

CHAPTER VI

RESULTS OF CALCULATION AND DISCUSSION

6.1 BINARY INTERACTION PARAMETERS

The optimal values of K_{ij} for a particular system in different equations of state are not the same. For Leiva EOS, the results of optimal K_{ij} for the different groups of binary systems as determined in this work are summarized in Tables 6.1 - 6.5

(a) Light Hydrocarbon Binaries (Upto n - decane)

The values of K_{ij} for these systems, except for binaries containing methane, were found to be close to 0.0 as shown in Table 6.1. This supports Soave's conclusion that K_{ij} 's equal zero for nonpolar hydrocarbon mixtures.

For Systems containing methane, the Leiva equation gives K_{ij} values in the range 0.0 - 0.05 as shown in Table 6.2 and Figure 6.1

(b) CO₂-Hydrocarbon Binaries

The optimum values of K_{ij} for systems containing CO₂ were found to lie in the range 0.0 - 0.15 as shown in Table 6.3 and Figure 6.2



(c) $\frac{N}{2}$ -Hydrocarbon Binaries

The optimum values of K_{ij} for these systems are in the range 0.0 - 0.20 as shown in Table 6.4 and Figure 6.3

(d) $\frac{N-CO}{2}$ Binaries

The optimum values of K_{ij} for these systems are 0.0 as shown in Table 6.5

(e) Methane - $\frac{CO}{2}$ Binaries

The optimum values of K_{ij} for these systems are in the range 0.00 - 0.15 as shown in Table 6.5 and Figure 6.4

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Table 6.1 Optimum Values of K_{12} and Bubble Point Deviations Using
Leiva EOS for Hydrocarbon-Hydrocarbon Systems

System	Experimental Data				K_{12} Optimum	AAD	
	Ref.	Temp., K	pressure, atm.	Np		$\Delta P/P\%$	ΔY_1
ETHANE-HEXANE	[36]	298.16	5 - 35	7	0.0000	2.30	0.0048
ETHANE-i-BUTANE	[37]	311.27	10.54- 48.43	12	0.0000	4.08	0.0058
		344.49	13.00- 52.99	10	0.0000	3.37	0.0124
		377.44	23.13- 48.98	9	0.0028	2.83	0.0196
		394.05	31.56- 41.29	5	0.0000	9.15	0.0630
ETHANE-DECANE	[38]	410.94	6.80-114.76	17	0.0000	10.94	0.0054
		444.27	6.80-116.67	18	0.0000	13.70	0.0092
		477.60	6.80-111.56	17	0.0000	13.80	0.0162
		510.90	6.80-100.75	15	0.0000	12.42	0.0372
BUTANE-DECANE	[39]	377.64	1.70- 15.31	9	0.0049	1.72	0.0010
		410.94	3.40-27.21	8	0.0000	2.11	0.0019
		444.27	3.41-41.95	3	0.0000	3.96	0.0059
		477.60	3.40-47.22	14	0.0005	5.64	0.0213
		510.94	6.80-48.57	14	0.0000	6.21	0.0340

Table 6.2 Optimum Values of K_{12} and Bubble Point deviations Using
Using Leiva EOS For METHANE-heavier Hydrocarbon Systems.

System	Experimental Data				K_{12} Optimum	AAD	
	Ref.	Temp., K	Pressure, atm	N_p		$\Delta P/P\%$	ΔY_1
ETHANE	[40]	130.38	1.91- 3.31	4	0.0161	1.04	0.0006
		144.27	1.86- 6.67	7	0.0125	0.41	0.0013
		158.16	1.76-13.55	10	0.0014	2.29	0.0023
		172.05	2.10-23.05	9	0.0050	0.96	0.0020
		186.12	2.50-38.65	11	0.0035	0.97	0.0026
		190.85	2.69-45.60	16	0.0033	0.99	0.0037
		192.40	2.65-46.60	13	0.0050	0.96	0.0069
		193.93	41.65-47.50	7	0.0130	0.38	0.0057
		195.45	35.50-48.50	8	0.0000	0.53	0.0088
		200.93	3.62-50.90	14	0.0000	3.70	0.0076
	[41]	260.00	17.80-65.18	13	0.0000	2.55	0.0219
		270.00	22.53-60.22	10	0.0000	1.48	0.0163
280-00		28.50-62.10	14	0.0000	3.16	0.0325	
n-PROPANE	[42]	130.37	1.84- 2.86	3	0.0170	1.33	0.0000
		144.26	2.11- 7.35	6	0.0244	2.18	0.0001
		158.15	1.70-13.70	8	0.0288	1.38	0.0003
		172.04	2.10-23.35	8	0.0248	0.84	0.0004
		187.54	2.79-39.85	9	0.0221	1.20	0.0009
		192.30	2.04-46.85	13	0.0186	1.10	0.0018

		195.20	2.08-48.25	14	0.0206	0.99	0.0028
		213.71	1.87-64.25	13	0.0121	3.54	0.0092
	[43]	277.00	6.80-100.27	21	0.0000	4.89	0.0238
		294.00	10.20-97.55	19	0.0000	4.86	0.0293
		310.00	13.60-92.04	20	0.0000	5.64	0.0326
n-BUTANE	[44]	166.46	1.36-19.26	8	0.0340	1.32	0.0001
		185-96	1.36-37.35	9	0.0331	1.64	0.0005
		194.11	1.36-46.06	10	0.0226	1.97	0.0011
		210.96	1.36-66.20	10	0.0155	1.98	0.0020
		227.56	3.40-81.44	8	0.0159	3.77	0.0025
		283.16	3.47-95.26	9	0.0009	1.29	0.0072
i-PENTANE	[45]	344.26	41.29-148.05	8	0.0000	6.03	0.0403
		377.56	33.94-129.18	7	0.0000	7.89	0.0443
		410.94	34.76-103.20	6	0.0000	8.23	0.0305
n-HEXANE	[46]	198.05	1.35-68.04	11	0.0435	7.02	0.0045
		210.15	1.37-95.26	10	0.0473	7.24	0.0037
		223.15	1.37-115.68	12	0.0465	5.32	0.0020
		248.15	1.37-149.70	19	0.0430	3.87	0.0026
		273.16	1.70-180-32	20	0.0339	3.90	0.0062
	[47]	298.16	10. -100.	10	0.0252	0.74	0.0075
		323.16	10. -100.	10	0.0146	0.38	0.0095
		348.16	10. -100.	10	0.0061	0.38	0.0109
		373.16	10. -100.	10	0.0000	0.79	0.0148
		423.16	20. -100.	9	0.0000	2.46	0.0387

Table 6.3 Optimum Values of K_{12} and Bubble Point Deviations Using
LEIva EOS For CO_2 -Hydrocarbon Systems

System	Experimental Data				K_{12} Optimum	AAD	
	Ref.	Temp., K	Pressure, atm	N_p		$\Delta P/P\%$	ΔY_1
ETHANE	[48]	250.00	14.23-18.51	13	0.1366	0.58	0.0100
PROPANE	[49]	244.27	4.97-13.42	10	0.1307	1.97	0.0057
		266.49	7.97-25.82	11	0.1314	1.97	0.0076
	[50]	277.60	6.81-37.41	10	0.1270	1.78	0.0090
	294.27	10.22-57.91	15	0.1266	1.02	0.0089	
	310.94	13.62-68.29	18	0.1265	0.68	0.0184	
	327.60	21.44-67.58	14	0.1272	0.53	0.0203	
	344.27	27.25-66.49	11	0.1371	0.43	0.0317	
n-BUTANE	[51]	310.94	4.09-74.60	20	0.1292	1.72	0.0063
		344.27	8.52-80.66	18	0.1224	2.36	0.0219
		377.60	17.33-74.26	13	0.1208	2.50	0.1135
		410.94	30.66-51.64	8	0.0550	2.42	0.1715
i-BUTANE	[51]	310.94	7.14-70.88	12	0.1200	1.71	0.0139
		344.27	21.36-65.03	7	0.1168	0.90	0.0178
		377.60	35.71-61.16	6	0.0952	4.21	0.0267
		394.27	35.65-47.69	4	0.0831	0.48	0.0160
PENTANE	[52]	277.66	2.25-37.06	10	0.1340	5.42	0.0042
		344.16	4.09-91.08	15	0.1193	3.29	0.0151
		377.16	8.99-95.17	9	0.1152	3.84	0.0261
HEPTANE	[53]	310.66	1.84-74.49	17	0.1078	2.36	0.0045
		394.27	11.16-131.36	11	0.0514	3.06	0.0001
		477.21	4.18-114.56	7	0.0000	3.83	0.0310

CO₂-hydrocarbon (continued)

DECANE	[54]	462.50	19.36-50.70	4	0.0478	0.85	0.0016
		476.96	14.25-50.10	4	0.0385	0.76	0.0011
		542.96	19.38-51.00	4	0.0000	0.69	0.0042
		583.66	19.76-50.40	4	0.0000	2.48	0.0317



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N₂-Hydrocarbon (continued)

n-BUTANE	[59]	310.94	35.29-273.86	6	0.1511	19.61	0.0498
		366.49	35.29-205.40	5	0.0496	3.28	0.1544
		399.83	35.29-137.27	4	0.0268	9.26	0.3407
		422.05	62.61- 82.98	4	0.0076	10.96	0.1347
HEXANE	[60]	310.94	17.03-340.62	11	0.1929	7.57	0.0088
		344.27	17.01-340.14	11	0.2042	3.69	0.0184
		377.60	17.03-340.62	11	0.1424	7.64	0.0410
		410.94	17.41-287.07	11	0.0000	15.29	0.0510
		444.27	34.06-199.54	8	0.0000	14.51	0.0984
HEPTANE	[61]	305.38	156.53-681.97	9	0.1896	4.43	0.0073
		352.60	143.64-682.16	6	0.0934	13.05	0.0107
		399.83	205.63-544.71	5	0.0050	11.81	0.0522
		463.16	12.00-238.50	13	0.0000	15.55	0.0801
		497.16	28.00-154.80	9	0.0000	18.40	0.0994
		497.16	31.00-130.50	8	0.0000	5.32	0.0500

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Table 6.5 Optimum Values of K_{12} and Bubble Point Deviations Using Leiva EOS for N_2 - CO_2 and METHANE- CO_2 Systems

System	Experimental Data				K_{12} Optimum	AAD	
	Ref.	Temp., K	Pressure, atm	N_p		$\Delta P/P\%$	ΔY_1
N_2 - CO_2	[62]	220.0	14.89-164.89	10	0.0000	5.40	0.0347
		240.0	20.73-159.37	17	0.0000	11.38	0.0639
		270.0	33.80-119.76	32	0.0000	8.96	0.0731
METHANE- CO_2	[63]	153.16	11.53- 11.60	3	0.0020	0.80	0.0007
		173.16	24.34- 25.18	4	0.1450	0.12	0.0036
		183.16	33.16- 35.38	5	0.1213	0.19	0.0007
		193.16	42.32- 46.75	8	0.1183	0.12	0.0055
		203.16	47.63- 52.67	10	0.1078	0.41	0.0267
		210.16	41.64- 57.50	11	0.1021	1.06	0.0235
		219.27	6.80- 63.83	11	0.0983	3.25	0.0253
		230.00	15.00- 70.47	14	0.0844	3.01	0.0301
		240.00	20.77- 76.71	12	0.0795	3.99	0.0465
		250.00	20.00- 79.88	10	0.0686	2.82	0.0345
	270.00	35.09- 84.08	9	0.0722	2.80	0.0260	

6.1.1 Temperature Dependence of K_{ij}

As shown in Figures 6.1 to 6.4, the K_{ij} values obtained in this study do vary to some degree with temperature. In all the binary systems studied, as the temperature increased, the K_{ij} value would either decreased or remained constant.

The binary interaction parameter for N_2 -hydrocarbon binaries is a strong function of temperature as shown in Figure 6.3. For CO_2 hydrocarbon (Lighter than pentane) binaries, at temperature below $1.1 T_c$ of CO_2 , the variation of K_{ij} with temperature is not significant as shown in Figure 6.2. However, at higher temperature Figure 6.2 does indicate of a possible trend in the variation of K_{ij} with temperature.

