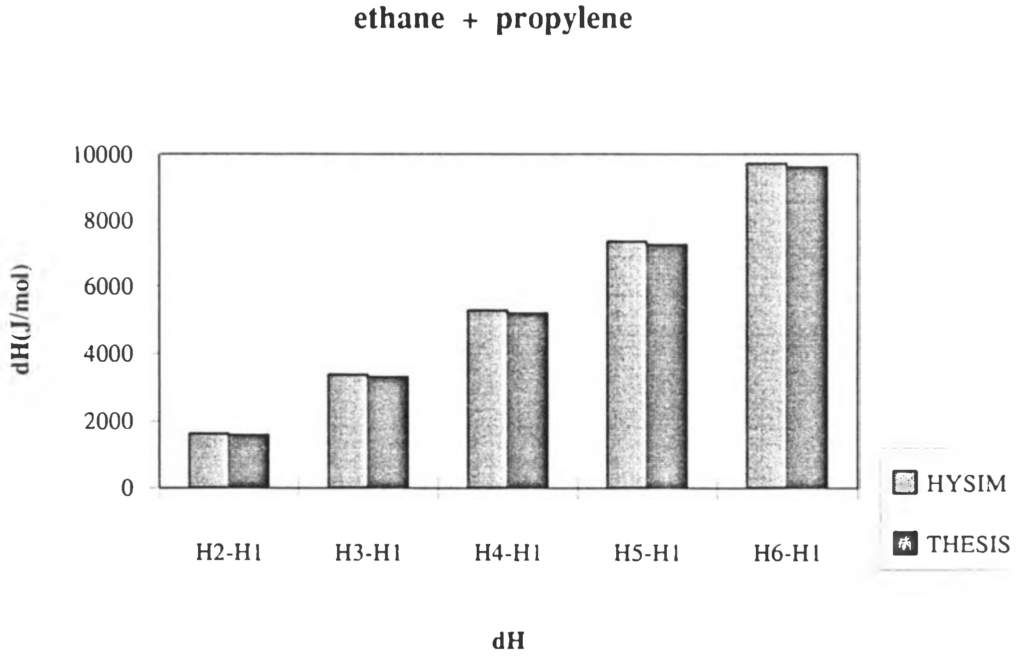

Figure 9.58 Comparison between the calculated values of enthalpy changes of ethane and propylene in liquid phase using SRK equation and those from HYSIM (at bubble-point pressure)

