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Technical Progress Report

to

DOE/PC/70024--T1

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Pittsburgh Energy Technology Center

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on

Synthesis Gas Solubility in Fischer-Tropsch Slurry

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DISCLAIMER

Summary

Solubility data were determined for ethylene in n-eicosane and for hydrogen, carbon monoxide, carbon dioxide, methane, and ethane in n-hexatriacontane.

Interaction constants in the modified Soave equation were determined and correlated for the solubility of hydroen, carbon monoxide, methane, ethane, and carbon dioxide in n-paraffin solvents.

Solubility Data

Figures 1-5 present the solubility of hydrogen, carbon monoxide, carbon dioxide, methane, and ethane respectively in n-hexatriacontane.

Figure 6 presents the solubility of ethylene in n-Eicosane

Figure 1.

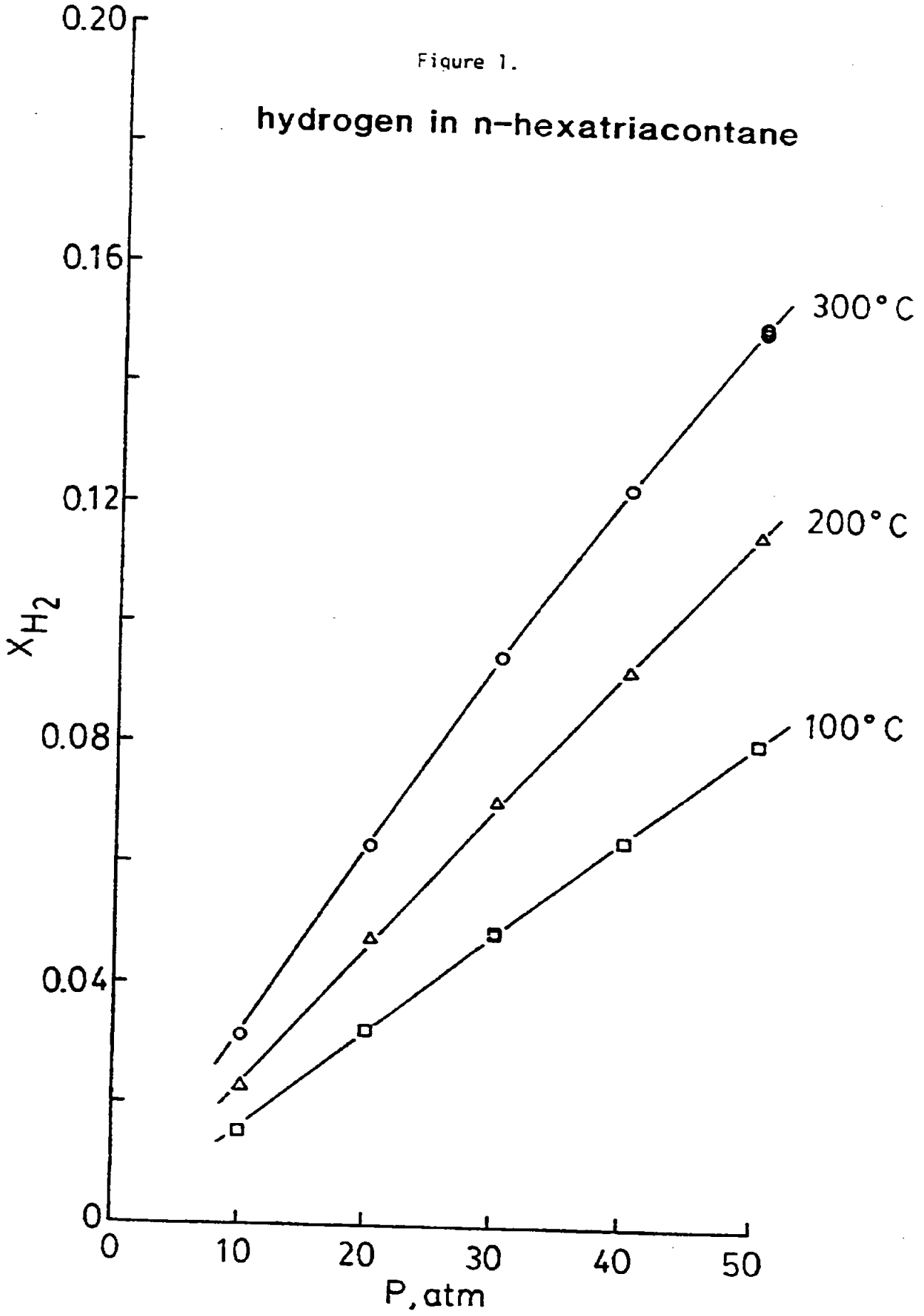

hydrogen in n-hexatriacontane
0.20
0.16
0.12
0.08
0.04
0
X_{H_2}
300° C
200° C
100° C
0
10
20
30
40
50
P, atm

Figure 2.