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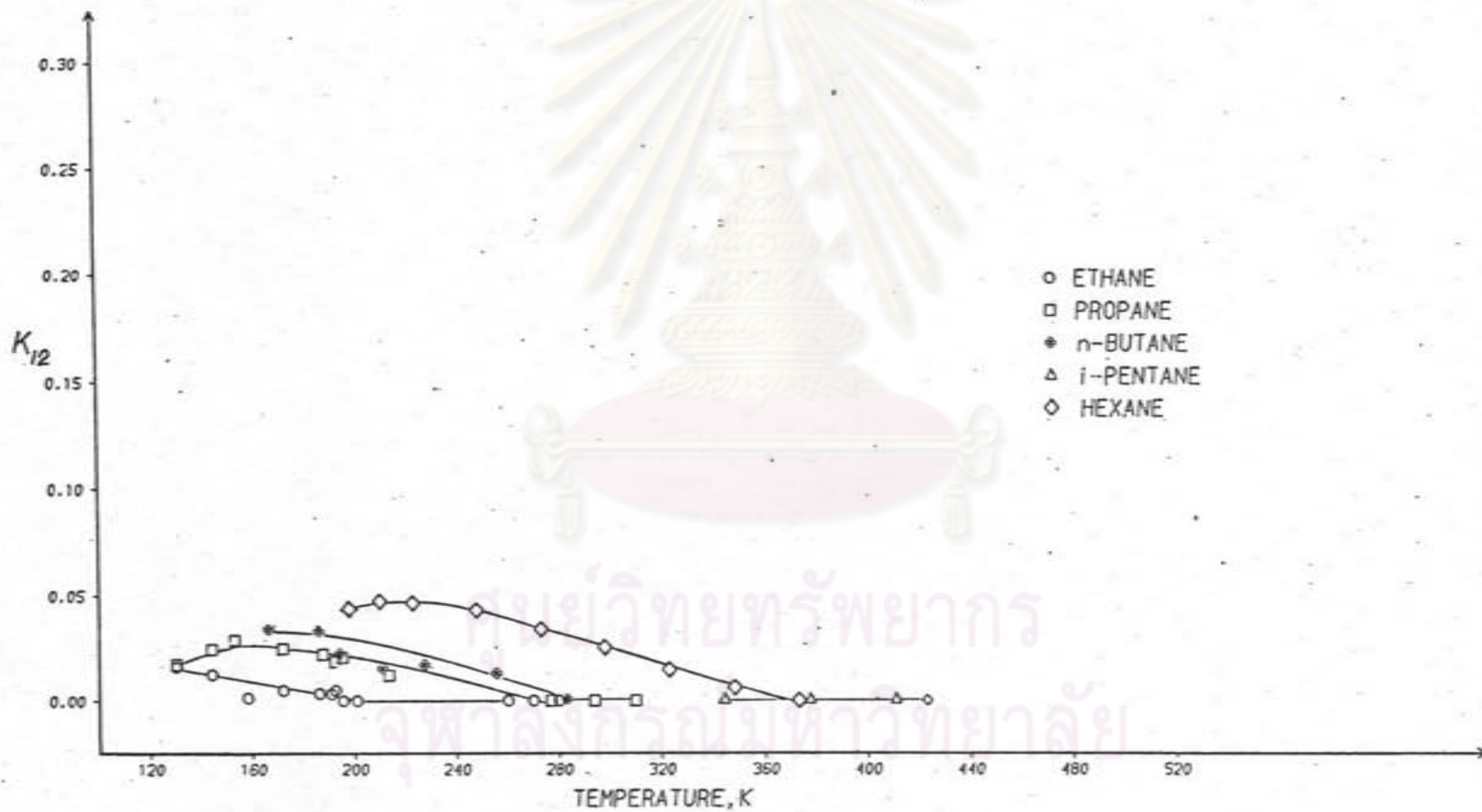


FIGURE 6.1 K_{12} AS A FUNCTION OF TEMPERATURE FOR METHANE-HEAVIER HYDROCARBON SYSTEMS.

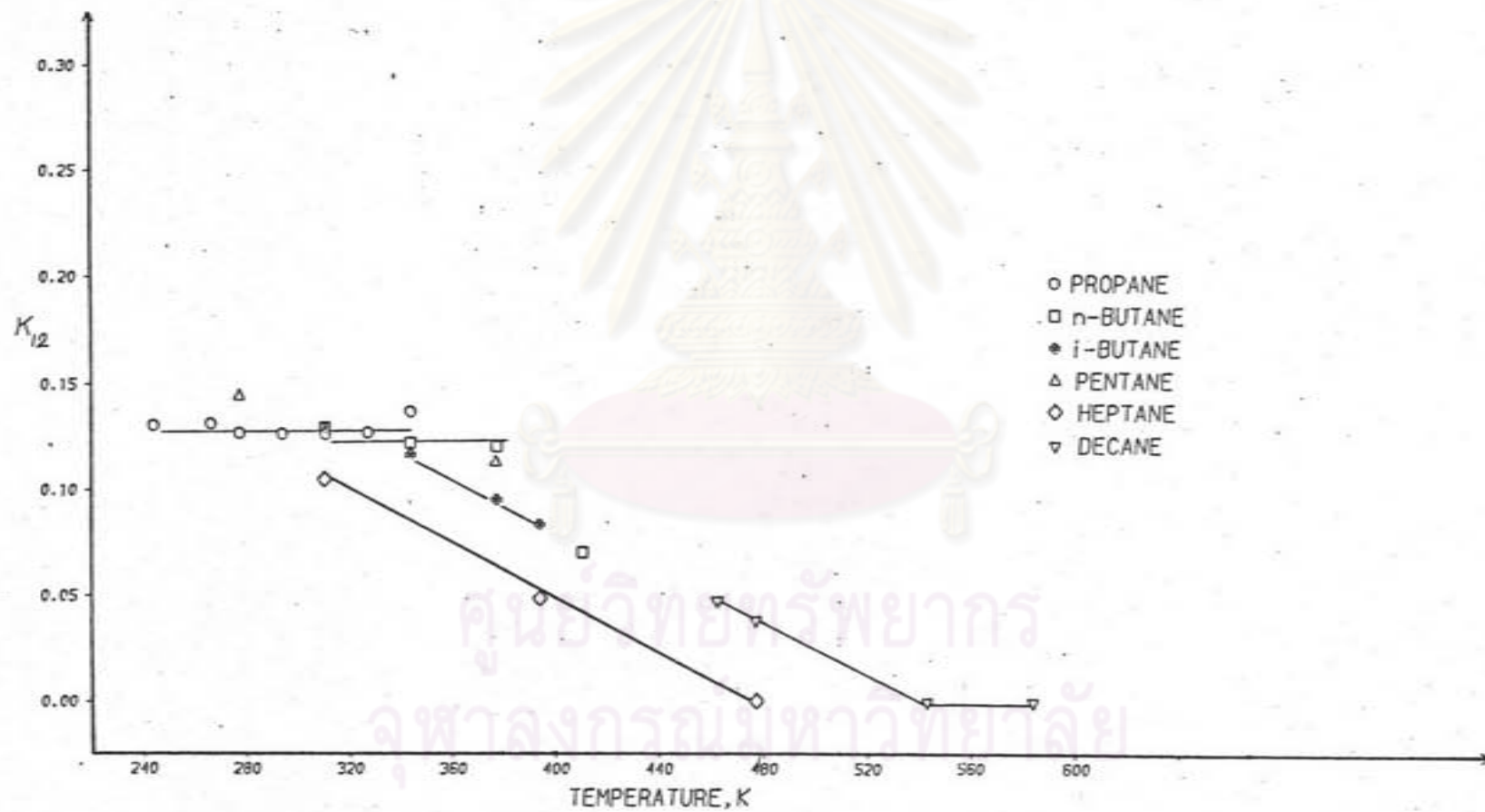


FIGURE 6.2 K_{12} AS A FUNCTION OF TEMPERATURE FOR CO_2 -HYDROCARBON SYSTEMS.

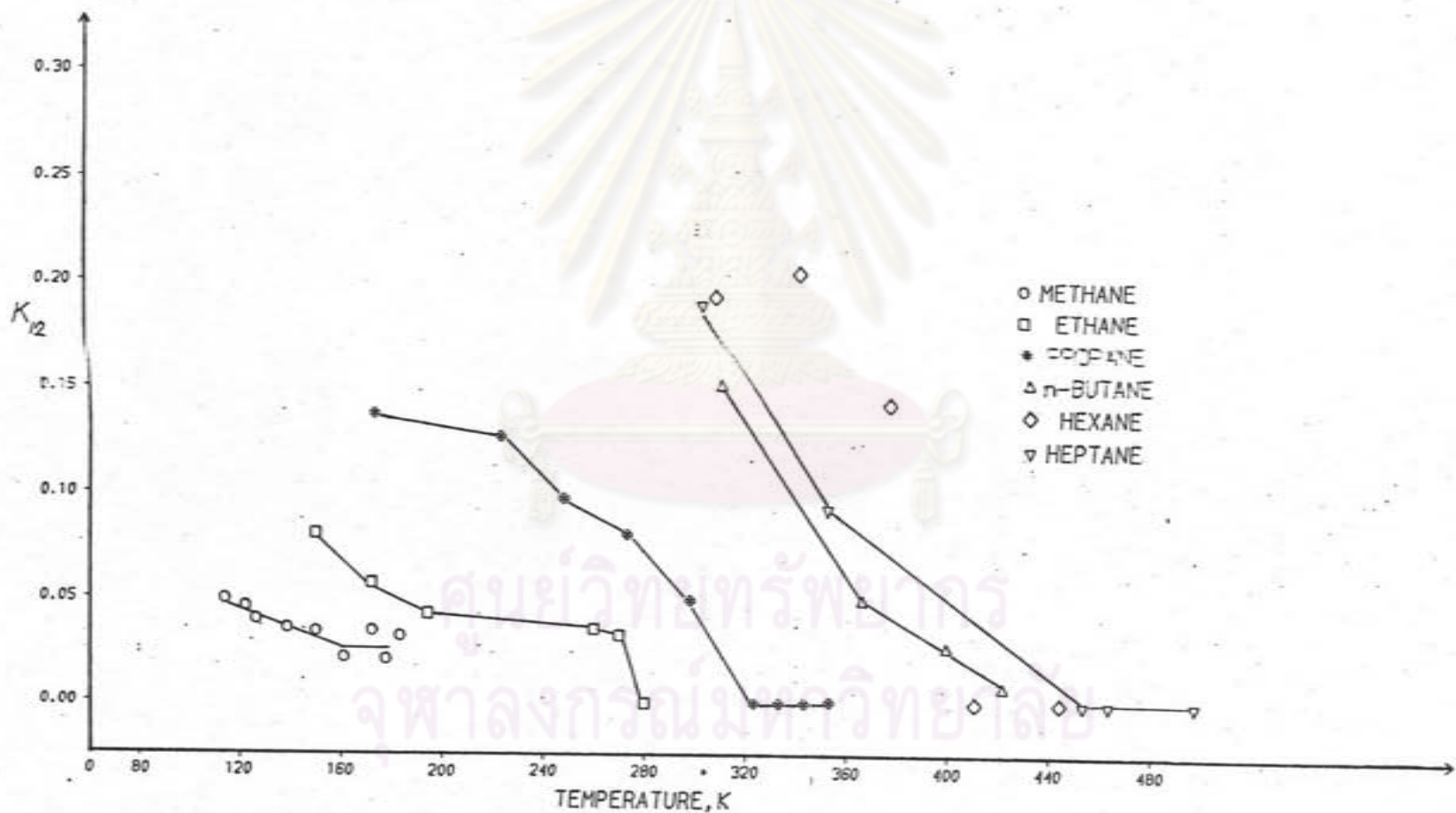


FIGURE 6.3 K_{12} AS A FUNCTION OF TEMPERATURE FOR N_2 -HYDROCARBON SYSTEMS.