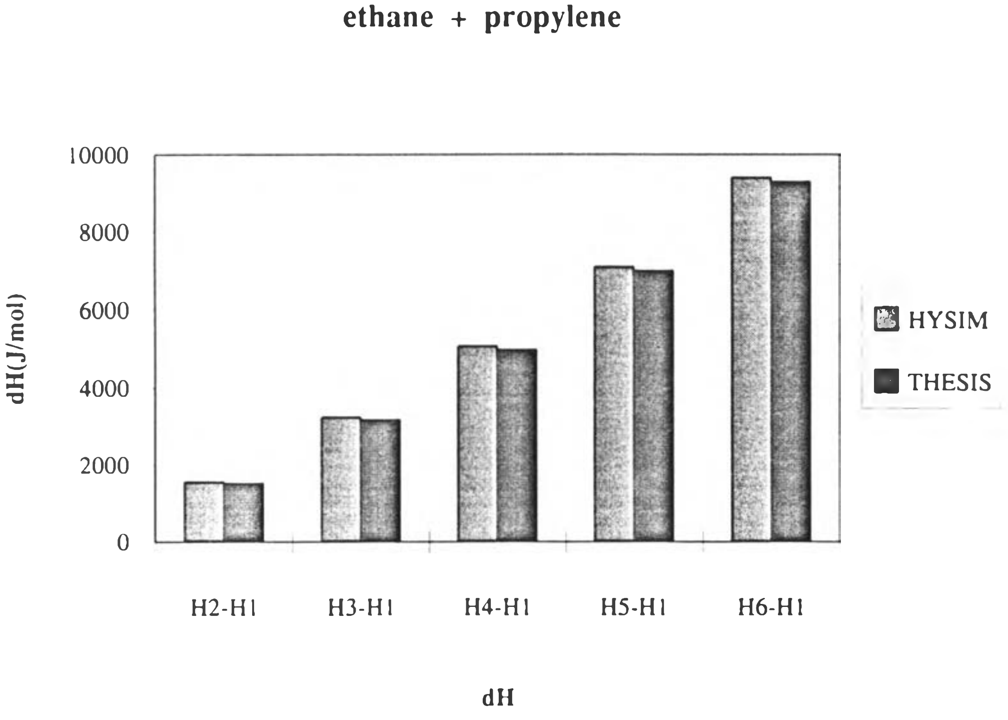

Figure 9.59 Comparison between the calculated values of enthalpy changes of ethane and propylene in liquid phase using PR equation and those from HYSIM (at bubble-point pressure)

The conclusion of enthalpy changes for multicomponent in liquid phase is shown in Table 9.30.

Table 9.30 Percent deviation of molar enthalpy changes for multicomponent in liquid phase

Compounds	Compositions	Deviation(SRK)	Deviation(PR)
1.ethane+ propylene	0.5 , 0.5	-1.404	-1.563

Deviation (SRK) = Percent deviation of SRK equation .

Deviation (PR) = Percent deviation of PR equation

Pure component

In gas phase, both SRK and PR equations can estimate molar enthalpy changes fairly well when it is compared with HYSIM and the percent deviation is less than 4.5%. The percent deviation of molar entropy changes is less than ± 2%. In liquid phase, SRK and PR equations can predict molar enthalpy changes and molar entropy changes'fairly well. The percent deviation is less than 2% when it is compared with HYSIM.

Multicomponent

In gas phase, the molar enthalpy changes, which is calculated by SRK and PR is higher than HYSIM and the percent deviation is less than 5%. In liquid phase, the per cent deviation of molar enthalpy changes is less than -2%.

The results show that this program is more accurate to predict molar enthalpy changes for pure component and multicomponent of both gas and liquid phase. For pure component, the molar entropy changes estimated by this work has percent deviation less than ± 2%. For calculating enthalpy changes by this program, we use reference state at temperature 273.15 K and pressure at the system pressure. If we require to calculate enthalpy changes between temperature T1 and temperature T2, we will calculate enthalpy changes between T1 and reference state($\Delta H1$) and then calculate enthalpy changes between T2 and reference state($\Delta H2$). Enthalpy changes between T1 and T2 equals to $\Delta H2-\Delta H1$. The procedure for calculating enthalpy changes compared with reference state is as follows:

1. Calculation enthalpy changes at ideal gas state from initial conditions A(273.15, P $)_{ideal}$ to final conditions B(T1, P$)_{ideal}$. An equation for calculating is

$$\Delta Hideal = \int_{273.15}^{T1} CpdT$$

ΔHideal = enthalpy changes at ideal gas state

Cp= heat capacity for calculating enthalpy at ideal gas state

2. Calculation of enthalpy changes between ideal gas state B(T1, P$)_{ideal}$ and real gas state C(T1, P$)_{real}$. Enthalpy changes for this step is enthalpy departure at temperature T1 and pressure P. It is computed from equation(6-68) in chapter VI.

3. Calculation total enthalpy changes. An equation for calculating is

$$\Delta H = \Delta Hideal + \left(H_p - H^o\right)_{T1}$$

ΔH = total enthalpy changes

$(H_p-H^o)_{T1}$ = enthalpy departure at temperature T1 and pressure P

This concept is also used in HYSIM therefore there is no significant difference between this program and HYSIM for calculating enthalpy changes. Calculation of entropy changes is also based on the same concept as calculation of enthalpy changes. Detail for calculating entropy changes is revealed in chapter IV.

Figure 9.60 shows the procedure to calculate total enthalpy changes when compare with reference state.