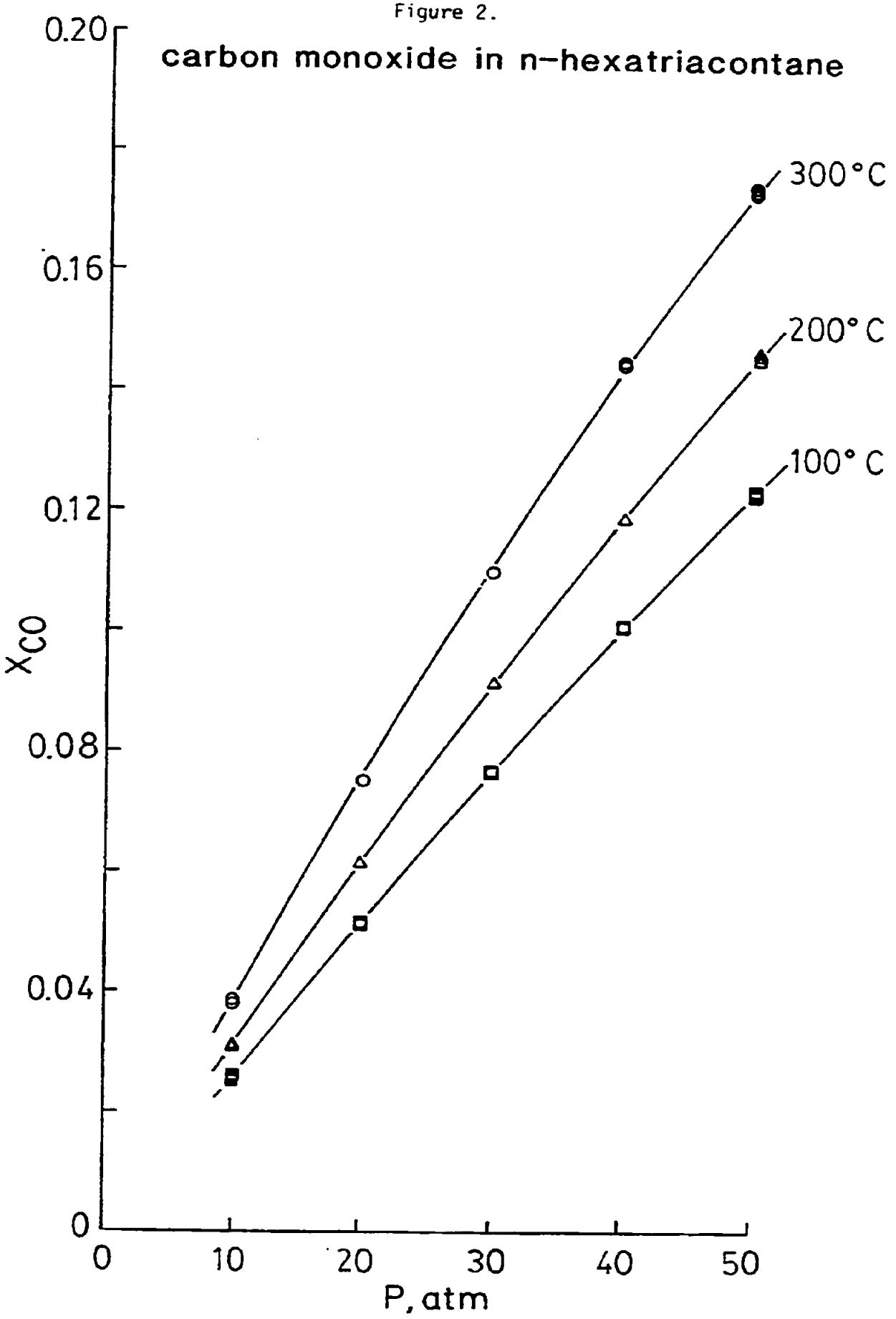

carbon monoxide in n-hexatriacontane
0.20
0.16
0.12
0.08
0.04
0
x_{CO}
300°C
200°C
100°C
0
10
20
30
40
50
P, atm

Figure 3.

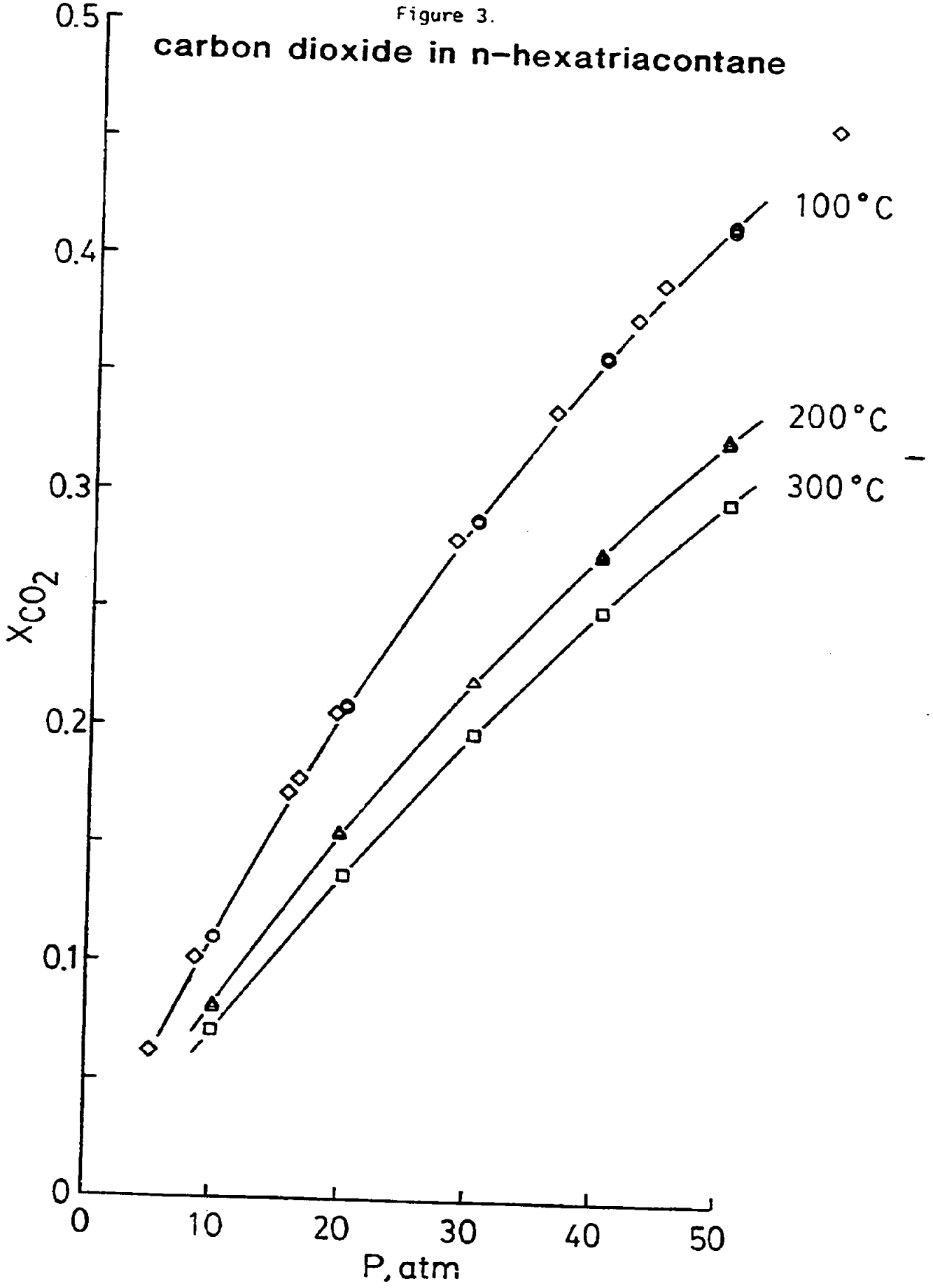

carbon dioxide in n-hexatriacontane
100 °C
200 °C
300 °C
X_{CO_2}
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
P, atm

Figure 4.