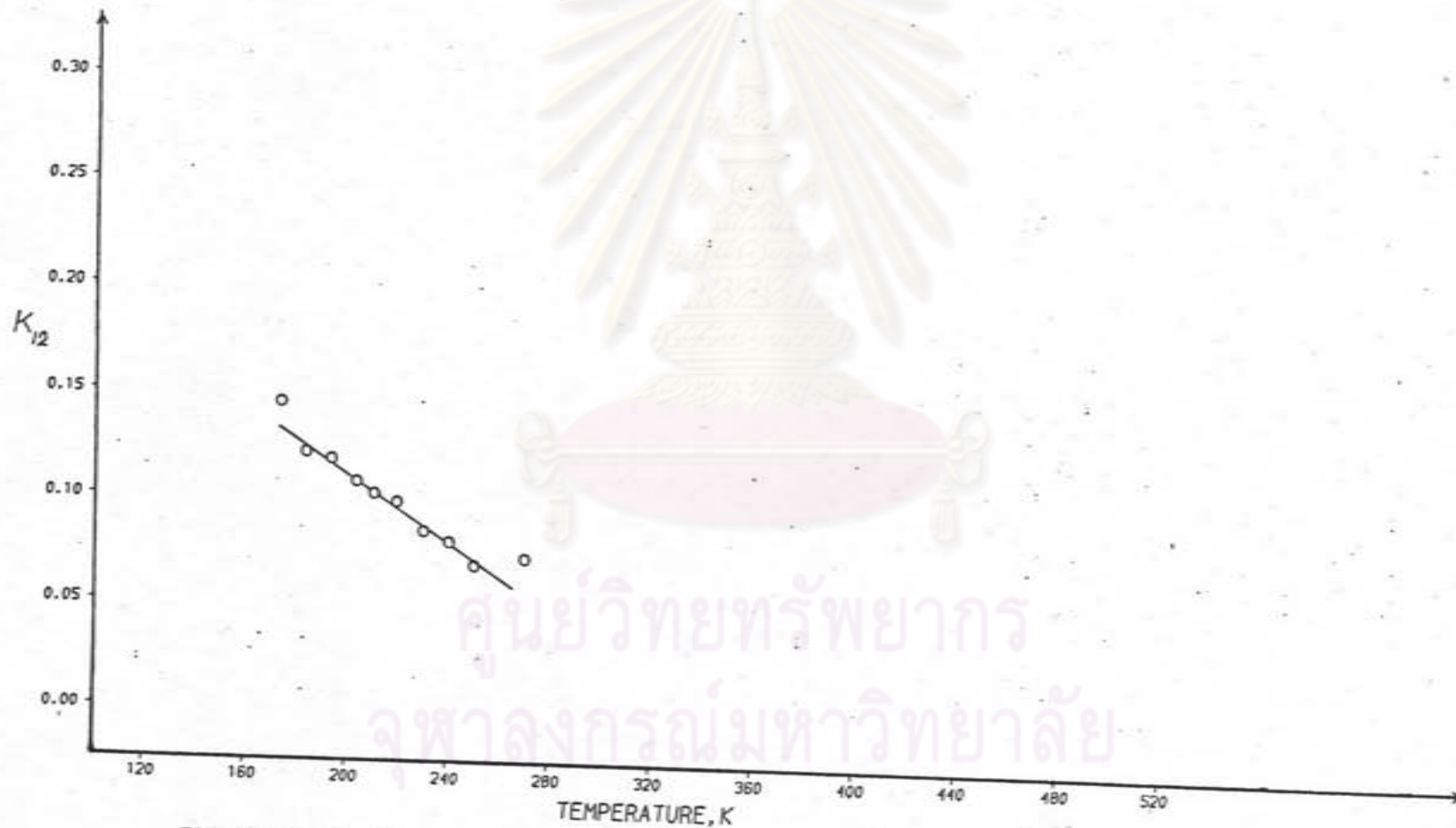


FIGURE 6.4 K_{12} AS A FUNCTION OF TEMPERATURE FOR METHANE - CO₂ SYSTEMS.

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6.1.2 Sensitivity

In order to test the effect of a small change of K_{ij} on the value of predicted P , a sensitivity analysis is necessary.

Sensitivity analysis of K_{ij} are shown in Figures 6.5, 6.6, 6.7 and 6.8 for systems of methane-propane, CO_2 -propane, CO_2 -i-butane and N_2 -propane respectively. The root mean square deviation, σ_P , was used as a mean for sensitivity analysis, and was defined as

$$\sigma_P = 100 \sqrt{\frac{S_P}{N_P}} \quad (6.1)$$

where S_P is the variance as defined by Equation (5.8)

N_P is the number of data points

In general, the sensitivity (flatness of the σ_P curves) were quite low at high temperature, and become high at low temperature. Figure 6.8 showed that a variation of ± 0.010 in interaction coefficients affected the prediction of P significantly at 173.16 K.

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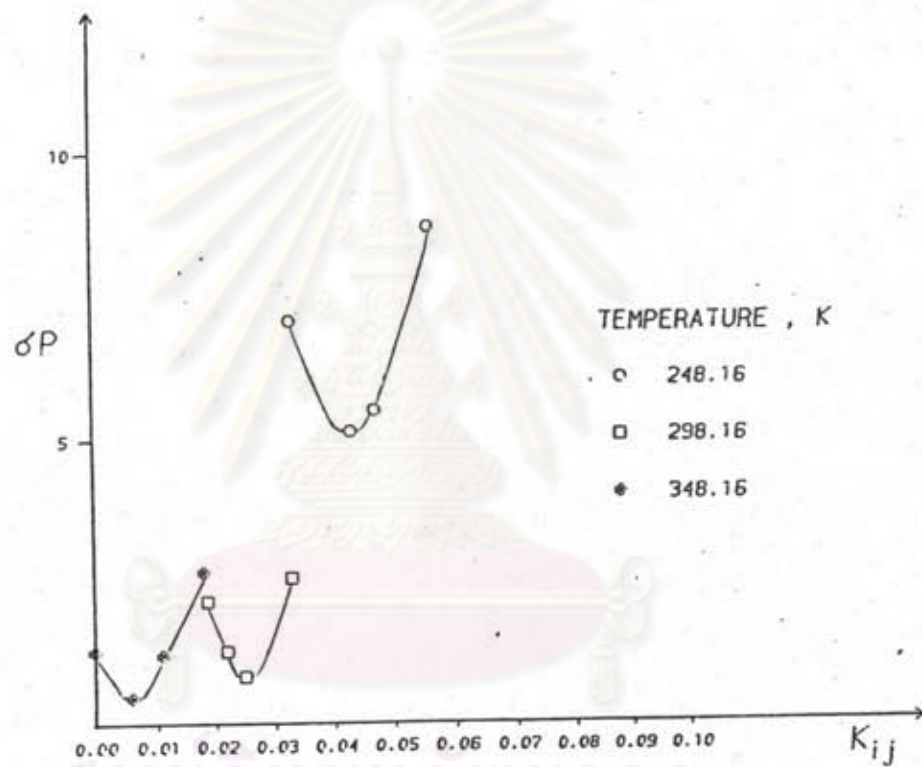


figure 6.5 Sensitivity Analysis for the METHANE-HEXANE SYSTEM.

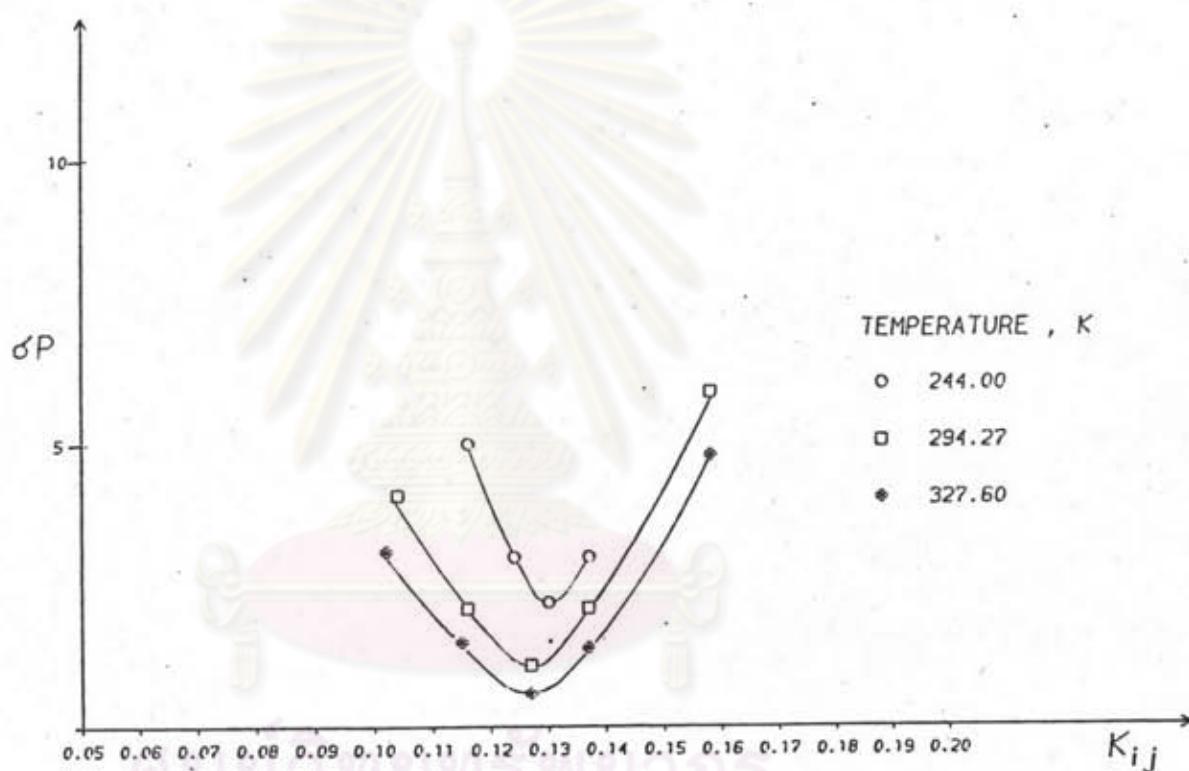


figure 6.6 Sensitivity Analysis for the CO₂-PROPANE SYSTEM.

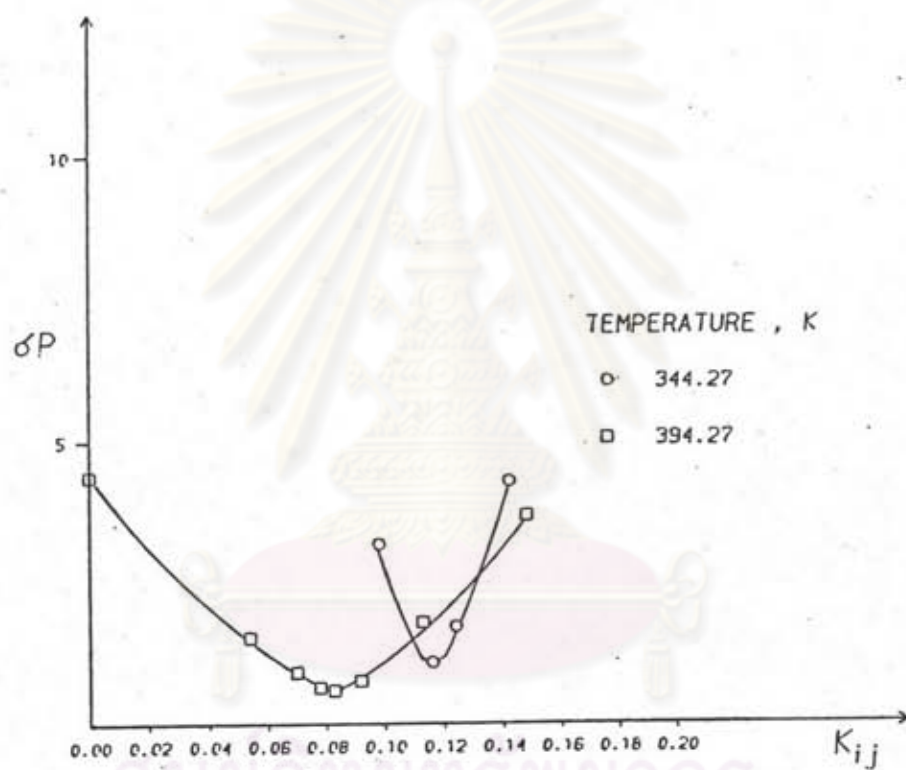


figure 6.7 Sensitivity Analysis for the CO₂-i-BUTANE SYSTEM.

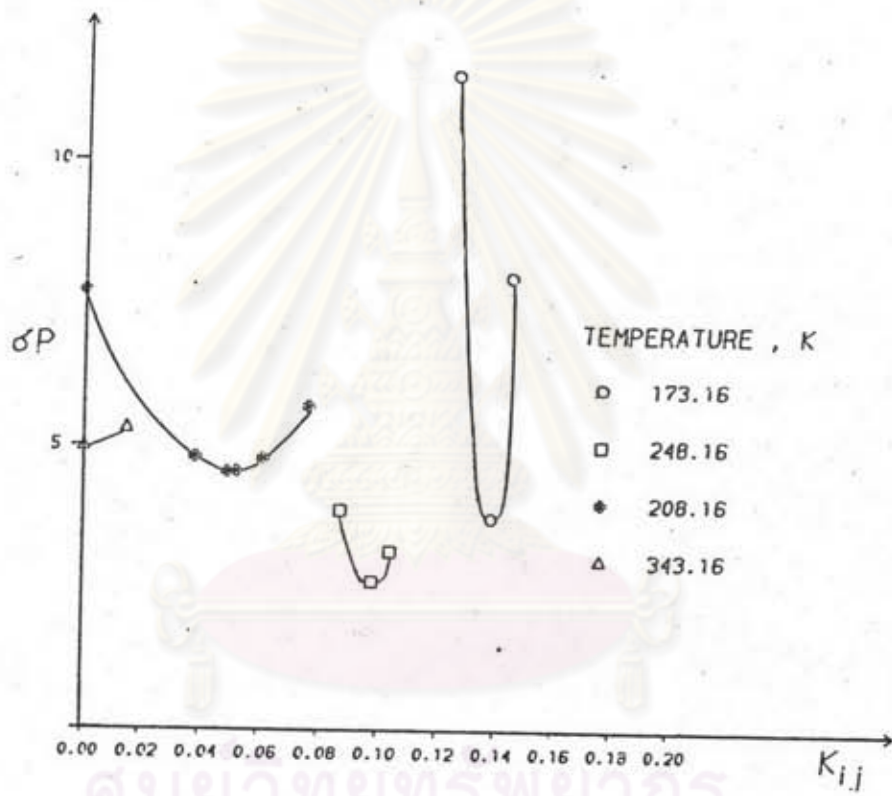


figure 6.8 Sensitivity Analysis for the N_2 -PROPANE SYSTEM.

