A STUDY OF MODIFIED EQUATIONS OF STATE FOR VAPOR-LIQUID EQUILIBRIUM PREDICTIONS

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PREFACE

This study was concerned with modifying equations of state to improve predicted saturated phase properties of several hydrocarbons and non-hydrocarbons at low temperatures. Experimental vapor pressures and saturated liquid volumes were used to modify two RK parameters and two BWR parameters simultaneously as functions of temperature. Three BWR parameters were simultaneously modified as functions of temperature by using experimental vapor pressures and saturated liquid volumes along with saturated vapor volumes.

Vapor-liquid equilibrium calculations were performed for binary mixtures using pure component RK and BWR parameters determined in this study and incorporating modified mixing rules for the parameters "a" and A_o.

I wish to express my sincere thanks to my major adviser, Dr. R. L. Robinson, Jr., for his advice and encouragement during this research. I would also like to thank the Oklahoma State University Computer Center for the use of their facilities. The financial support of the School of Chemical Engineering is gratefully acknowledged. Finally, I am deeply grateful to my parents and brothers for their financial support and constant encouragement during this study.

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CHAPTER I

INTRODUCTION

An equation of state, relating the pressure, volume, temperature, and composition, is a tool for calculating the thermodynamic properties of pure components and their mixtures. More than one hundred equations of state have been proposed since 1873, but none can entirely successfully represent the experimental data over the entire practical range of conditions. Among these equations of state, the Redlich-Kwong (RK) equation (30) has been shown to be the best two-constant equation of state, while the Benedict-Webb-Rubin (BWR) equation (7, 8) is the most frequently employed equation of state which involved several constants.

The RK equation of state is less accurate than the BWR equation, but it is more often employed because of its simplicity. The RK equation was originally proposed for predicting thermodynamic properties at temperatures above the critical temperature for any pressure. The BWR equation was specifically designed to describe the behavior of light hydrocarbons and their mixtures for reduced temperatures higher than 0.6 and for reduced densities up to 1.8. At the saturated phase boundary, both equations of state exhibit considerable deviation from experimental results. However, the equations can be improved by modifying one or more of the parameters.

There were three primary objectives of this study. The first of these objectives was to determine which parameters of the BWR equation are most suitable for modification. Second, the parameters for pure components were modified as functions of temperature to improve prediction of saturated phase properties. The third objective was to apply the modified pure component parameters to vapor-liquid equilibrium calculations for binary mixtures and to improve the mixing rules.

Several parameters of pure light hydrocarbons and non-hydrocarbons were modified. The binary system chosen for vapor-liquid equilibrium calculations were methane-hydrogen sulfide system and n-pentane-hydrogen sulfide system. Empirical interaction coefficients were introduced into the mixing rules of the parameter "a" for the RK equation and A_o for the BWR equation.

CHAPTER II

BACKGROUND

Redlich-Kwong Equation of State

The Redlich-Kwong equation of state (30) is essentially empirical. It contains two individual parameters which can be evaluated from the critical properties. The equation has been discussed by several authors, including Barner, Pigford, and Schreiner (6), Estes and Tully (19), Robinson and Jacoby (31), and Wilson (39). Several studies of the RK equation, presented by Ader, Ozkardesh, and Schreiner (1), Edmister and Yarborough (16), and Shah and Thodos (35), have shown that the RK equation is the best two-constant equation of state for predicting thermodynamic properties of hydrocarbons and non-hydrocarbons.

The RK equation was originally proposed for predicting pressure-volume-temperature (p-v-T) behavior at temperatures above the critical temperature for any pressure. At temperatures below the critical temperature, the deviation of the predicted values from experimental data increases with decreasing temperature.

The basic RK equation often produces large errors when used for predicting saturated phase properties. In order to improve the accuracy of the RK equation in the two phase region, Chueh and Prausnitz (11, 12) proposed that two pairs of constants, one for liquid phase and one for vapor phase, should be used. Wilson (39, 40) has proposed to use the original constant b at all temperatures and to make the constant "a" a function of temperature. Recently, Zudkevitch and Joffe (43) modified the constants of the RK equation as functions of temperature to represent the experimental vapor pressures and saturated liquid densities with the help of a generalized fugacity coefficient correlation for saturated vapor.

The poor results resulting from application of RK equation to mixtures are due in part to the inflexible mixing rules for the composition dependence of the constants. Chueh and Prausnitz (12), and Zudkevitch and Joffe (43) have suggested modifications of the mixing rule of constant "a" to improve the vapor-liquid equilibrium calculations for binary mixtures. Results presented by Zudkevitch and Joffe appeared sufficiently promising to be followed up and developed in this study.