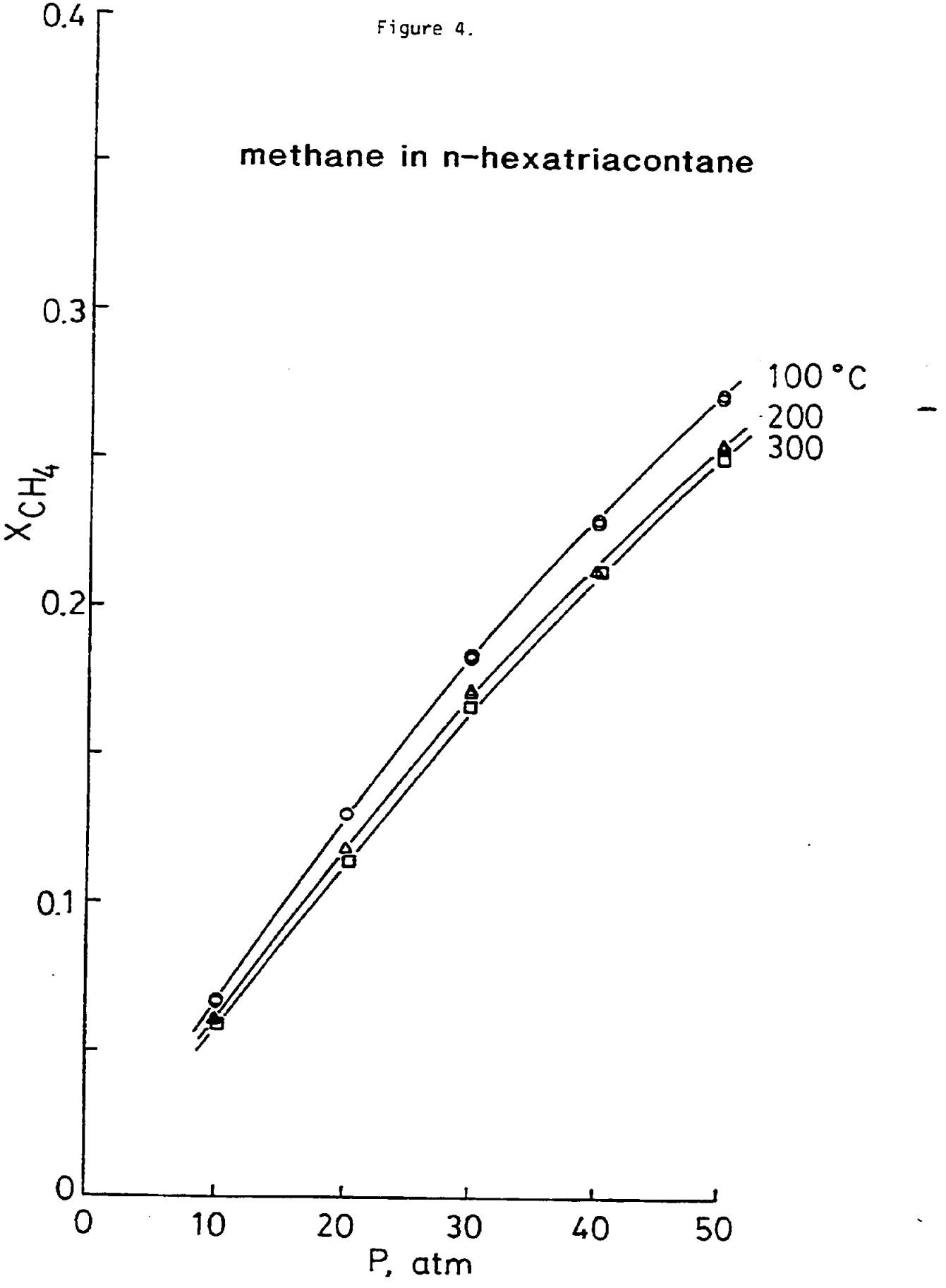

methane in n-hexatriacontane
0.4
0.3
0.2
0.1
0
X_{CH_4}
100 °C
200
300
0
10
20
30
40
50
P, atm

Figure 5.