6.1.3 Vitality of K_{ij}

The incorporation of the binary interaction parameter in the mixing rule of an equation of state increases the accuracy over that can be obtained with no interaction parameter as shown in Figures 6.9 through 6.11. Solid curves are obtained from the Leiva EOS with the optimized K_{ij} and dotted curves are obtained from the Leiva EOS with $K_{ij} = 0.0$.

For system in which K_{ij} has a value much greater than zero, K_{ij} cannot be neglected as shown in Figure 6.9. This figure belongs to CO₂-PROPANE system which has a relatively high value of K_{ij} ($K_{ij} = 0.1037$ at 244.27 K and $K_{ij} = 0.1371$ at 344.27 K). The average deviation between the experimental and calculated bubble point pressure is less than 2 per cent when interaction parameters are used and greater than 11 per cent for no interaction parameters. Similar result is illustrated in Figure 6.10 for N₂-PROPANE system.

For METHANE-ETHANE system at low temperature, the values of K_{ij} are extremely small ($K_{ij} = 0.0014$ and 0.0035 at 158.16 K and 185.12 K respectively), the calculated results do not significantly affected the cases with no interaction parameters as shown in Figure 6.11.

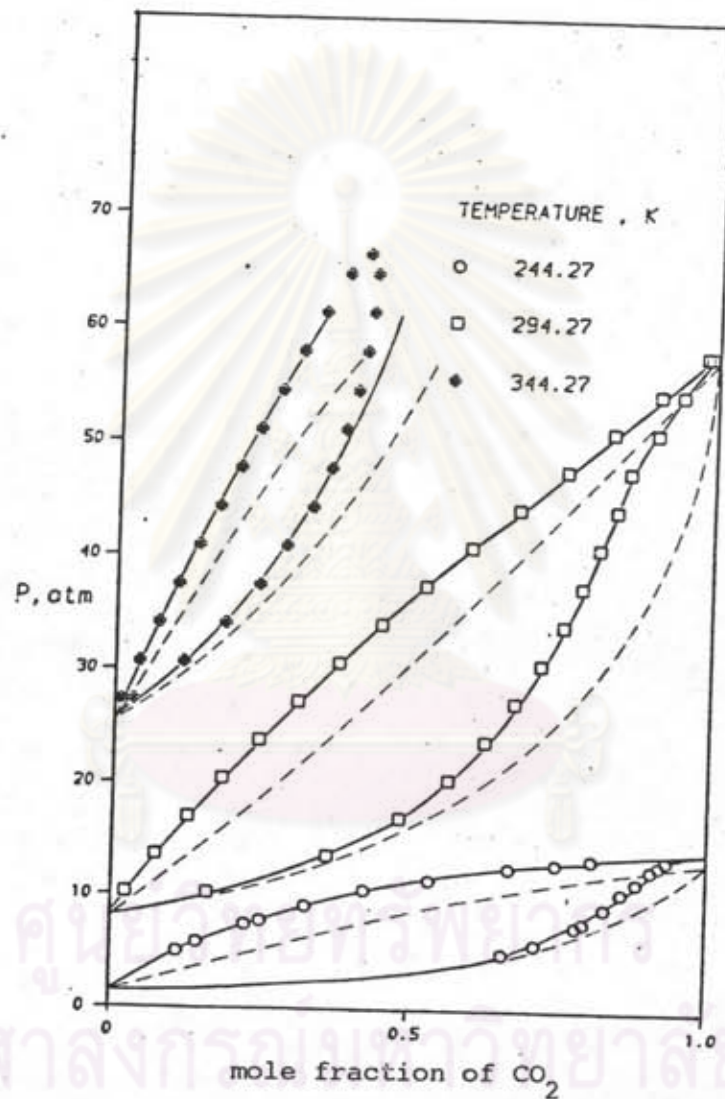


Figure 6.9. Comparison of Calculated and Experimental VLE for CO₂ - PROPANE System.

(— = with K_{ij} , --- = without K_{ij})

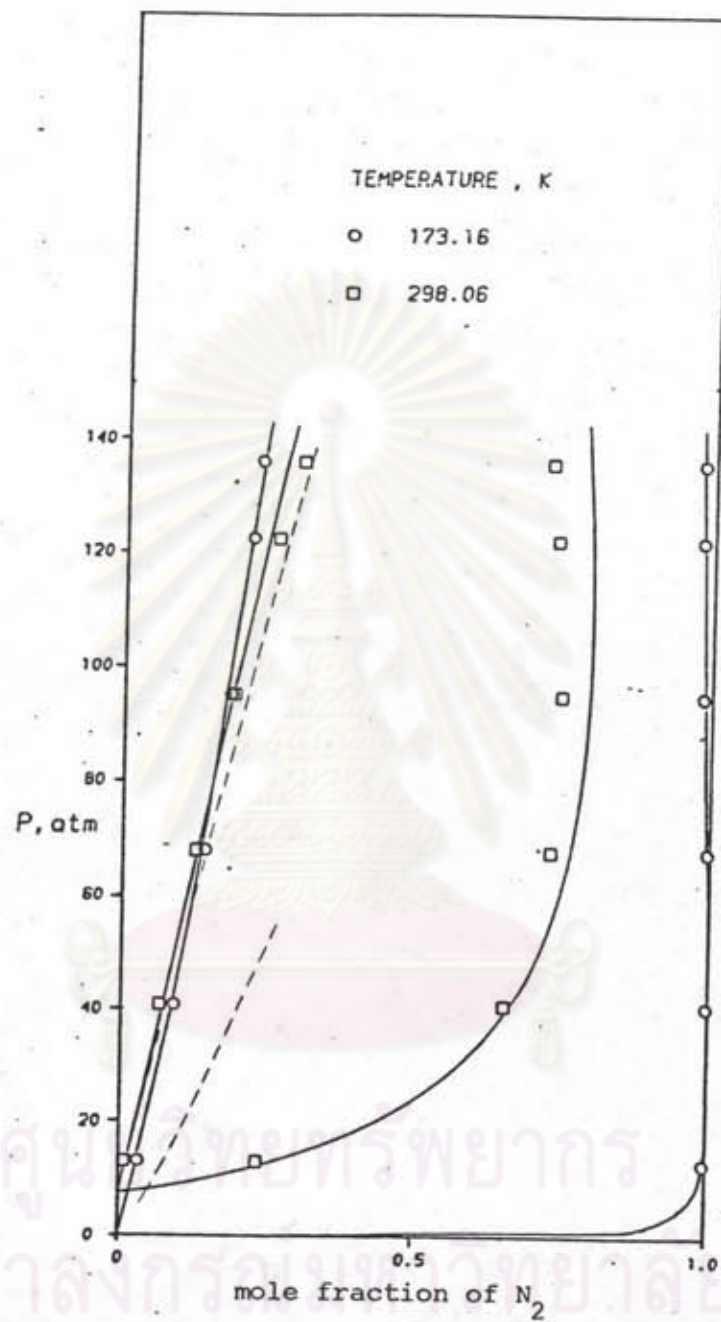


Figure 6.10 Comparison of Calculated and Experimental VLE for N₂ - PROPANE System.

(--- = with K_{ij} , - - - = without K_{ij})

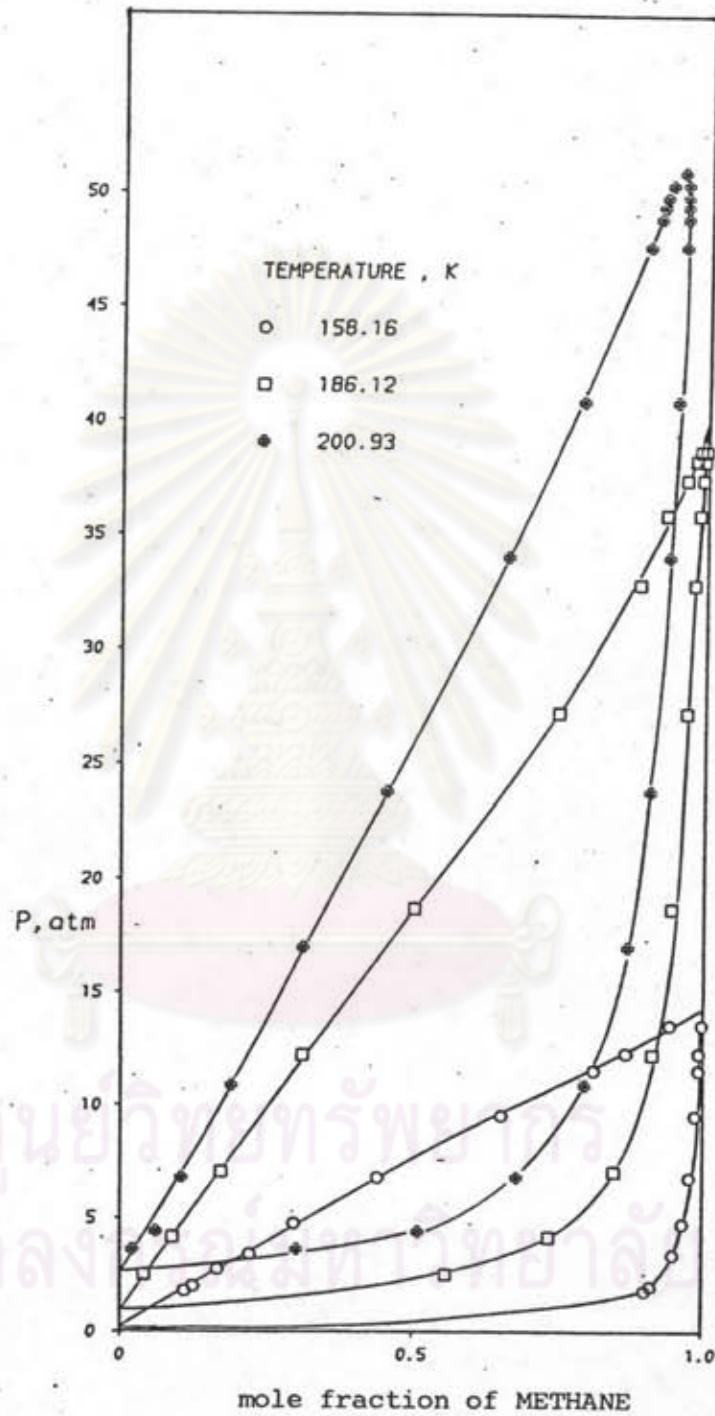


FIGURE 6.11 Comparison of Calculated and Experimental VLE for METHANE-ETHANE System

6.2 LEIVA EOS FOR VLE CALCULATIONS

6.2.1 Binary Systems

The interaction parameters determined for the binary systems (Table 6.1 - 6.5) were then used in bubble point calculations. A Summary of the average absolute deviations (AAD) in relative pressure ($\Delta P/P$) and equilibrium vapor composition (ΔY_1) over a wide range of pressure are reported in Table 6.1 - 6.5

The AAD is defined as

$$\Delta P/P = \frac{\sum_{N_p} |\Delta P/P|_i}{N_p} \quad (6.2)$$

$$\Delta Y_1 = \frac{\sum_{N_p} |\Delta Y_1|_i}{N_p} \quad (6.3)$$

where N_p is the number of data points

The results for the different groups of the binary systems can be summarized as follows.

(a) Light Hydrocarbon Binaries

Figures 6.11 to 6.14 present comparisons of predicted and experimental phase boundaries for a number of light-hydrocarbon binaries containing methane. The calculated P values generally agree very well with the experimental at low temperature. The AAD of calculated pressure were all less than 3% and calculated vapor compositions differ from experimental values by less than 0.003 mole

fraction as shown in Table 6.2. However, at high temperature (where methane is in a supercritical state) accuracy of the prediction is seen to degenerate as the critical pressure is approach, the AAD of the calculated P shifted to within the range of 3-9% and the calculated vapor compositions differ from experimental values by less than 0.04 mole fraction.