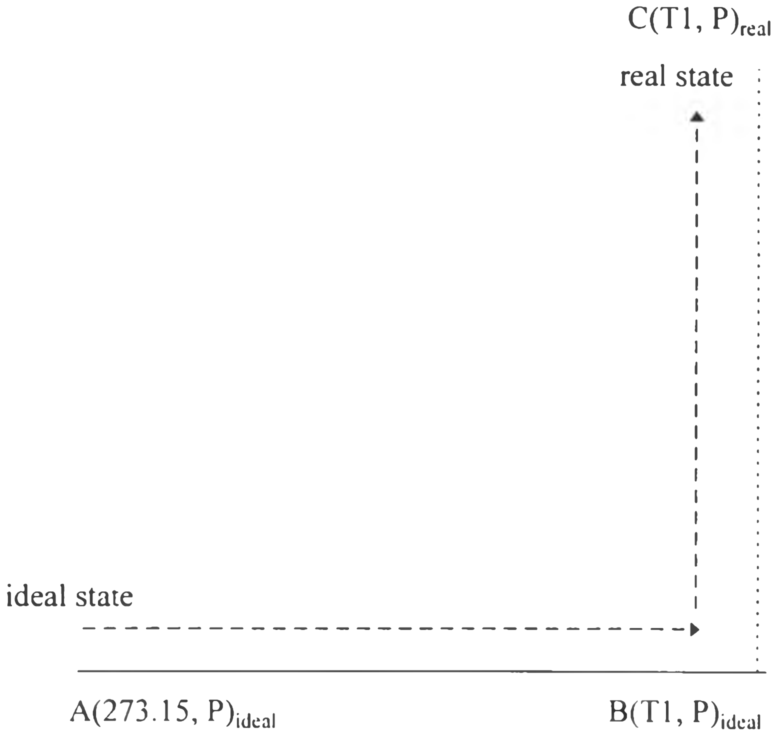

Figure 9.60 Enthalpy changes when it is compared with reference state

9.6 FUGACITY COEFFICIENT

RK, SRK, and PR equations can predict only fugacity coefficient of gas phase. In liquid phase these equations can not predict the fugacity coefficient. For liquid phase, estimation of fugacity coefficient must use activity coefficient. In this work, the fugacity coefficient is estimated by RK, SRK, and PR equations. Percent deviation is calculated from $\left(\frac{Vth - Vrh}{Vrh}\right) * 100$. Vrh refers to the values derive from reference data. Vth refers to the values calculated by this work.

For gas phase

9.6.1 Pure component

Three compounds are tested by this program. Ammonia is tested at saturated condition(temperatue 373.15 K and at various pressure). Ethylene is tested at temperature 323.15 K, pressure 50.662 bars and 1-butene at temperature 473.15 K, pressure 70 bars. The conclusion of testing is shown in Table 9.31. Fugacity coefficient is compared with reference data (Walas S.M.,1985).

Table 9.31 Percent deviation of fugacity coefficient in gas phase for pure component

Compounnd	D(SRK)	D(PR)	D(RK)
1. ammonia	1.270	0.405	1.656
2. 1-butene	2.361	-2.472	-1.204
2. ethylene	-1.362	-4.387	1.656

D(SRK) = Percent deviation of SRK equation.
D(PR) = Percent deviation of PR equation.
D(RK) = Percent deviation of RK equation.

9.6.2 Multicomponent

A mixture of nitrogen and n-butane at temperature 460.93 K and pressure 41.368 bars is introduced to test fugacity coefficient. The results of prediction are compared with reference data (Van Ness and Abbott,1982).

Table 9.32 Percent deviation of fugacity coefficient in gas phase for multicomponent

Compounnd	Compositions	D(SRK)	D(PR)	D(RK)
1. nitrogen	0.4974	0.426	-0.383	-1.036
2. n-butane	0.5026	0.762	-2.704	-1.228

D(SRK) = Percent deviation of SRK equation
D(PR) = Percent deviation of PR equation
D(RK) = Percent deviation of RK equation

The results show that estimation of fugacity coefficient for pure component and multicomponent in gas phase, which are calculated by RK, SRK, and PR equations has percent deviation less than ±4.5% when it is compared with reference data. RK, SRK, and PR equations can predict only fugacity coefficient in gas phase. For liquid phase, There is no the information to calculate fugacity coefficient from PVT data. Deshpande(1985) suggested activity coefficient model for estimating fugacity coefficient of liquid phase.