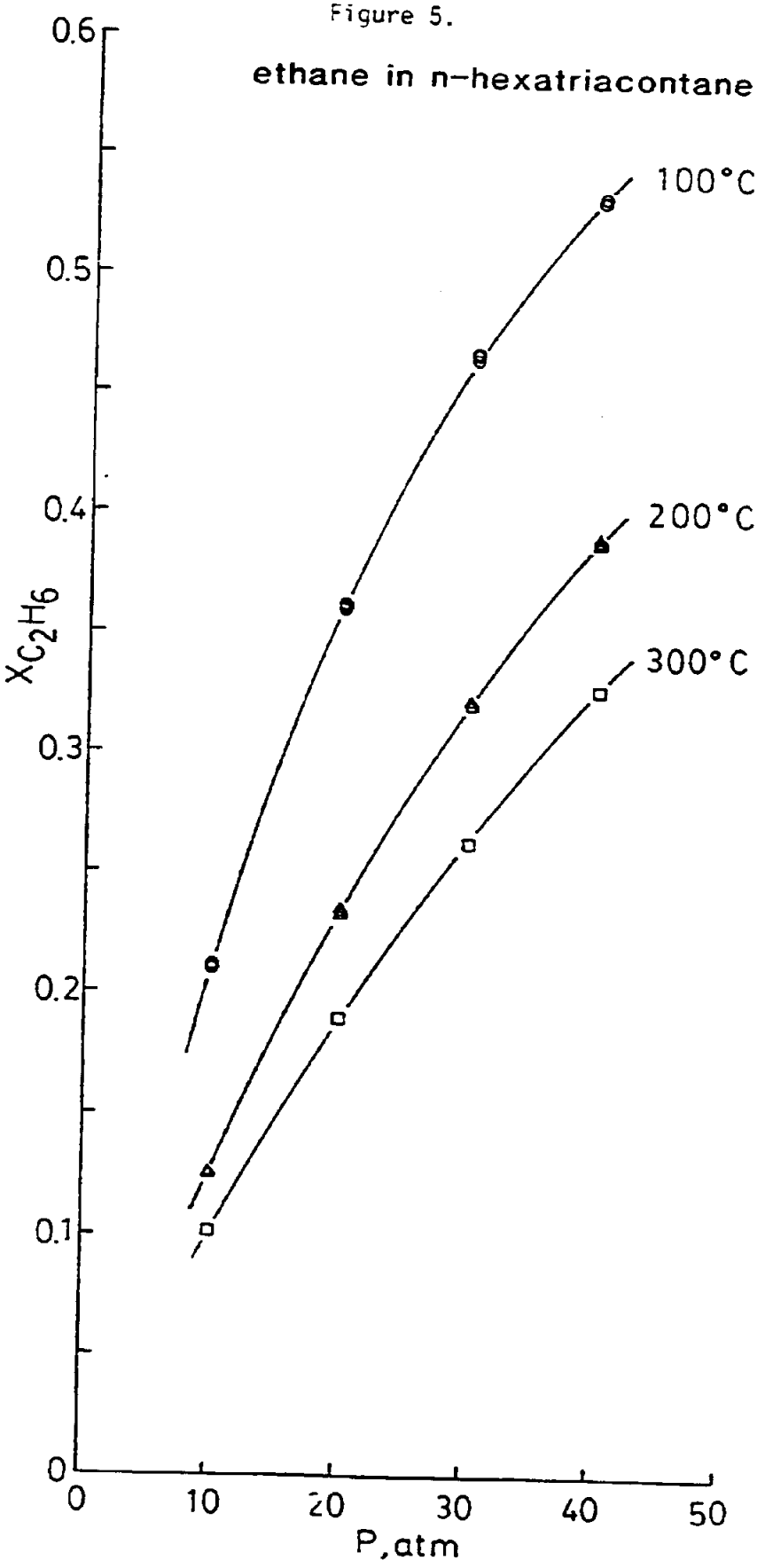
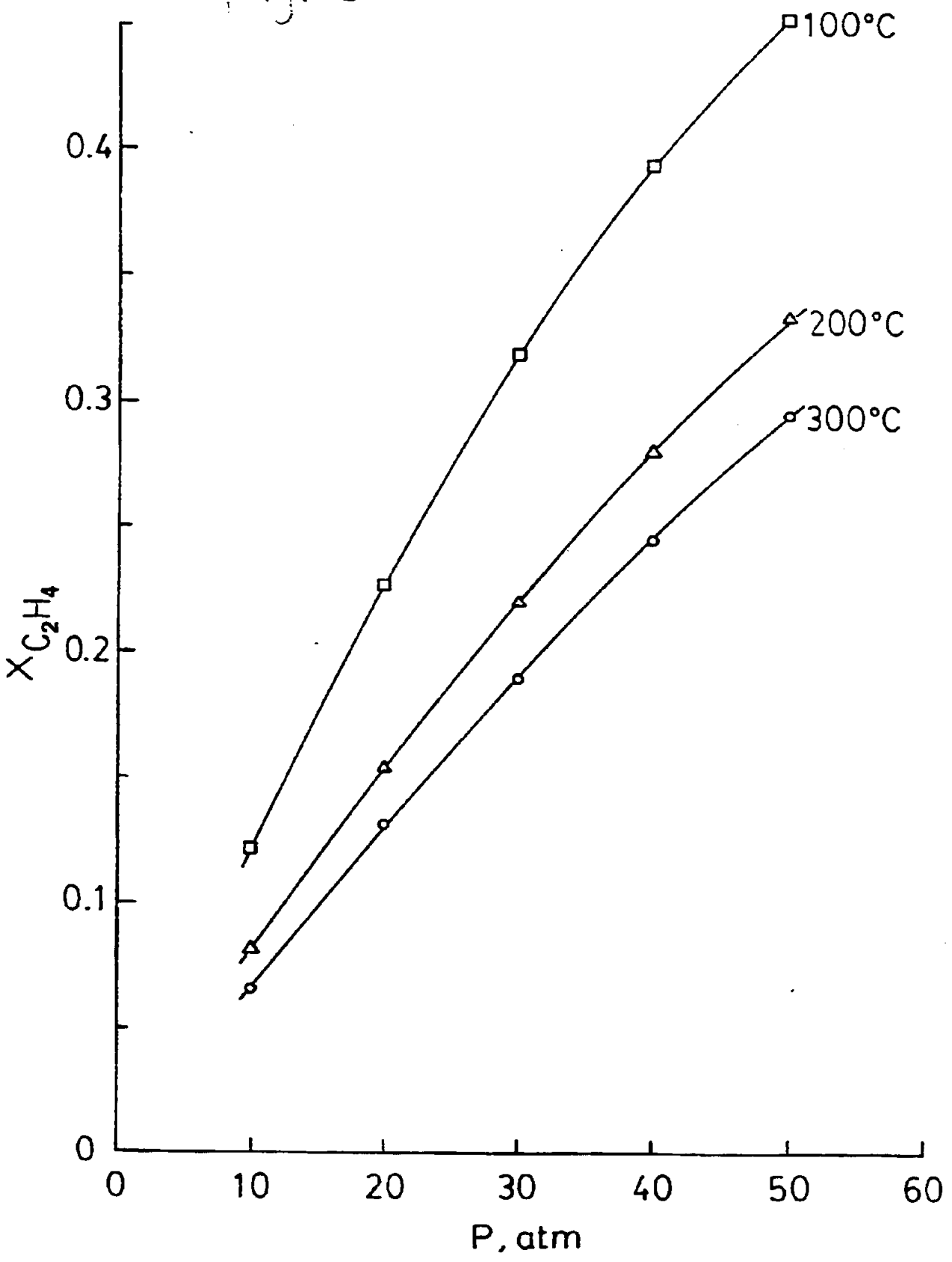

ethane in n-hexatriacontane
100°C
200°C
300°C
$X_{C_2H_6}$
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
P, atm

Fig. 6



Solubility of Ethylene in n-Eicosane

Correlation of the Interaction Constants

We have completed the correlation of all our solubility data with the modified Soave equation of state. The Flory-Huggins-Huron-Vidal (FHHV) mixing rules are used to replace the classical van der Waals one-fluid mixing rules in the correlation. The correlation method has been described in detail in our previous reports. The interaction constant A_{ij} in the FHHV mixing rules determined from the solubility data has been reported previously for the gas/n$-C_{20}$ and gas/n$-C_{28}$ interactions. The A_{ij} values for gas/n$-C_{36}$ are now presented in Table 1. We have correlated the A_{ij} for all the mixtures of gas/n-paraffin from this research project in terms of the molecular weight M of the n-paraffin as follows:

$$A_{ij} = A_{ij}^{\infty} [1 - \exp(-M/M_o)] \qquad (1)$$

The coefficients of A_{ij}^{∞} and M_o are given in Table 2. The calculated solubilities with the correlated A_{ij} of Equation 1 are in general comparable with results from the optimal A_{ij}. The comparison is illustrated in Table 1 for n$-C_{36}$ mixtures. Figures 7 and 8 compare the optimal A_{ij} with Equation 1. The A_{ij} value at a constant temperature increase with M to approach an asymptotic value for very heavy paraffin.