The AAD of bubble point calculations for light-hydrocarbon not containing methane are shown in Table 6.1. The percent AAD of predicted bubble point pressures lay in the range 1.72 - 13.80 and calculated vapor compositions differ from experimental values by less than 0.07 mole fraction. Figure 6.14 present comparisons of predicted and experimental phase boundaries for ethane-i-butane system.

(b) CO_2 -Hydrocarbon binaries

Figures 6.9 and 6.15 present comparisons between experimental and model predictions of bubble point pressures and vapor compositions for CO_2 -PROPANE, CO_2 -HEPTANE respectively. As in the case of METHANE-Containing binaries, predictions of behavior at low temperatures were better than those at high temperature. The percent AAD of predicted bubble point pressures lay in the range 0.43 to 0.52 and calculated vapor compositions differ from experimental values by less than 0.03 mole fraction (Table 6.3)

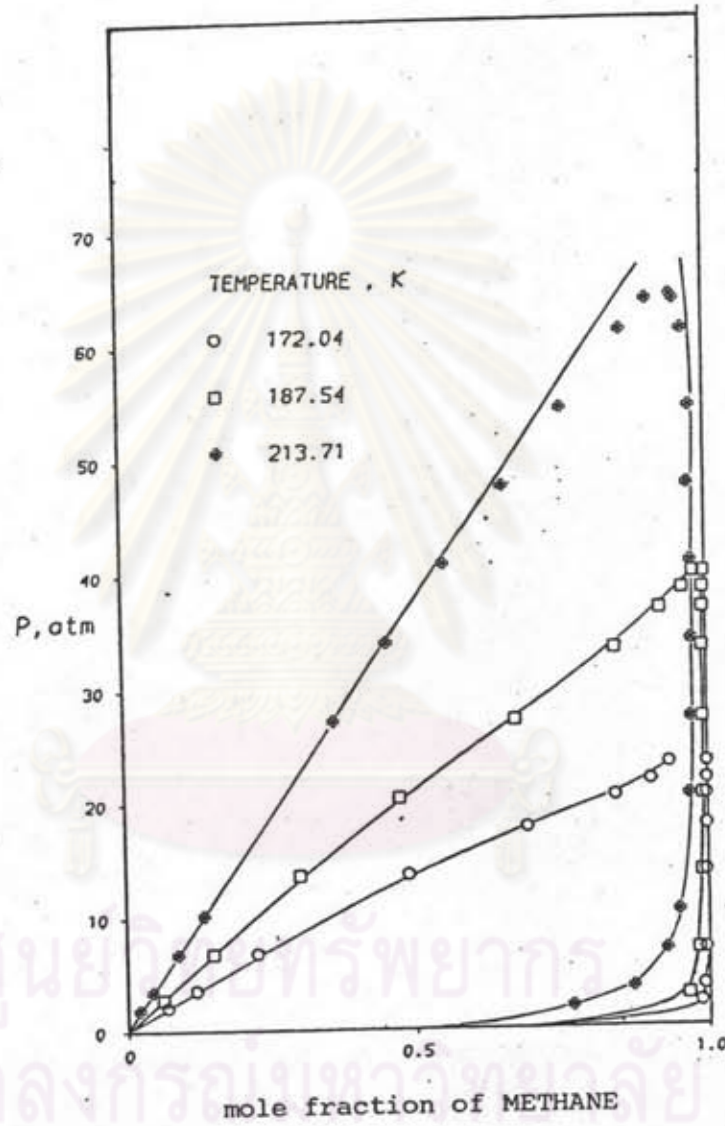


figure 6.12 Comparison of Calculated and Experimental VLE for METHANE-PROPANE SYSTEM.

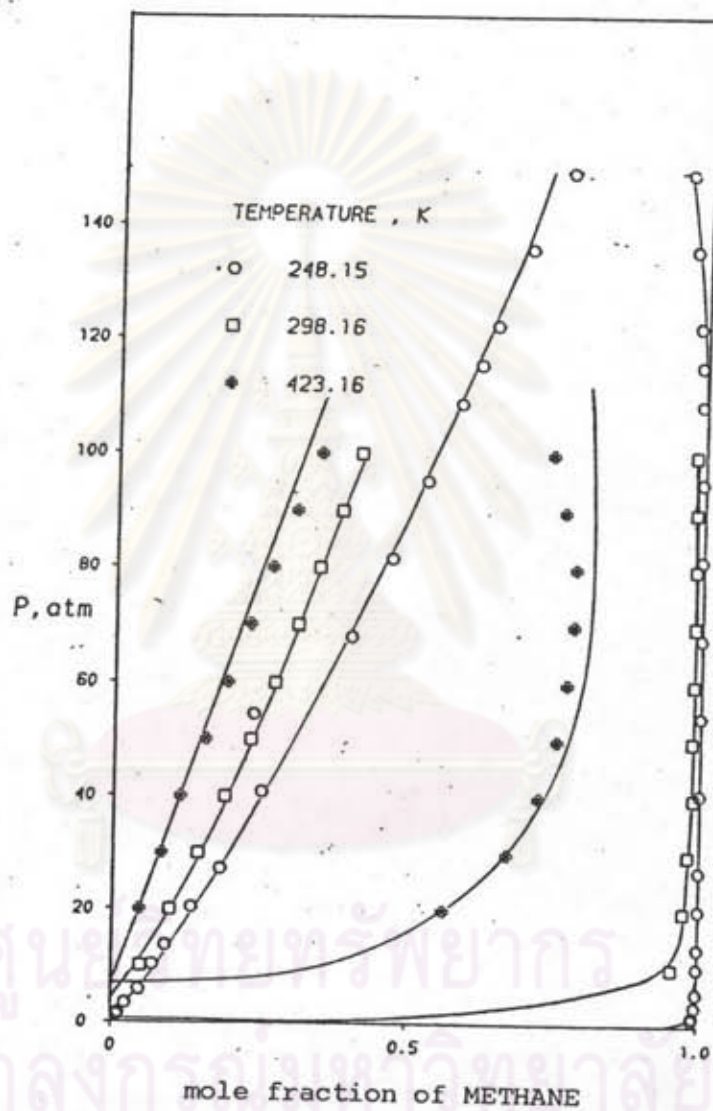


figure 6.13 Comparison of Calculated and Experimental VLE for METHANE-HEXANE SYSTEM.

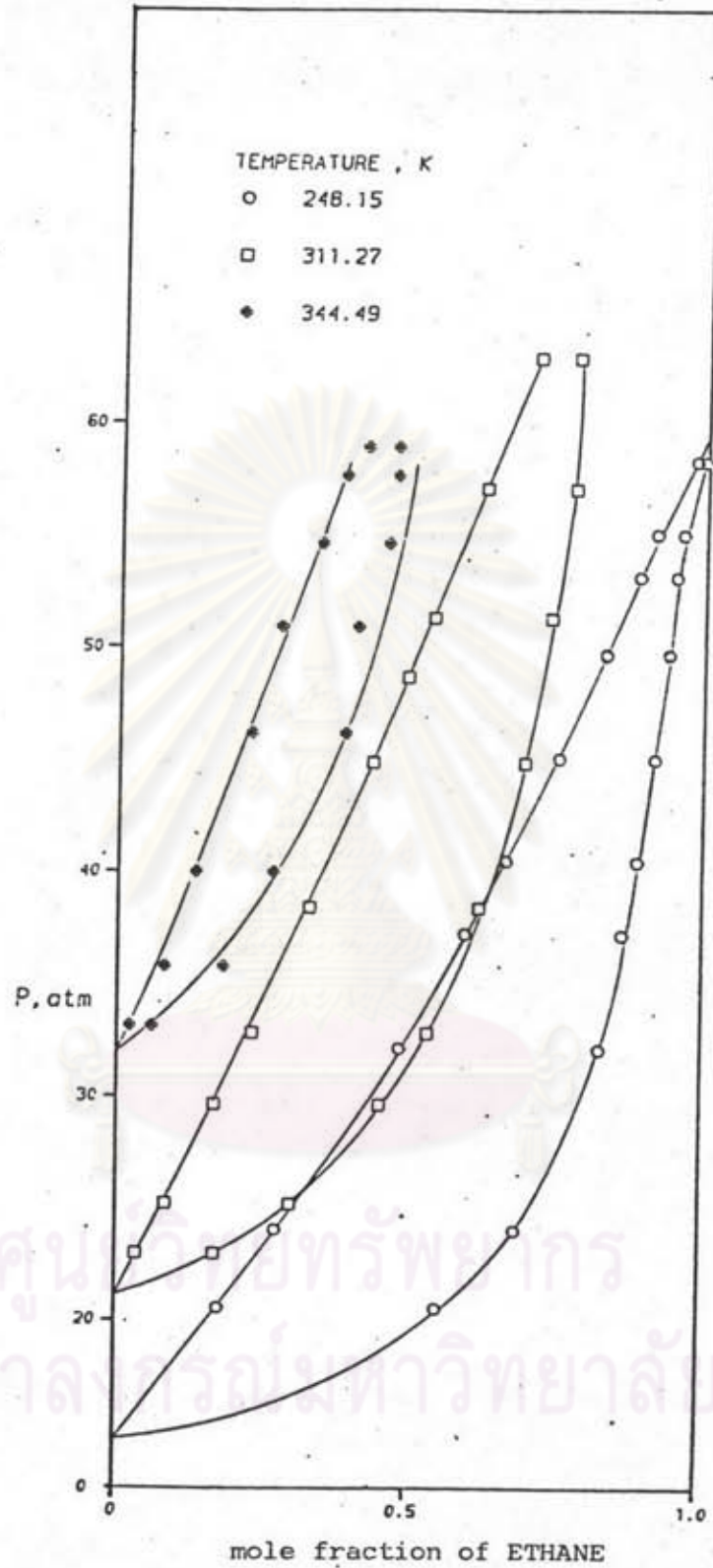


figure 6.14 Comparison of Calculated and Experimental VLE for ETHANE-i-BUTANE SYSTEM.

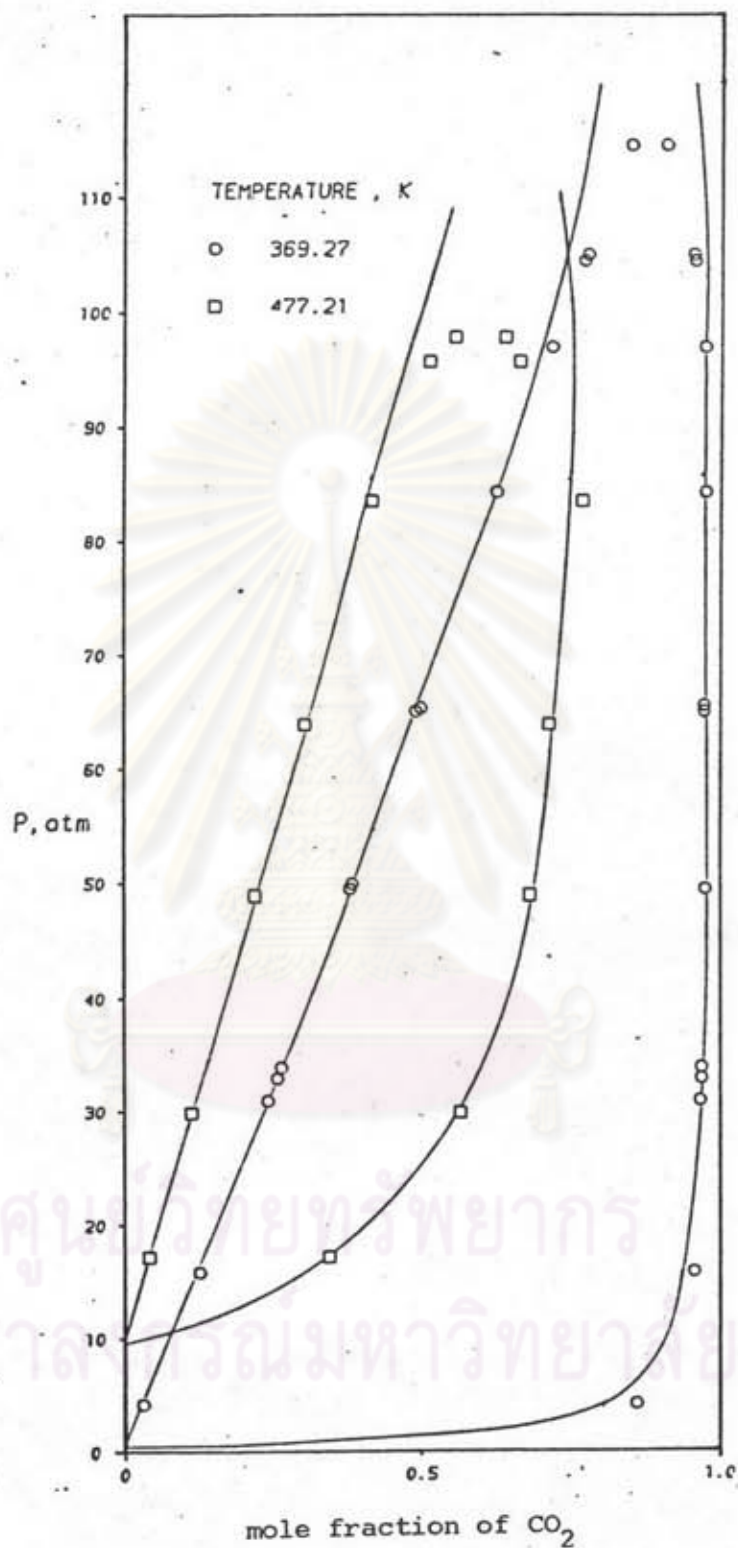


figure 6.15 Comparison of Calculated and Experimental VLE for CO₂-HEPTANE SYSTEM.

c) N_2 -Hydrocarbon Binaries

The AAD of bubble point calculations of these binaries are shown in Table 6.4. For N_2 -METHANE binary, the AAD did not exceed 1.66 percent for bubble point pressure predictions and less than 0.03 mole fraction for calculated vapor composition. For N_2 -larger hydrocarbon molecules binaries, the AAD became larger and in some cases it reached 19.67 percent for calculated P and 0.34 mole fraction for calculated vapor composition.