Benedict-Webb-Rubin Equation of State

The Benedict-Webb-Rubin equation of state (7, 8) is an eight-parameter equation and is now more than 30 years old. It has been discussed by many authors (2, 4, 13, 18, 36). The BWR equation was primarily developed to accurately represent the phase behavior of pure components and their mixtures for reduced temperatures greater than 0.6 and reduced densities less than 1.8. The BWR equation can also accurately predict vapor-liquid equilibria for light hydrocarbons (9).

The considerable errors induced in predicting thermodynamic properties of pure components at low temperatures indicate that the BWR parameters must be modified (27). Most authors have chosen one parameter such as C_o (5, 9, 10, 23, 28, 38, 44) or γ (5, 25, 32). Some authors chose two parameters for modification (14, 20). Recently, Starling and

Powers (37) described C_o and "a" as linear functions of reciprocal temperature. Multiproperty analysis was used to determine the new constants.

The BWR equation of state may be applied to mixtures by using mixing rules. But at low temperatures or for dissimilar components, the equation gives poorer results. Stotler and Benedict (38) and Furr (20) have proposed the modified mixing rule for A_o and found empirical interaction coefficients for binary mixtures. These methods have been applied to several mixtures (22, 41, 42). Modification of the BWR equation constant A_{o12} is successful in predicting volumetric properties.

CHAPTER III

PRELIMINARY INVESTIGATIONS

The RK equation of state contains only two parameters which can be simultaneously modified to predict correct values of two saturated phase properties. The BWR equation contains eight parameters. Thus, improvement in several property predictions should be possible by simultaneously modifying more parameters as functions of temperature. Several preliminary investigations were required to determine which of the eight parameters had the greatest effect on calculated saturated phase properties.

Calculations of Sensitivities of Saturated Phase Properties to Changes in Benedict-Webb-Rubin Parameters

The BWR equation (7) of state is a pressure explicit equation of the form:

$$P = \frac{RT}{V} + \left(B_oRT - A_o - \frac{C_o}{T^2}\right)\frac{1}{V^2} + (bRT - a)\frac{1}{V^3} + \frac{a\alpha}{V^6} + \frac{c}{T^2V^3}\left(1 + \frac{\gamma}{V^2}\right)\exp\left(-\frac{\gamma}{V^2}\right) \tag{3-1}$$

where P is the pressure; V, volume; T, temperature; R, gas constant; and B_o, A_o, C_o, b, a, α, c, and γ are adjustable parameters.

The effects of each BWR parameter on saturated phase properties for pure methane was calculated at the range of reduced temperatures from

0.3 through 1.0. "Absolute sensitivity" is defined as the change in the saturated phase property per per cent change in each parameter, expressed as:

$$\text{Absolute vapor pressure sensitivity} = C_i \left(\frac{\Delta P}{\Delta C_i}\right)$$

$$\text{Absolute liquid volume sensitivity} = C_i \left(\frac{\Delta V^L}{\Delta C_i}\right)$$

$$\text{Absolute vapor volume sensitivity} = C_i \left(\frac{\Delta V^V}{\Delta C_i}\right)$$

$$\text{Absolute saturated fugacity sensitivity} = C_i \left(\frac{\Delta f}{\Delta C_i}\right) .$$

The following steps show the procedure used to find the sensitivities of saturated phase properties:

1. Fix all parameters.
2. Calculate saturated phase properties, vapor pressure, liquid volume, vapor volume, and saturated phase fugacity, at certain reduced temperatures.
3. Increase the parameters one at a time and repeat step 2.
4. Calculate the sensitivities.
5. Repeat steps 3 and 4 for other parameter C_i, i.e., i from 1 to 8.
6. Repeat for another reduced temperature.

A detailed procedure of this sensitivity calculation is shown in Appendix A.

In order to determine which parameters have the greatest effect on saturated phase properties, the sensitivity of A_o was used as the basis for comparison. The general forms of the relative sensitivities are

$$\text{Relative vapor pressure sensitivity} = \frac{C_1\left(\frac{\Delta P}{\Delta C_1}\right)}{A_o\left(\frac{\Delta P}{\Delta A_o}\right)}$$

$$\text{Relative liquid volume sensitivity} = \frac{C_1\left(\frac{\Delta V^L}{\Delta C_1}\right)}{A_o\left(\frac{\Delta V^L}{\Delta A_o}\right)}$$

$$\text{Relative vapor volume sensitivity} = \frac{C_1\left(\frac{\Delta V^V}{\Delta C_1}\right)}{A_o\left(\frac{\Delta V^V}{\Delta A_o}\right)}$$

$$\text{Relative saturated fugacity sensitivity} = \frac{C_1\left(\frac{\Delta f}{\Delta C_1}\right)}{A_o\left(\frac{\Delta f}{\Delta A_o}\right)} .$$

The plots of the absolute sensitivity to A_o are shown in Figures 1 and 2. At reduced temperatures below 0.5, both the vapor pressure and saturated fugacity are less sensitive to A_o. With increasing temperature, the sensitivities of vapor pressure and saturated fugacity become very significant. The liquid volume is less sensitive to A_o at reduced temperatures lower than 0.3, while the vapor volume is less sensitive at reduced temperatures near 1.0.