Figures 9-12 show the comparison of the calculated solubilities for synthesis mixtures H_2+CO in n$-C_{28}$ with experimental data. The calculations are of a predictive nature. Experimental solubility data are not used for adjustment of the equation constants. The predicted results agree well with the data.

Table 1 Comparison of the Modified Soave Equation Calcuated Gas Solubilities with Experimental Data in n-Hexatriacontane

Gas	T, C	data pts	Optimal Aij: Aij mole/mL	Optimal Aij: Deviations in p, % RMS	AAD	BIAS	Correlated Aij: Aij mole/mL	Correlated Aij: Deviations in p, % RMS	AAD	BIAS
H2	100	5	0.260	6.1	4.9	-0.4	0.258	6.3	4.7	-2.0
	200	5	0.243	7.0	5.3	-0.8	0.241	6.9	5.2	-2.4
	300	5	0 237	6.2	5.2	-0.7	0.236	6.2	5.1	-1.4
CO	100	5	0.181	4.6	3.9	-0.2	0.179	4.8	4.0	-2.0
	200	5	0.170	5.0	4.3	-0.4	0.168	5.6	4.1	-3.0
	300	5	0.166	4.7	4.1	-0.4	0.166	4.7	4.1	-0.4
CH4	100	5	0.101	3.1	2.4	-0.2	0.100	3.5	2.5	-1.9
	200	5	0.0981	3.6	2.9	-0.2	0.0978	3.5	2.7	-0.6
	300	5	0.102	4.6	4.0	-0.6	0.102	4.6	4.0	-0.6
CO2	100	5	0.110	5.7	4.7	-0.6	0.109	6.1	4.8	-2.7
	200	5	0.0960	4.7	3.6	-0.3	0.0947	4.9	3.5	-2.6
	300	5	0.0908	4.9	4.1	-0.4	0.0901	5.0	3.8	-1.7
C2H6	100	4	0.0475	2.0	1.9	-0.1	0.0470	2.4	1.8	-1.5
	200	4	0.0468	3.4	2.8	-0.2	0.0463	3.7	2.8	-1.2
	300	4	0.0483	2.8	2.2	-0.1	0.0492	3.6	3.3	2.2

Table 2 Correlation of A_{ij} by Molecular Weight of n-Paraffins

Solute	M_o	A_{ij}^{∞}, mol/cm³		
		100°C	200°C	300°C
H_2	127.30	0.2632	0.2456	0.2406
CO	140.75	0.1842	0.1723	0.1707
CH_4	146.06	0.1032	0.1009	0.1050
C_2H_6	188.16	0.05046	0.04967	0.05277
CO_2	137.02	0.1121	0.09710	0.09240