The relatively high deviations of calculated bubble point pressures from experimental measurements indicates that the Leiva equation may be unacceptable for binary phase equilibrium calculations involving N_2 .

Figure 6.16 and 6.10 give isothermal pressure composition diagrams for N_2 -METHANE and N_2 -PROPANE mixtures

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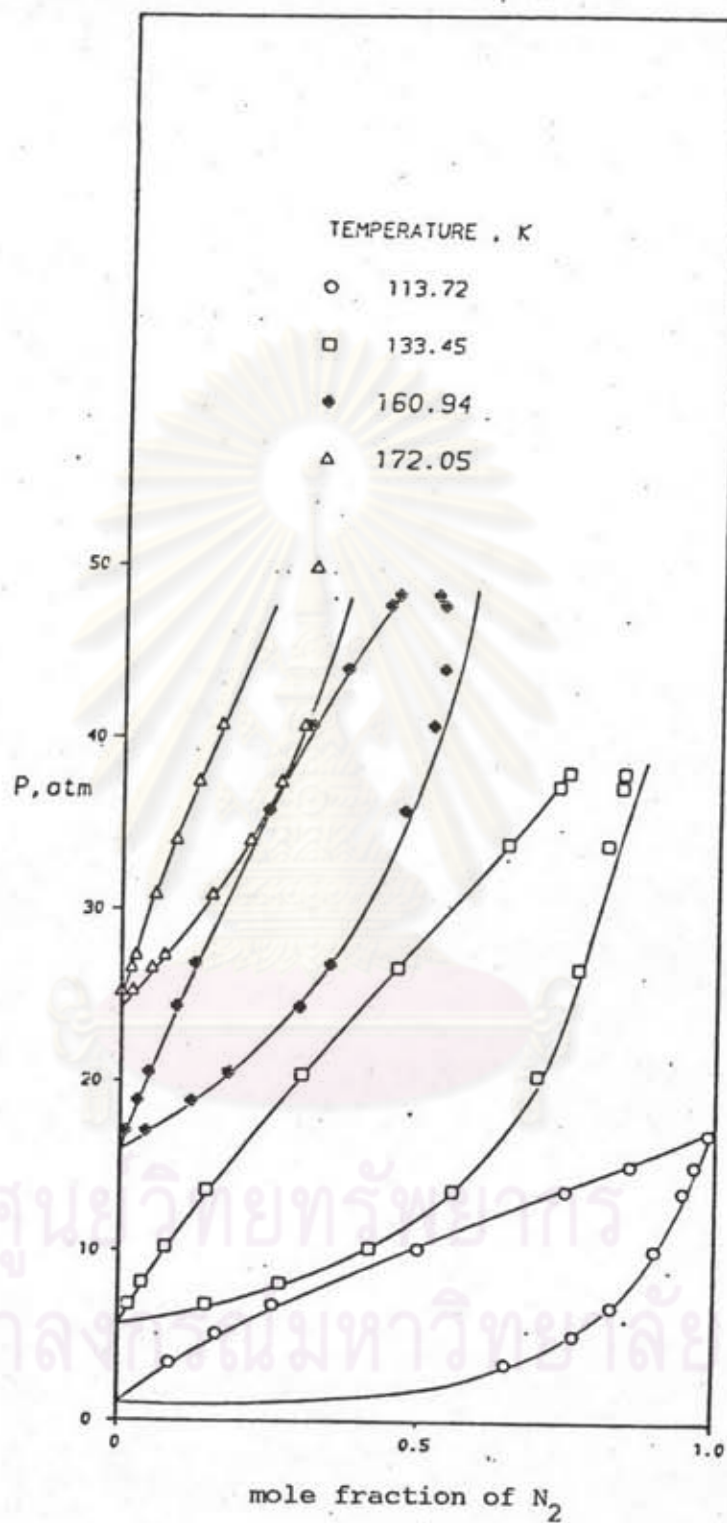


figure 6.16 Comparison of Calculated and Experimental VLE for N₂-METHANE SYSTEM.

6.2.2 Multicomponent Systems

The Leiva equation was tested for multicomponent VLE predictions against the synthetic natural gas mixtures investigated by Yamaborough [68]. For the Leiva equation, the K_{ij} were derived from Table 6.1 - 6.5 (Figure 6.1 - 6.4). In most cases, interpolation and extrapolation of the tabulated data were required. The results are presented in Table 6.6 and 6.9 for the K_{ij} values for mixtures of n-paraffin hydrocarbon with and without the nonhydrocarbon components respectively.

Table 6.7 and 6.10 present the percent AAD in bubble point calculations for mixtures of n-paraffin hydrocarbon with and without N_2 , CO_2 at 366.49 K respectively. For hydrocarbon - hydrocarbon binaries, the binary interaction parameters were all set to zero. In general, the agreement between experimental and model predictions are good. However, the percent AAD in calculated P become larger when mixture containing N_2 and CO_2 . In Table 6.10 the percent AAD in bubble point calculations is also presented at 310.94 and 338.72 K.

ศูนย์วิทยทรัพยากร
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Table 6.6 Values of Binary Interaction Parameters for n-Paraffin Hydrocarbon Mixture at 360.49 K.

i	j	K_{ij}
METHANE	ETHANE	0
	PROPANE	0
	PENTANE	0
	HEPTANE	0
	DECANE	0
ETHANE	PROPANE	0
	PENTANE	0
	HEPTANE	0
	DECANE	0
PROPANE	PENTANE	0
	HEPTANE	0
	DECANE	0
PENTANE	HEPTANE	0
	DECANE	0
HEPTANE	DECANE	0

Table 6.7 Deviations in Bubble Point Pressure Calculation for n-paraffin Hydrocarbon at 366.49 K, 17-206 atm, using Leiva EOS

$ \Delta P/P _{av} \cdot 100\%$		9.66
ΔY	METHANE	0.0196
	ETHANE	0.0027
	PROPANE	0.0029
	PENTANE	0.0060
	HEPTANE	0.0050
	DECACANE	0.0027

Table 6.8 % AAD in K-value for n-paraffin Hydrocarbon at 366.49 K

METHANE	8.494
ETHANE	2.954
PROPANE	3.476
PENTANE	8.583
HEPTANE	18.876
DECANE	20.082



Table 6.9 Values of Binary Interaction Parameters for n-Paraffin Hydrocarbon Mixtures, Containing N_2 and CO_2 .

i	j	K_{ij}			
		310.94 K	338.72 K	366.49 K	
N_2	METHANE	0.025	0.025	0.025	
	CO_2	0	0	0	
	ETHANE	0	0	0	
	PROPANE	0.020	0	0	
	PENTANE	0.050	0.050	0.050	
	HEPTANE	0.170	0.120	0.083	
	DECANE	0.100	0.100	0.100	
METHANE	CO_2	0.010	0	0	
	ETHANE	0	0	0	
	PROPANE	0	0	0	
	PENTANE	0	0	0	
	HEPTANE	0.020	0.010	0	
	DECANE	0	0	0	
	CO_2	ETHANE	0.137	0.137	0.130
PROPANE		0.130	0.130	0.130	
PENTANE		0.120	0.120	0.120	
HEPTANE		0.100	0.082	0.067	
DECANE		0.138	0.125	0.100	
ETHANE		PROPANE	0	0	0
		PENTANE	0	0	0
	HEPTANE	0	0	0	
	DECANE	0	0	0	
PROPANE	PENTANE	0	0	0	
	HEPTANE	0	0	0	
	DECANE	0	0	0	
PENTANE	HEPTANE	0	0	0	
	DECANE	0	0	0	
HEPTANE	DECANE	0	0	0	

Table 6.10 Deviations in Bubble Point Pressure Calculation for multicomponent System

		310.94K 15-206 atm	338.72K 17-206 atm	366.49K 17-206 atm
$ \Delta P/P _{av} \cdot 100\%$		6.67	11.88	13.87
ΔY	N ₂	0.001	0.0003	0.0020
	METHANE	0.0309	0.0193	0.018E
	CO ₂	0.0005	0.0004	0.0007
	ETHANE	0.0033	0.0038	0.0026
	PROPANE	0.0030	0.0034	0.0078
	PENTANE	0.0052	0.0055	0.0046
	HEPTANE	0.0036	0.0038	0.0038
	DECANE	0.0027	0.0024	0.0028

Table 6.11 % AAD in K-value for Multicomponent System.

	310.94K	338.72K	366.49K
N ₂	10.379	-8.817	2.212
METHANE	3.945	12.971	7.784
CO ₂	20.182	14.519	17.801
ETHANE	2.816	4.573	4.653
PROPANE	5.285	5.880	4.010
PENTANE	10.936	11.602	12.725
HEPTANE	19.931	19.729	23.116
DECANE	41.004	28.105	36.596

6.3 COMPARISONS WITH THE SOAVE EOS

6.3.1 The Binary VLE Calculations

Comparisons of the calculated VLE results were made between the Leiva equation and the SOAVE equation. The data set used for this study was a representative one composed mainly of substances important to natural gas system. The following 3 binary systems at 21 isothermal conditions were studied; CO₂-PROPANE, METHANE-CO₂, METHANE-HEXANE.

The optimum values of K_{ij} obtained for the 3 binary systems for both equations are shown in Figure 6.17 and Table 6.12 - 6.16. The temperature effect on the K_{ij} values obtained with SOAVE equation is more profound.

The calculated results of these two methods for 3 binary systems are presented in Table 6.12 -6.14. The two methods are compared on the basis of root mean square (RMS) deviations in relative pressure and vapor composition.

The RMS is defined as

$$RMS = 100 \sqrt{\frac{d_i^2}{N_p}} \quad (6.3)$$

where d_i is the error (either absolute or relative) and N_p is the number of data points.