9.7 VAPOR-LIQUID EQUILIBRIA

The results of estimation vapor-liquid equilibria are compared with reference data or those from HYSIM package. Percent deviation is calculated from $\left(\frac{Vth - Vrh}{Vrh}\right) * 100$. Vrh refers to the values derived from HYSIM or reference data. Vth refers to the values calculated by this program.

9.7.1 Bubble-point pressure

The results of estimation bubble-point pressure are compared with those from reference data and those from HYSIM. A mixture of two components and three components is introduced to test bubble point pressure.

1. A mixture of ethane(1) and propylene(2) is tested at temperature 261 K and various composition of a mixture(0 to 1). For example, mole fraction of ethane and propylene equals to 0.1 and 0.9. The results are compared with reference data (Sandler,1989).

Table 9.33 Percent deviation of bubble point pressure calculated by this work and HYSIM compared with reference data for ethane and propylene

Methods	D(y1)	D(y2)	D(P)	H(y1)	H(y2)	H(P)
1. Raoult's law	2.804	-6.419	-1.172	-	-	-
2. SRK	0.160	-0.367	-0.119	0.187	-0.428	0.093
3. PR	0.026	-0.060	-1.091	0.089	-0.203	-1.111

D(y1), D(y2) = Percent deviation of vapor fractions calculated by this work compared with reference data for bubble-point pressure

D(P) = Percent deviation of bubble-point pressure calculated by this work compared with reference data

H(y1), H(y2) = Percent deviation of vapor fractions calculated by HYSIM compared with reference data for bubble-point pressure

H(P) = Percent deviation of bubble-point pressure calculated by HYSIM compared with reference data

Table 9.34 shows percent deviation of bubble-point pressure calculated by this work compared with those from HYSIM for ethane and propylene.

Table 9.34 Percent deviation of bubble-point pressure calculated by this work compared with those from HYSIM for ethane and propylene

Methods	D(y1)	D(y2)	D(P)
1. SRK	0.026	-0.060	-0.212
2. PR	0.062	-0.143	0.139

D(y1), D(y2) = Percent deviation of vapor fractions calculated by this work compared with those from HYSIM for bubble-point pressure

D(P) = Percent deviation of bubble-point pressure calculated by this work compared with those from HYSIM

2. A mixture of n-pentane(1), propane(2), and methane(3) is tested at various temperature and composition. The results are compared with reference data(Prausnitz and Chueh, 1968). Table 9.35 shows percent deviation of bubble point pressure calculated by this work and HYSIM compared with reference data for n-pentane, propane, and methane.

Table 9.35 Percent deviation of bubble point pressure calculated by this work and HYSIM compared with reference data for n-pentane, propane, and methane

Methods	D(y1)	D(y2)	D(y3)	D(P)	H(y1)	H(y2)	H(y3)	H(P)
1. SRK	-2.33	-0.83	0.87	-3.85	-5.43	-1.00	2.15	-1.15
2. PR	-0.89	0.49	0.07	-4.79	-1.16	0.03	0.16	-1.21

D(y1), D(y2), D(y3) = Percent deviation of vapor fractions calculated by this work compared with reference data for bubble-point pressure

D(P) = Percent deviation of bubble-point pressure calculated by this work compared with reference data

H(y1), H(y2), H(y3) = Percent deviation of vapor fractions calculated by HYSIM compared with reference data for bubble-point pressure

H(P) = Percent deviation of bubble-point pressure calculated by HYSIM compared with reference data

Table 9.36 shows percent deviation of bubble-point pressure calculated by this work compared with those from HYSIM for n-pentane, propane, and methane

Table 9.36 Percent deviation of bubble-point pressure calculated by this work compared with those from HYSIM for n-pentane, propane, and methane