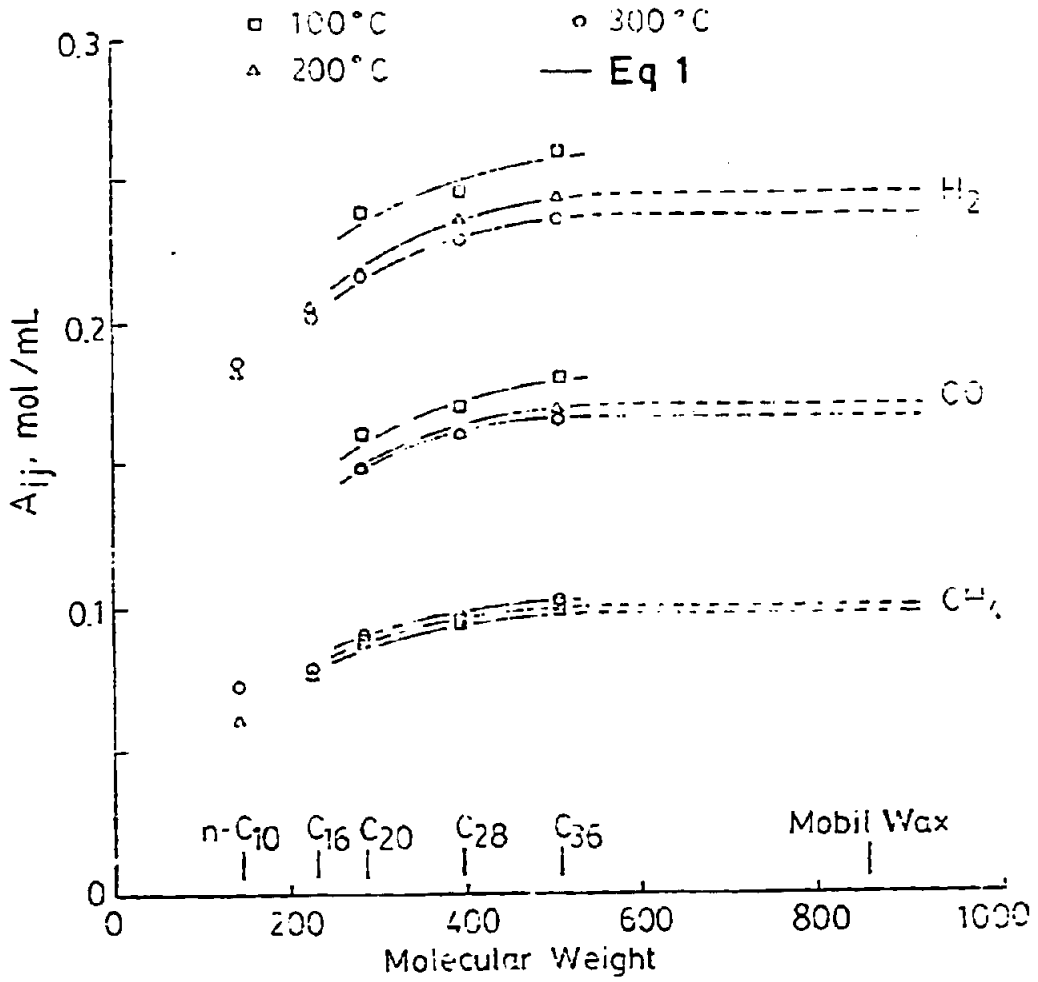


Figure 7. Plot of A_{ij} vs Molecular Weight of n-Paraffins

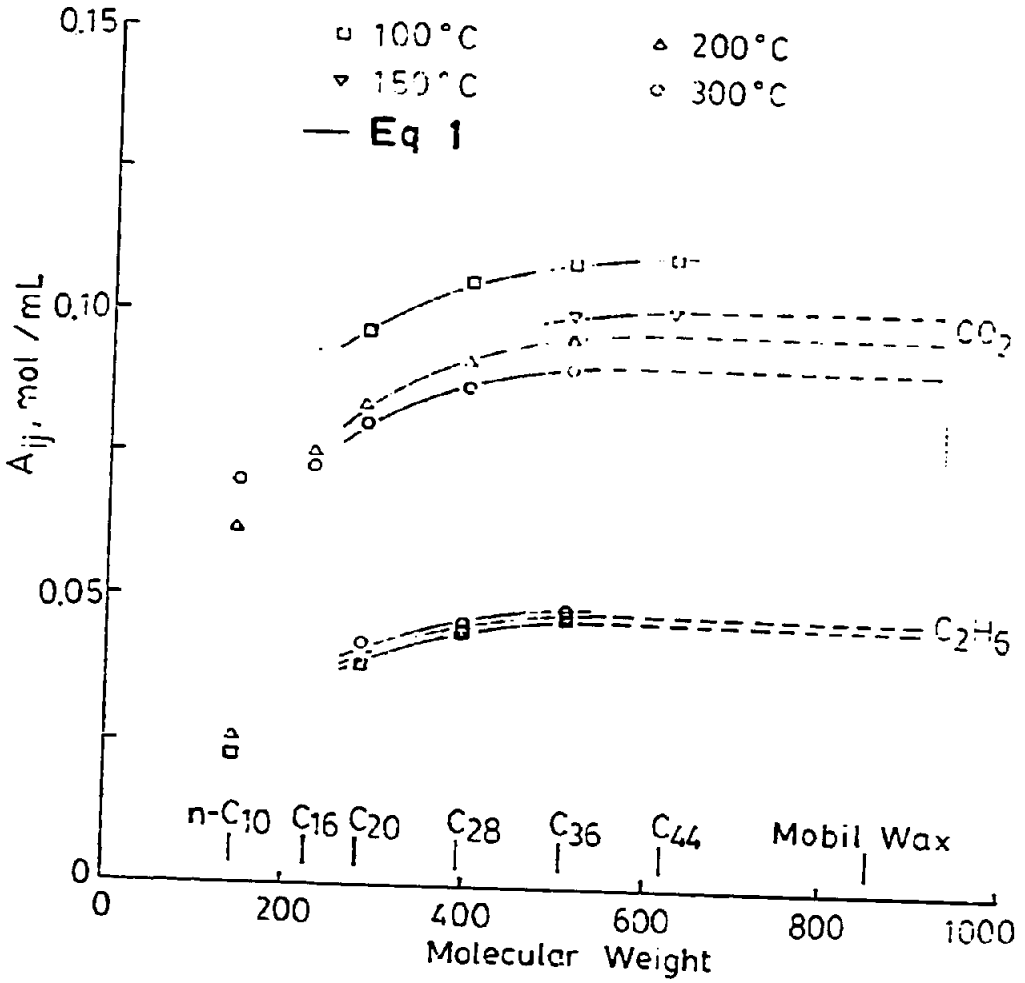


Figure 8 . Plot of A_{ij} vs Molecular Weight of n-Paraffins

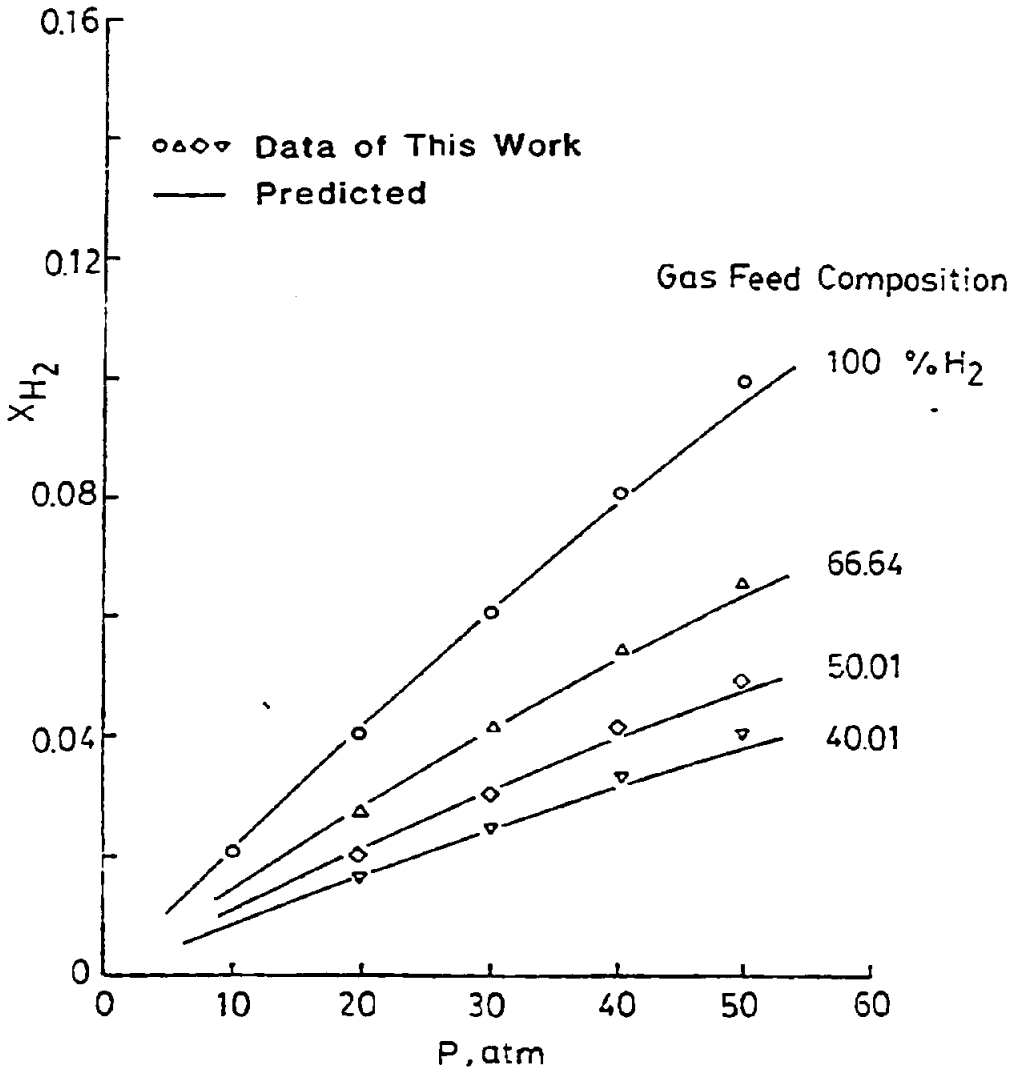