At low temperature, the results are found to be comparable among these equations which all show good agreement with the

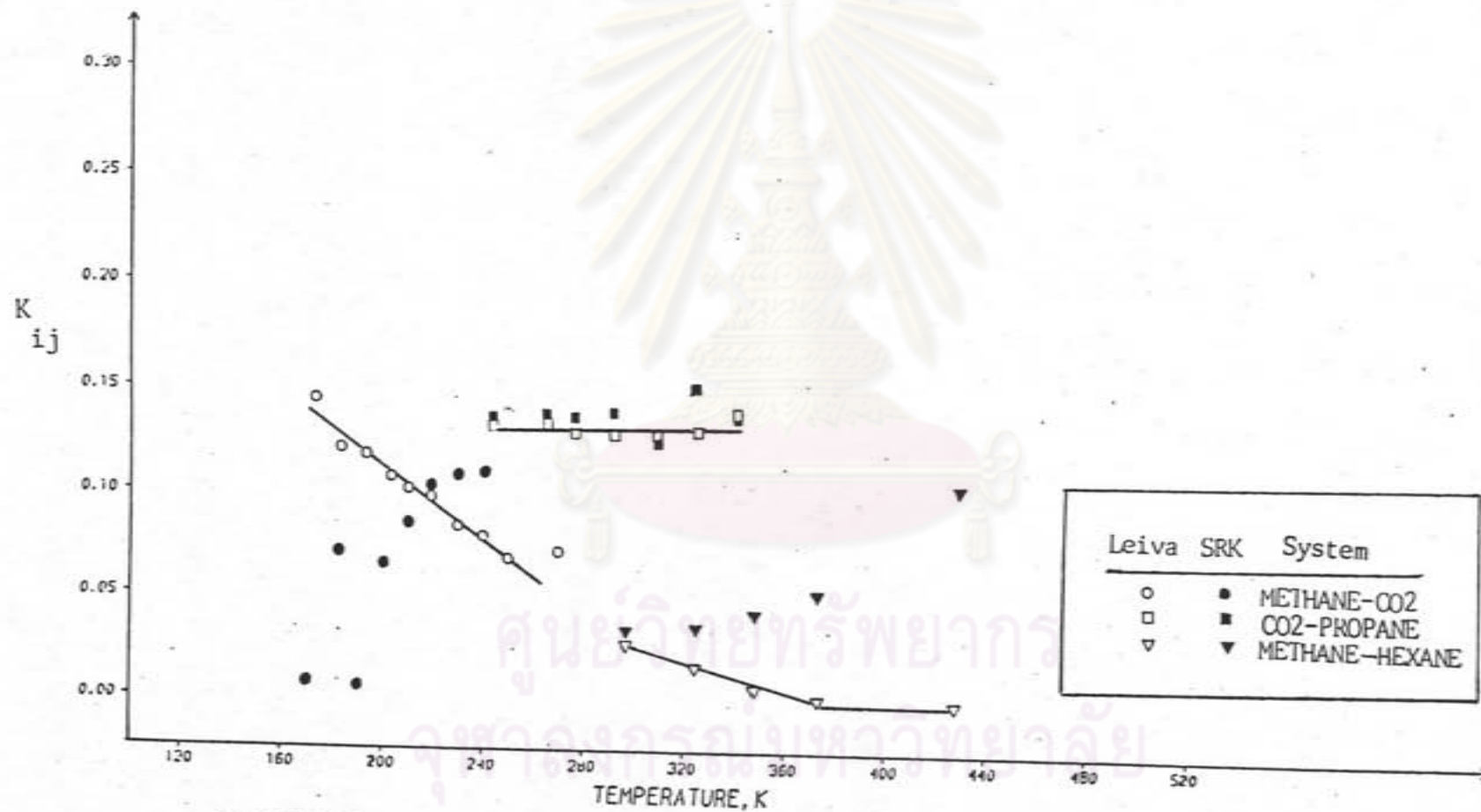


FIGURE 6.17 K_{12} AS A FUNCTION OF TEMPERATURE

literature data. However, at high temperature better results have been obtained with the Leiva equation.

As an example, Table 6.13 and 6.14 presents a comparison between the experimental data of Hamam and LU (1976) and the calculated values for the CO₂-PROPANE system at two temperatures, 294.27 and 344.27 K. At temperature 294.27 K, the experimental data are predicted with errors in the calculated pressure of less than 2 percent from both equations as shown in Table 6.13. However at higher temperature, at 344.27 K, the temperature is above the critical temperature of CO₂. From Figure 6.18, it can be seen qualitatively that, in the lower pressures region up to about 35 atm for the 344.27 curve both equations are in good agreement. However at higher pressures up to the critical region, the agreement is better with Leiva equation. The quantitative superiority of the Leiva equation can be seen in Table 6.14, that the error in relative pressure ($\Delta P/P$) are greatly reduced using Leiva EOS for high pressures region.

It was found in this study that one significant drawback of the SOAVE EOS was in the difficulty in obtaining its solution (roots) by normal method at high pressure above a certain pressure. Consequently one cannot obtain correct saturated pressure near critical point using the SOAVE EOS (marked by * in Table 6.14).

Figure 6.19 gives the METHANE-CO₂ pressure - composition diagram at 210.16 and 219.27 K.

Table 6.12 Optimum Values of K_{ij} and Bubble Point Deviation for $\text{CO}_2(1)$ -Propane(2) Mixtures. Comparison between SRK and Leiva Equations of State.

Temp., K	No. of Points	Optimum K_{12}		$\Delta P/P \%$		$\Delta Y1$		CPU time	
		SRK	Leiva	SRK	Leiva	SRK	Leiva	SRK	Leiva
244.26	10	0.1341	0.1307	2.22	2.20	0.0056	0.0064	0.90	0.84
266.49	11	0.1356	0.1310	2.24	2.23	0.0072	0.0088	1.16	1.09
277.60	10	0.1317	0.1270	1.77	2.27	0.0088	0.0105	1.18	1.14
294.27	15	0.1350	0.1266	0.66	1.12	0.0056	0.0089	2.53	2.16
310.94	18	0.1231	0.1265	5.43	0.68	0.0208	0.0184	3.96	3.92
327.60	14	0.1492	0.1272	8.95	0.53	0.0536	0.0465	3.32	2.96
344.27	11	0.1350	0.1371	15.44	1.58	0.0425	0.0473	5.65	2.99
Overall Average				5.24	1.52	0.0206	0.0209		

Table 6.13 Experimental and Calculated Results for CO₂-PROPANE System at 294.27 K.

NO.	EXPERIMENTAL			CALCULATED P, atm		$\Delta P/P \%$	
	P, atm	Y ₁	X ₁	SOAVE	Leiva	SOAVE	Leiva
1	10.22	0.1618	0.0245	10.23	10.10	0.09	1.13
2	13.62	0.3589	0.0742	13.48	13.36	1.01	1.89
3	17.03	0.4812	0.1274	16.85	16.75	1.05	1.66
4	20.44	0.5634	0.1834	20.27	20.19	0.83	1.23
5	23.84	0.6235	0.2423	23.71	23.67	0.55	0.73
6	27.25	0.6718	0.3048	27.19	27.19	0.22	0.22
7	30.66	0.7148	0.3727	30.77	30.83	0.35	0.55
8	34.06	0.7518	0.4443	34.32	34.45	0.77	1.15
9	37.47	0.7814	0.5173	37.77	37.96	0.79	1.13
10	40.87	0.8092	0.5937	41.17	41.41	0.72	1.31
11	44.28	0.8368	0.6722	44.58	44.84	0.68	1.25
12	47.69	0.8673	0.7516	48.03	48.23	0.70	1.13
13	51.09	0.9011	0.8275	51.37	51.43	0.55	0.67
14	54.50	0.9417	0.9046	54.74	54.60	0.44	0.18
15	57.91	0.9874	0.9805	57.70	57.38	0.36	0.91
	ADD					0.61	1.02
	RMS					0.66	1.12

Table 6.14 Experimental and Calculated Results for CO₂-PROPANE System
at 344.27 K

NO.	EXPERIMENTAL			CALCULATED P, atm		$\Delta P/P\%$	
	P, atm	Y1	X1	SOAVE	Leiva	SOAVE	Leiva
1	27.25	0.0315	0.0099	27.44	27.25	0.72	0.29
2	30.66	0.1153	0.0409	30.55	30.76	0.37	0.32
3	34.06	0.1832	0.0726	33.68	34.23	1.11	0.51
4	37.47	0.2377	0.1043	36.78	37.67	1.84	0.55
5	40.87	0.2800	0.1370	39.91	41.18	2.34	0.76
6	44.28	0.3218	0.1698	43.00	44.65	2.89	0.83
7	47.69	0.3513	0.2019	45.94	47.99	3.67	0.63
8	51.09	0.3743	0.2328	48.69	51.15	4.71	0.11
9	54.50	0.3930	0.2666	*45.82	54.52	15.93	0.04
10	57.91	0.4068	0.2998	47.22	57.75	18.46	0.28
11	61.31	0.4162	0.3348	47.83	61.01	21.99	0.50
ADD						6.73	0.44
RMS						10.15	0.50

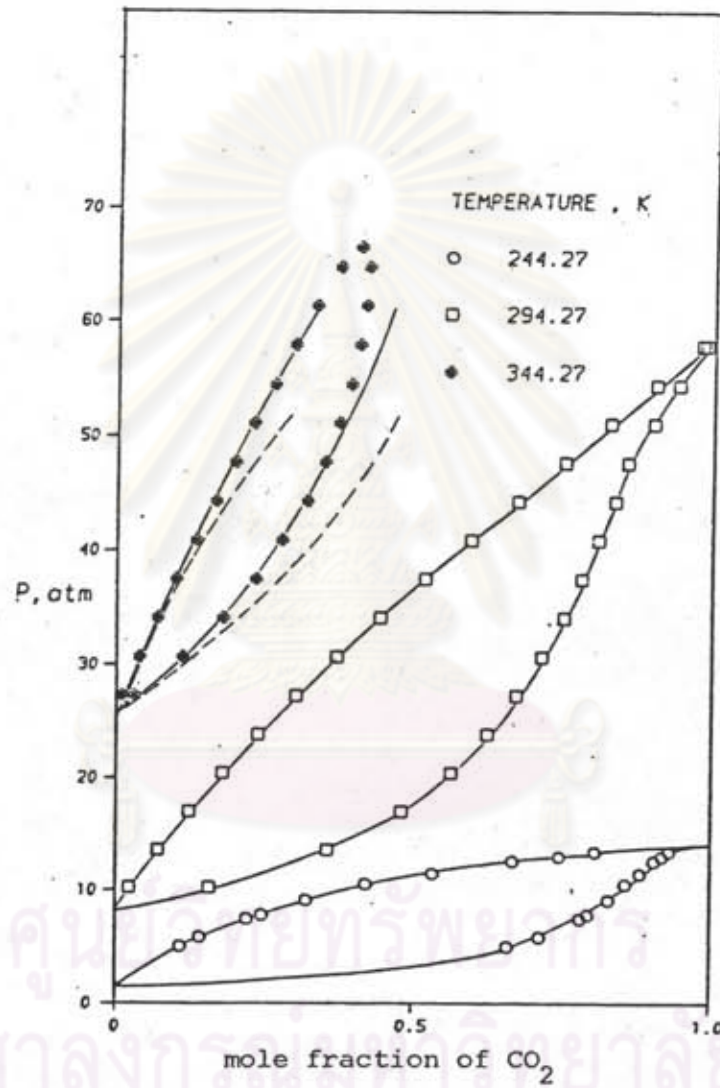


figure 6.18 Comparison of Predicted VLE for CO₂-PROPANE SYSTEM

(— = Leiva, --- = SRK).

Table 6.15 Optimum Values of K_{12} and Bubble Point Deviation for Methane(1)-CO₂(2) Mixtures, Comparison Between SRK and Leiva Equations of State.

Temp., K	No.of Points	Optimum K_{12}		$\Delta P/P$ %		ΔY_1		CPU time	
		SRK	Leiva	SRK	Leiva	SRK	Leiva	SRK	Leiva
153.16	3	0.0003	0.0020	2.96	0.80	0.0008	0.0008	0.43	0.42
173.16	4	0.0008	0.1450	0.42	0.14	0.0028	0.0037	0.76	0.68
183.16	5	0.0733	0.1213	0.22	0.20	0.0018	0.0008	1.15	1.07
193.16	8	0.0003	0.1183	4.22	0.12	0.0127	0.0055	3.28	2.68
203.16	10	0.0644	0.1078	3.16	1.29	0.0190	0.0233	4.27	3.14
210.16	11	0.0902	0.1021	6.36	4.26	0.0445	0.0232	2.70	2.67
219.27	11	0.1004	0.0983	6.71	3.60	0.0330	0.0342	2.13	2.50
240.27	12	0.1009	0.0795	6.85	4.42	0.0148	0.0547	3.56	3.06
270.00	9	0.1100	0.0722	7.28	3.30	0.0344	0.0446	2.03	1.98
Overall Average				4.24	1.99	0.0182	0.0212		

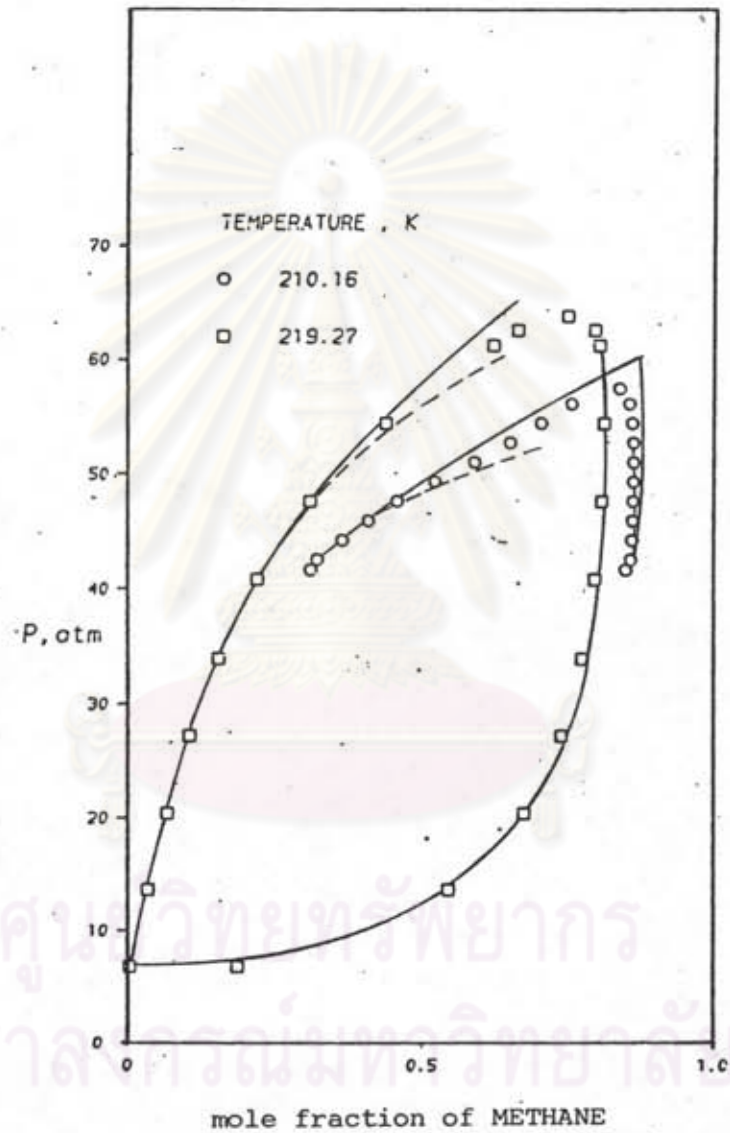


figure 6.19 Comparison of Predicted VLE for METHANE-CO₂ SYSTEM

(— = Leiva, --- = SRK).