Methods	D(y1)	D(y2)	D(y3)	D(P)
1. SRK	3.28	0.18	-1.25	-2.73
2. PR	0.28	0.46	-0.09	-3.63

D(y1), D(y2), D(y3) = Percent deviation of vapor fractions calculated by this work compared with those from HYSIM for bubble-point pressure

D(P) = Percent deviation of bubble-point pressure calculated by this work compared with those from HYSIM

3. A mixture of propane(1), ethane(2), and methane(3) is tested at various temperature and composition. The results are compared with reference data (Prausnitz and Chueh, 1968). Table 9.37 shows percent deviation of bubble point pressure for propane, ethane, and methane compared with reference data.

Table 9.37 Percent deviation of bubble-point pressure calculated by this work and HYSIM compared with reference data for propane, ethane, and methane

Methods	D(y1)	D(y2)	D(y3)	D(P)	H(y1)	H(y2)	H(y3)	H(P)
1. SRK	-2.33	0.53	0.24	-1.16	-2.86	0.41	0.33	-0.22
2. PR	-0.56	1.67	-0.17	-2.02	-0.52	1.39	-0.13	-0.85

D(y1), D(y2), D(y3) = Percent deviation of vapor fractions calculated by this work compared with reference data for bubble-point pressure

D(P) = Percent deviation of bubble-point pressure calculated by this work compared with reference data

H(y1), H(y2), H(y3) = Percent deviation of vapor fractions calculated by HYSIM compared with reference data for bubble-point pressure

H(P) = Percent deviation of bubble-point pressure calculated by HYSIM compared with reference data

Percent deviation of bubble-point pressure calculated by this work compared with those from HYSIM for propane, ethane, and methane is shown in Table 9.38.

Table 9.38 Percent deviation of bubble-point pressure calculated by this work compared with those from HYSIM for propane, ethane, and methane

Methods	D(y1)	D(y2)	D(y3)	D(P)
1. SRK	0.55	0.125	-0.087	-0.93
2. PR	-0.039	0.27	-0.04	-1.17

D(y1), D(y2), D(y3) = Percent deviation of vapor fractions calculated by this work compared with those from HYSIM for bubble-point pressure

D(P) = Percent deviation of bubble-point pressure calculated by this work compared with those from HYSIM

9.7.2 Dew point pressure

Estimation of dew point pressure of a mixture of ethane (1) and propylene (2) is tested at temperature 261 K and various composition (y_i = 0-1). The results are compared with reference data (Prausnitz and Chueh, 1968).

Percent deviation of dew-point pressure calculated by this work and HYSIM compared with reference data for ethane and propylene is shown in Table 9.39.

Table 9.39 Percent deviation of dew-point pressure calculated by this work and HYSIM compared with reference data for ethane and propylene

Methods	D(x1)	D(x2)	D(P)	H(x1)	H(x2)	H(P)
1. Raoult's law	-5.08	6.89	-4.49	-	-	-
2. SRK	-0.25	0.34	-0.32	-0.28	0.38	-0.12
3. PR	-0.07	0.09	-1.16	-0.21	0.28	-1.40

D(x1), D(x2) = Percent deviation of liquid fractions calculated by this work compared with reference data for dew-point pressure

D(P) = Percent deviation of dew-point pressure calculated by this work compared with reference data

H(x1), H(x2) = Percent deviation of liquid fractions calculated by HYSIM compared with reference data for dew-point pressure

H(P) = Percent deviation of dew-point pressure calculated by HYSIM compared with reference data

Table 9.40 shows percent deviation of dew-point pressure calculated by this work compared with those from HYSIM for ethane and propylene.

Table 9.40 Percent deviation of dew-point pressure calculated by this work compared with those from HYSIM for ethane and propylene

Methods	D(x1)	D(x2)	D(P)
1. SRK	-0.029	-0.039	-0.205
2. PR	0.143	-0.191	0.240

D(x1), D(x2) = Percent deviation of liquid fractions calculated by this work compared with those from HYSIM for dew-point pressure

D(P) = Percent deviation of dew point-pressure calculated by this work compared with those from HYSIM

9.7.3 Bubble-point temperature

Estimation of bubble-point temperature of a mixture of ethane (1) and propylene (2) is testd at pressure 2 bars and various composition (x_i = 0-1). The results are compared with those from HYSIM.