Figure 9 . Comparison of Calculated H_2 Solubilities in Synthesis Gas Mixtures in n-Octacosane with Experimental Data at 200° C

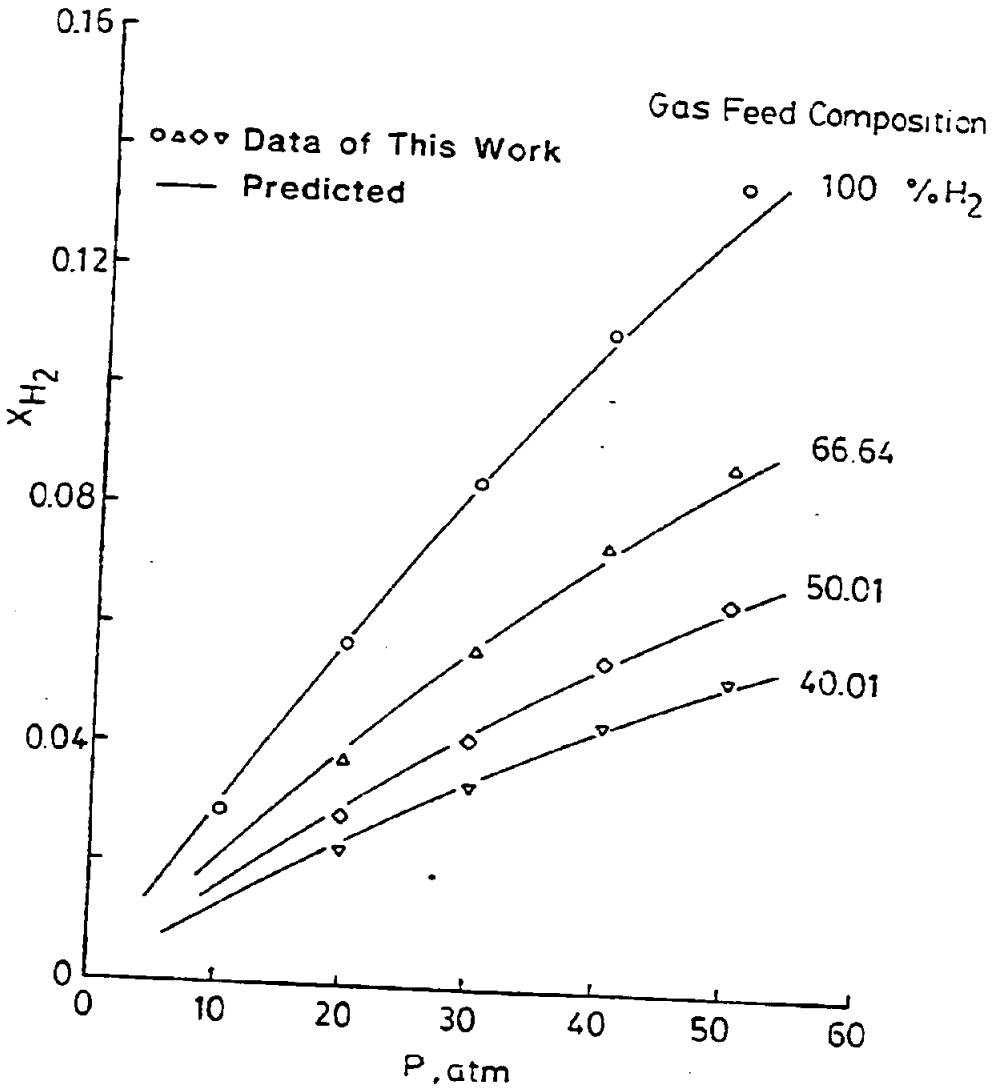


Figure 10. Comparison of Calculated H_2 Solubilities in Synthesis Gas Mixtures in n-Octacosane with Experimental Data at 300° C