Table 6.16 Optimum Values of K_{12} and Bubble Point Deviation for Methane(1)-Hexane(2) Mixtures, Comparison between SRK and Leiva Equations of State.

Temp., K	No.of Points	Optimum K_{12}		$\Delta P/P\%$		ΔY_1		CPU time	
		SRK	Leiva	SRK	Leiva	SRK	Leiva	SRK	Leiva
298.16	10	0.0372	0.0252	0.76	0.85	0.0091	0.0095	1.07	1.00
323.16	10	0.0398	0.0146	0.55	0.56	0.0129	0.0137	1.04	0.93
348.16	10	0.0482	0.0061	0.37	0.47	0.0095	0.0123	1.00	0.98
373.16	10	0.0594	0.0000	0.65	0.95	0.0213	0.0208	1.06	1.00
423.16	9	0.1160	0.0000	1.82	3.19	0.0301	0.0484	1.32	1.10
Overall Average				0.83	1.20	0.0166	0.0209		

6.3.2 Ternary VLE calculations

For comparison between the Leiva equation and the SRK equation in predicting multicomponent VLE values, the ternary systems of N₂-methane-CO₂, N₂-methane-ethane and methane-ethane-propane system at 9 isothermal conditions were studied.

Consider the ternary systems of N₂ (1)-methane(2) - CO₂ (3) and N₂ (1) - methane(2) - ethane(3), the temperature selected are above the critical temperature of N₂ and methane. The K_{ij} were obtained from binary experimental data of Stryjek et.al. [55] at 183.16 K and was assumed independent of temperature. Table 6.17, 6.19 and 6.21 summarize the optimize K_{ij} values used in Leiva and Soave equations.

Results of evaluation are given in Table 6.18, 6.20 and 6.22. The Leiva equation again yield better results at high temperature.

ศูนย์วิทยทรัพยากร
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Table 6.17 Values of Binary Interaction Coefficient for Mixtures of Nitrogen(1), Methane(2) and Carbon dioxide(3).

	at 220 K		at 233 K		at 240 K	
	SRK	Leiva	SRK	Leiva	SRK	Leiva
N ₂ + methane	0.0661	0.0322	0.0661	0.0322	0.0661	0.0322
N ₂ + CO ₂	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
methane + CO ₂	0.0902	0.0882	0.1004	0.0983	0.1004	0.0714

Table 6.18 Deviations in Bubble Point Pressure Calculation for Mixtures of Nitrogen(1), Methane(2) and Carbon dioxide(3)

	at 220 K 60-120 atm		at 233 K 80 atm		at 240 K 70-90 atm		
	SRK	Leiva	SRK	LEiva	SRK	Leiva	
$\Delta P/P_{av} \%$	7.48	3.27	4.89	2.32	4.93	2.16	
ΔY	N ₂	0.0224	0.0352	0.0045	0.0210	0.0101	0.0408
	methane	0.0157	0.0072	0.0047	0.0382	0.0535	0.0612
	CO ₂	0.0069	0.0323	0.0091	0.0591	0.0505	0.0666

Table 6.19 Values of Binary Interaction Coefficient for Mixtures of Nitrogen(1), Methane(2) and Ethane(3)

		at 260 K		at 270 K		at 280 K	
		SRK	Leiva	SRK	Leiva	SRK	Leiva
N ₂	+ methane	0.0661	0.0322	0.0661	0.0322	0.0661	0.0322
N ₂	+ ethane	0.0661	0.0359	0.0796	0.0328	0.0591	0.0000
	methane + ethane	0.0105	0.0000	0.0175	0.0000	0.0385	0.0000

Table 6.20 Deviations in Bubble Point Pressure Calculation for Mixtures of Nitrogen(1), Methane(2) and Ethane(3)

		at 260 K 50-75 atm		at 270 K 35-85 atm		at 280 K 50-75 atm	
		SRK	Leiva	SRK	LEiva	SRK	Leiva
$ \Delta P/P _{av} \%$		0.83	3.12	1.83	3.14	10.02	4.40
ΔY	N ₂	0.0047	0.0285	0.0142	0.0475	0.0396	0.0537
	methane	0.0036	0.0134	0.0017	0.0061	0.0118	0.0149
	ethane	0.0064	0.0418	0.0131	0.0534	0.0491	0.0685

Table 6.21 Values of Binary Interaction Coefficient for Mixtures of Methane(1), Ethane(2) and Propane(3)

	at 199.83 K		at 227.6 K		at 255.38 K	
	SRK	Leiva	SRK	Leiva	SRK	Leiva
methane + ethane	0.000	0.000	0.000	0.0000	0.000	0.000
methane + propane	0.000	0.015	0.000	0.0100	0.000	0.002
ethane + propane	0.000	0.000	0.000	0.000	0.000	0.000

Table 6.22 Deviations in Bubble Point Pressure Calculation for Mixtures of Methane(1), Ethane(2) and Propane(3)

		at 199.83 K		at 227.6 K		at 255.38 K	
		6-40 atm		6-68 atm		54-88 atm	
		SRK	Leiva	SRK	Leiva	SRK	Leiva
$ \Delta P/P _{av}$ 100%		1.64	1.51	3.20	3.66	3.61	7.84
ΔY	methane	0.0036	0.0050	0.0107	0.0145	0.0193	0.0455
	ethane	0.0037	0.0042	0.0209	0.0224	0.0087	0.0190
	propane	0.0024	0.0019	0.0043	0.0060	0.0106	0.0263

6.3.3 Liquid Molar Volume Calculations

Table 6.23 presents the percent average absolute deviations (% AAD) in liquid molar volume and vapor molar volume obtained from the SRK equation and the Leiva equation for the systems of CO₂-PROPANE and METHANE-HEXANE. As can be seen, the Leiva equation is superior to the Soave equation in liquid molar volume calculation. The average error from the Leiva equation is within 2 per cent of the experimental value for both systems, Soave equation overpredicted by 13 per cent for CO₂-PROPANE and 15 per cent for METHANE-HEXANE system. Figure 6.20 gives a comparison among the liquid molar volumes predicted by both equations and the experimental liquid molar volume of CO₂-PROPANE system at 327.6 K



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Table 6.23 Comparison of the Errors (AAD) in Liquid molar volumes and Vapor Molar Volumes Predicted by the SRK and the Leiva EOS.

System	Temp., K	No. of Points	$\Delta VL/VL\%$		$\Delta VV/VV\%$	
			SRK	Leiva	SRK	Leiva
CO ₂ - Propane	277.60	10	10.90	0.78	1.33	2.01
	294.27	15	15.19	1.00	1.62	3.18
	310.94	18	14.90	2.40	1.49	7.53
	327.60	15	16.82	1.42	3.72	5.79
	344.27	13	9.64	3.58	18.95	9.78
Overall Average			13.49	1.84	5.42	5.66
Methane-Hexane	298.16	6	13.62	2.15	4.40	4.59
	323.16	6	13.94	1.79	5.33	6.14
	348.16	6	13.90	2.08	3.66	3.63
	373.16	7	14.81	0.97	7.81	7.79
	423.16	8	18.76	2.14	9.67	9.98
Overall Average			15.01	1.83	6.17	6.43

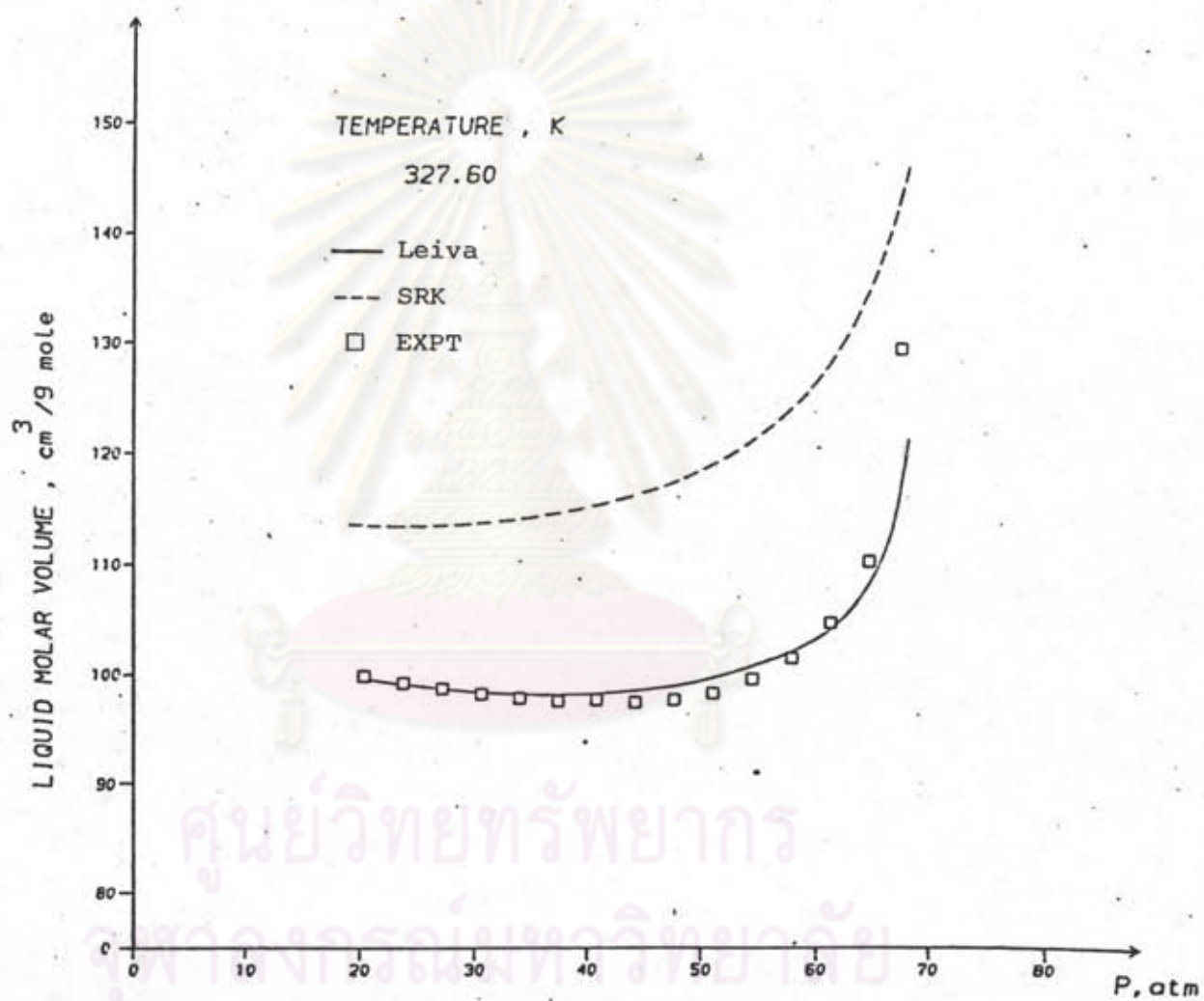


figure 6.20 Comparisons of Predicted Liquid Molar Volumes for
 $\text{CO}_2(1)$ -PROPANE(2) MIXTURE at 327.60 K.