Table 9.41 Percent deviation of bubble-point temperature calculated by this work compared with those from HYSIM for ethane and propylene

Methods	D(y1)	D(y2)	D(T)
1. SRK	-0.103	0.254	0.025
2. PR	-0.087	0.212	-0.072

D(y1), D(y2) = Percent deviation of vapor fractions calculated by this work compared with those from HYSIM for bubble-point temperature

D(P) = Percent deviation of bubble point temperature calculated by this work compared with those from HYSIM

9.7.4 Dew point temperature

Estimation of dew point temperatureof a mixture of ethane(1) and propylene (2) is testd at pressure 2 bars and various composition (y_i = 0-1). The results are compared with those from HYSIM. Table 9.42 shows percent deviation of dew point temperature calculated by this work compared with those from HYSIM for ethane and propylene

Table 9.42 Percent deviation of dew-point temperature calculated by this work compared with those from HYSIM for ethane and propylene

Methods	D(x1)	D(x2)	D(T)
2. SRK	0.267	-0.111	-0.005
3. PR	0.084	-0.043	-0.106

D(x1), D(x2) = Percent deviation of liquid fractions calculated by this work compared with those from HYSIM for dew-point temperature

D(T) = Percent deviation of dew point temperature calculated by this work compared with those from HYSIM

9.7.5 Isothermal flash calculation

1. A mixture of ethane and heptane, at temperature 430 K, pressure 10 bars, mole fractione of ethane 0.2654 and mole fractions of heptane 0.7346, is tested by this program. The results are compared with those from HYSIM.

Table 9.43 Percent deviation of isothermal flash calculated by this work compared with those from HYSIM for ethane and heptane

Methods	Compounds	Dx	Dy	Dk	DL	DV
SRK	ethane	3.97	0.12	-3.71	-0.57	-0.68
	heptane	-0.22	-0.10	-3.71		
PR	ethane	4.35	0.17	-4.01	0.65	-0.76
	heptane	-0.24	-0.17	0.09		

$$\text{Deviation} = \left(\frac{Zth - Zhy}{Zhy}\right) * 100$$

Zhy refers to the values computed by HYSIM

Zth refers to the values computed by this work

Dx = Percent deviation of mole fractions in liquid phase

Dy = Percent deviation of mole fractions in gas phase

Dk= Percent deviation of equilibrium constants

DL= Percent deviation of mole of liquid which is separated by flash calculation

DV= Percent deviation of mole of vapor which is separated by flash calculation

2. A mixture of methane, ethane and propane, at temperature 283.15 K, pressure 13.79 bars, mole fractione of methane 0.1, mole fractions of ethane 0.2, and mole fractions of propane 0.7, is tested by the program. The results of testing are compared with those from HYSIM.

Table 9.44 Percent deviation of isothermal flash calculated by this work compared with those from HYSIM for methane,ethane, and propane

Methods	Compounds	Dx	Dy	Dk	DL	DV
SRK	methane	2.12	0.49	-1.50	0.46	-1.06
	ethane	0.56	-0.20	-0.78		
	propane	-0.18	-0.13	0.05		
PR	methane	2.40	0.67	-1.88	0.61	-1.44
	ethane	0.62	-0.20	0.83		
	propane	-0.22	-0.23	0.00		

$$\text{Deviation} = \left(\frac{Zth - Zhy}{Zhy}\right) * 100$$

Zhy refers to the values computed by HYSIM.

Zth refers to the values computed by this work.

Dx = Percent deviation of mole fractions in liquid phase.

Dy = Percent deviation of mole fractions in gas phase.

Dk= Percent deviation of equilibrium constants

DL= Percent deviation of mole of liquid which is separated by flash calculation.

DV= Percent deviation of mole of vapor which is separated by flash calculation.