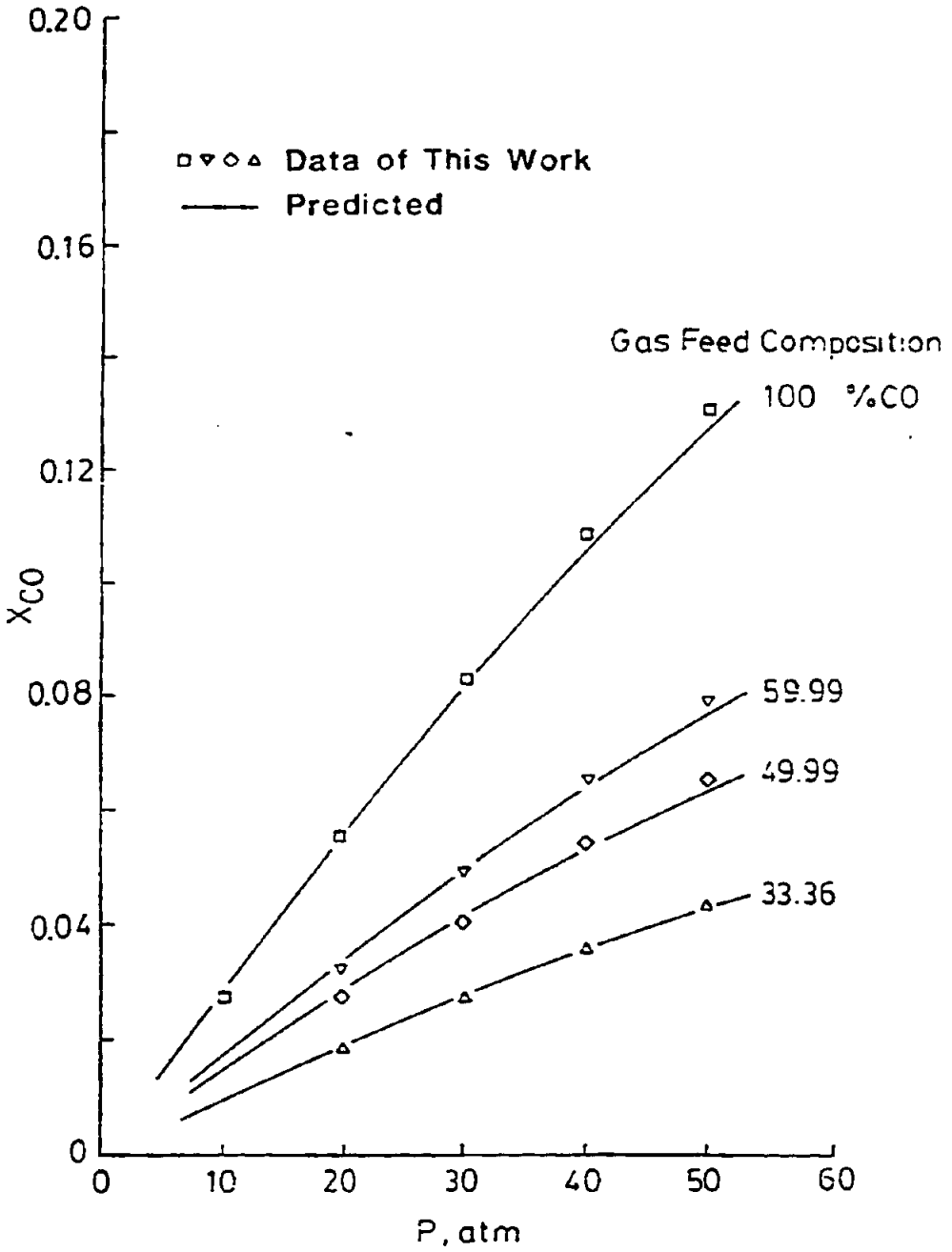


Figure 11. Comparison of Calculated CO Solubilities in Synthesis Gas Mixtures in n-Octacosane with Experimental Data at 200° C

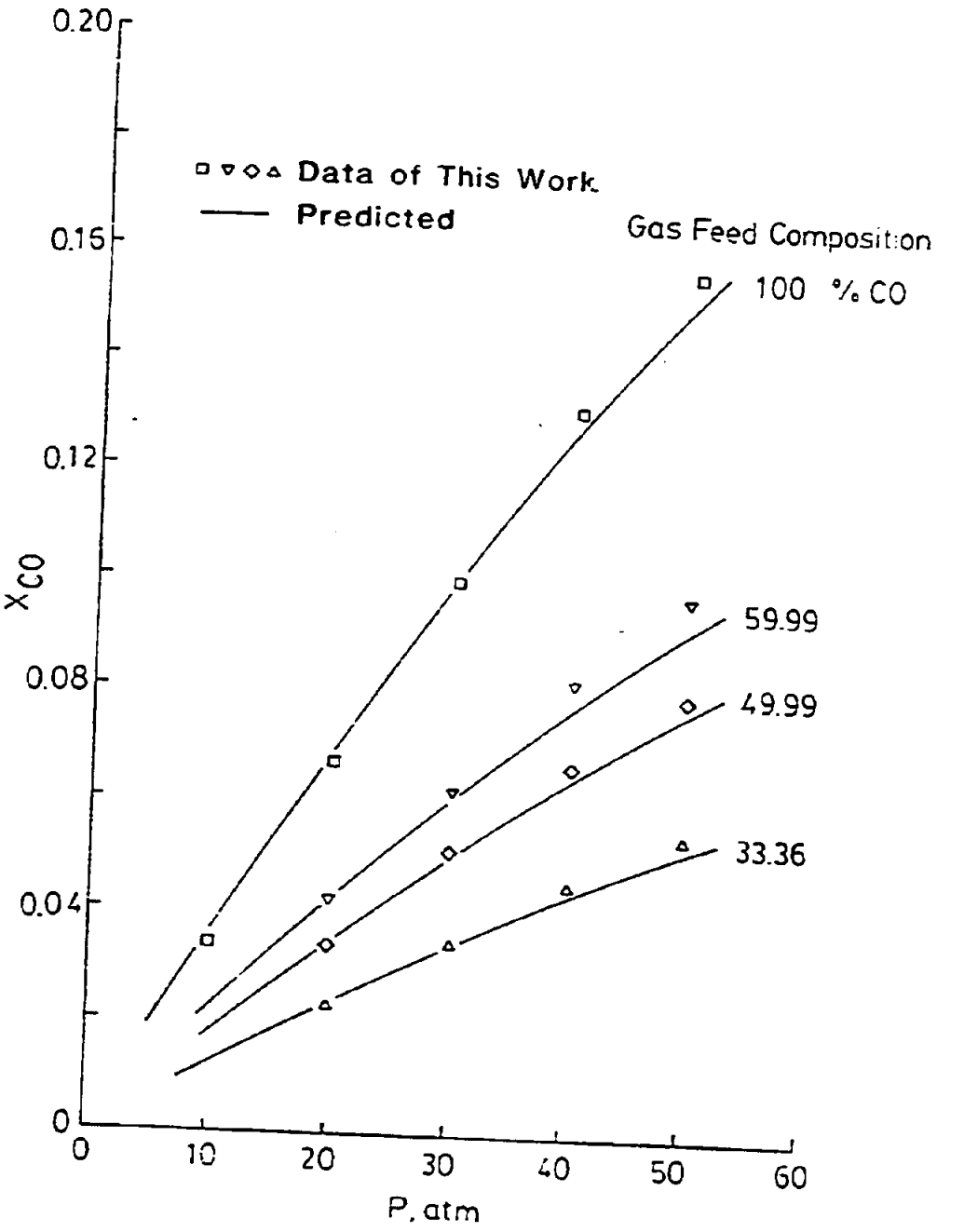


Figure 12. Comparison of Calculated CO Solubilities in Synthesis Gas Mixtures in n-Octacosane with Experimental Data at 300° C