Bubble-point pressure

The results show that a mixture of two components, of which bubble point pressure is calculated by SRK and PR equations has percent deviation less than ±2% and a mixture of three components has percent deviation less than ±5% when it is compared with reference data. Raoult's law has percent deviation more than SRK and PR. When this program is compared with HYSIM, a mixture of two component has percent deviation less than ±0.5% and a mixture of three component has percent deviation less than ±4%. Prediction of vapor fractions for bubble point pressure by this program, is more accurate than that of HYSIM.

Dew -point pressure

A mixture of two component, of which dew point pressure is calculated by SRK and PR equations has percent deviation less than ±5% when compare with reference data. This program compare with HYSIM has percent deviation less than ±0.5%.

Bubble-point temperature and dew-point temperature

SRK and PR equations can predict bubble point temperature and dew point temperature accurately. The percent deviation has less than ± 0.5% when it is compared with HYSIM.

Isothermal flash calculation

SRK and PR can calculate isothermal flash accurately when it is compared with HYSIM. The percent deviation of mole fractions in liquid, mole fraction in vapor and equilibrium constants are less than ±4% and the percent deviation of liquid and vapor, which are separated by isothermal flash, are less than ±2%.

The results show that this program can predict vapor-liquid equilibrium accurately. The percent deviation of calculation vapor-liquid equilibrium is a range of ±5%, compared with those of HYSIM. SRK and PR equations are confirmed that they are suitable for calculating vapor-liquid equilibria for nonpolar mixtures. These equations based on mixing rules are not satisfactory for mixtures containing strongly polar and hydrogen-bonded fluids in addition to common gases and hydrocarbons (Robert C. Ried, John M. Praausnitz and Bruce E. Poling, 1987). For those mixtures, the assumption of simple mixing is poor because strong polarity and hydrogen bonding can produce significant segregation. For example, a mixture of water and benzene are only partially miscible at ordinary temperatures because an attraction force between water molecules tends to keep these molecules together and prevent their random mixing with benzene molecules. Water is polar molecules because it has dipole moment values equal to 1.8 debyes. Benzene is nonpolar molecules and dipole moment equal to 0 debyes.

9.8 LIQUID VISCOSITY

Liquid viscosity is tested by the program, compared with reference data (Reid, Prausnitz and Poling, 1987). Four groups of compound used to test, are hydrocarbon (ethane at 298.15 K, n-butane at 268.15 K, 2-methylpentane at 298.15 K, 2-methylhexane at 298.15 K, 2-methylbutane at 298.15 K, cyclopentane at 298.15 K, cyclohexane at 298.15 K, ethylene at 273.15 K, 1-hexene at 298.15 K, benzene at 298.15 K), inorganic compound(argon at 88.15 K, chlorine at 298.15 K, carbondioxide at 298.15 K, nitrogen at 73.15 K), alcohol(methanol at 298.15 K, ethanol at 298.15 K), and halogenated hydrocarbon(carbontetrachloride at 298.15 K, chloroform at 298.15 K).

Table 9.45 shows the conclusion of the percent deviation for liquid viscosity when it is compared with reference data.

Table 9.45 Summary of the percent deviation for liquid viscosity

Compounds	Percent deviation (%)
1. Hydrocarbons	-7.63
2. Inorganic compounds	-0.15
3. Alcohols	-1.84
4. Halogenated hydrocarbons	-1.07

From table 9.45, this program can predict liquid viscosity fairly well when it is compared with reference data. Percent deviation is less than ±8%. The viscosities of liquids decrease with increasing temperature either under isobaric conditions or as saturated liquids. The equations for predicting liquid viscosities should not be used outside the range of temperature which is recommended in this program.

9.9 DATABASE SYSTEM

In this work, we applied Microsolft Excel program is utilized for input basic data which will be stored in form of text files. Excel program is selected because it provides worksheets in form of table which can be used as relational model. Database management system(DBMS) has been developed in C^{++} language using the concept of object-oriented programming. It is used to link the database system to other programs which are developed in the same language. Computer run time for this program is less than 1 minute when it run by a personal computer with a pentium CPU.