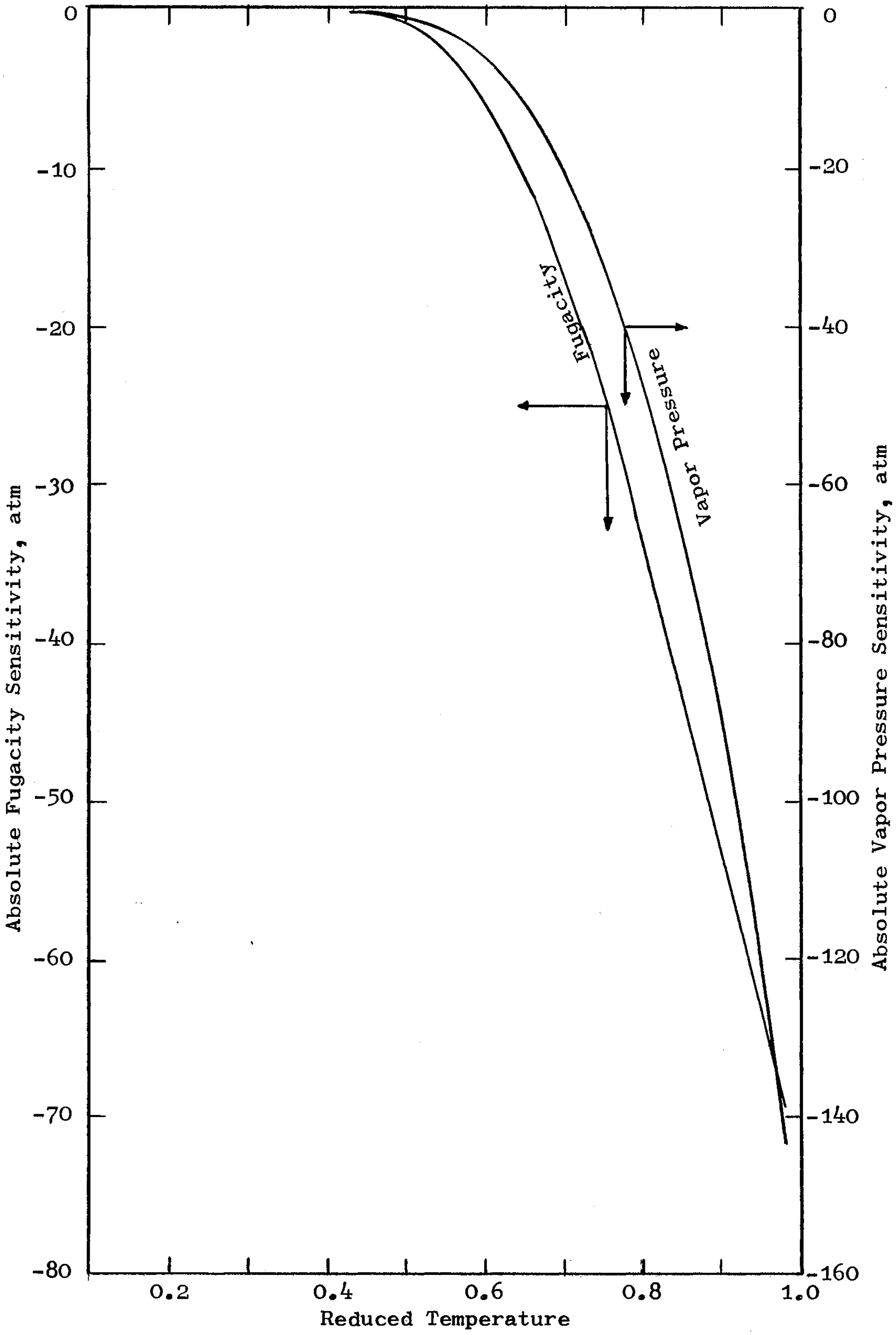


Figure 1. Absolute Sensitivity of Vapor Pressure and Fugacity to A_o

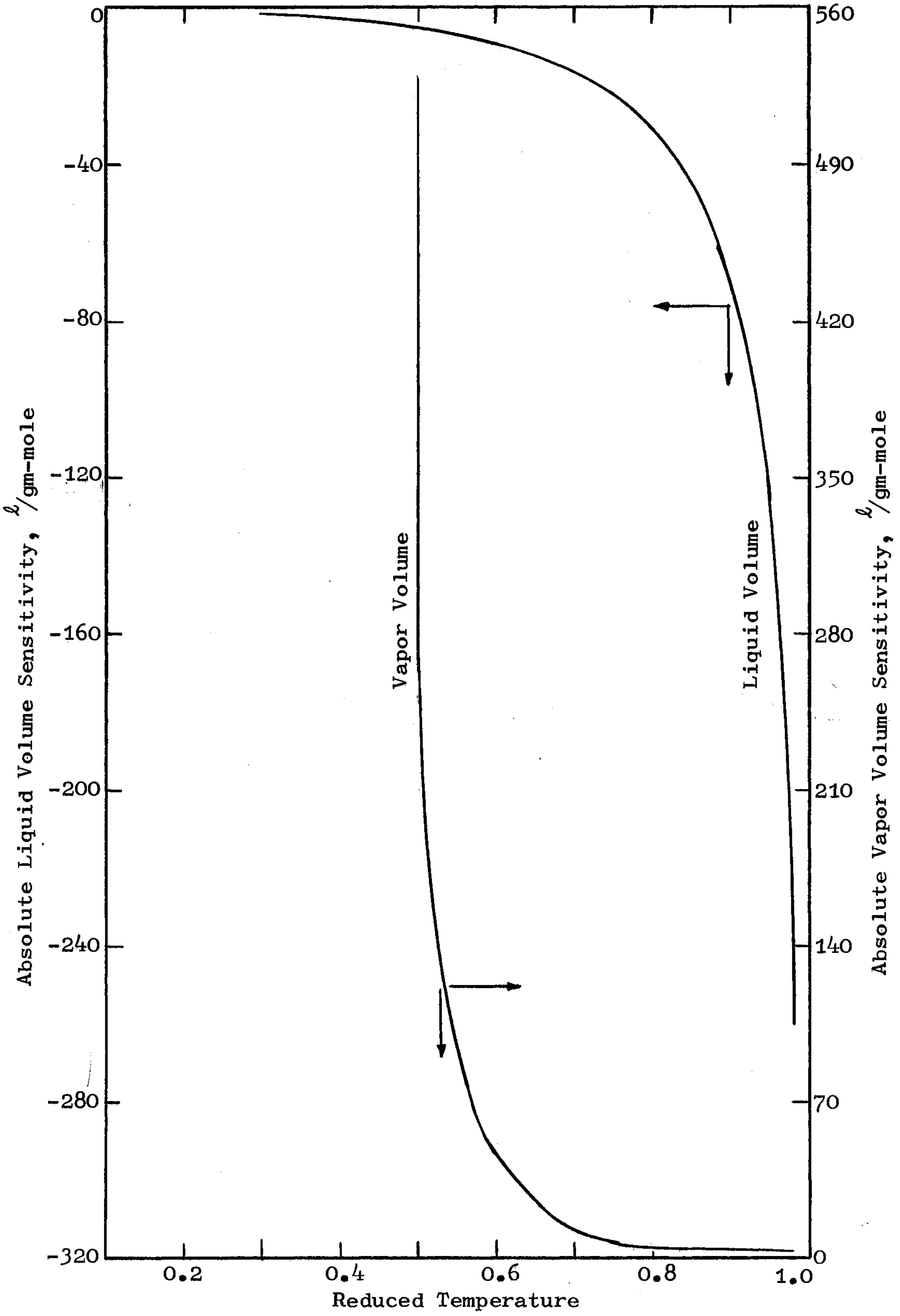


Figure 2. Absolute Sensitivity of Liquid Volume and Vapor Volume to A_o

Results of the relative sensitivities are shown in Figures 3 through 6. At low reduced temperatures, the comparison of the sensitivities to each parameter is shown in Table I.

TABLE I

TABULAR RESULTS OF THE RELATIVE SENSITIVITIES AT LOW REDUCED TEMPERATURES

	Vapor Pressure	Liquid Volume	Vapor Volume	Fugacity
Increasing Sensitivity ↑	C_o	α	C_o	C_o
	c	a	γ	c
	γ	C_o	c	γ
	α	A_o	A_o	α
	A_o	γ	α	A_o

The results of this preliminary investigation indicated that C_o, α, and c may be most suited for modification to predict more accurate values of saturated phase properties.

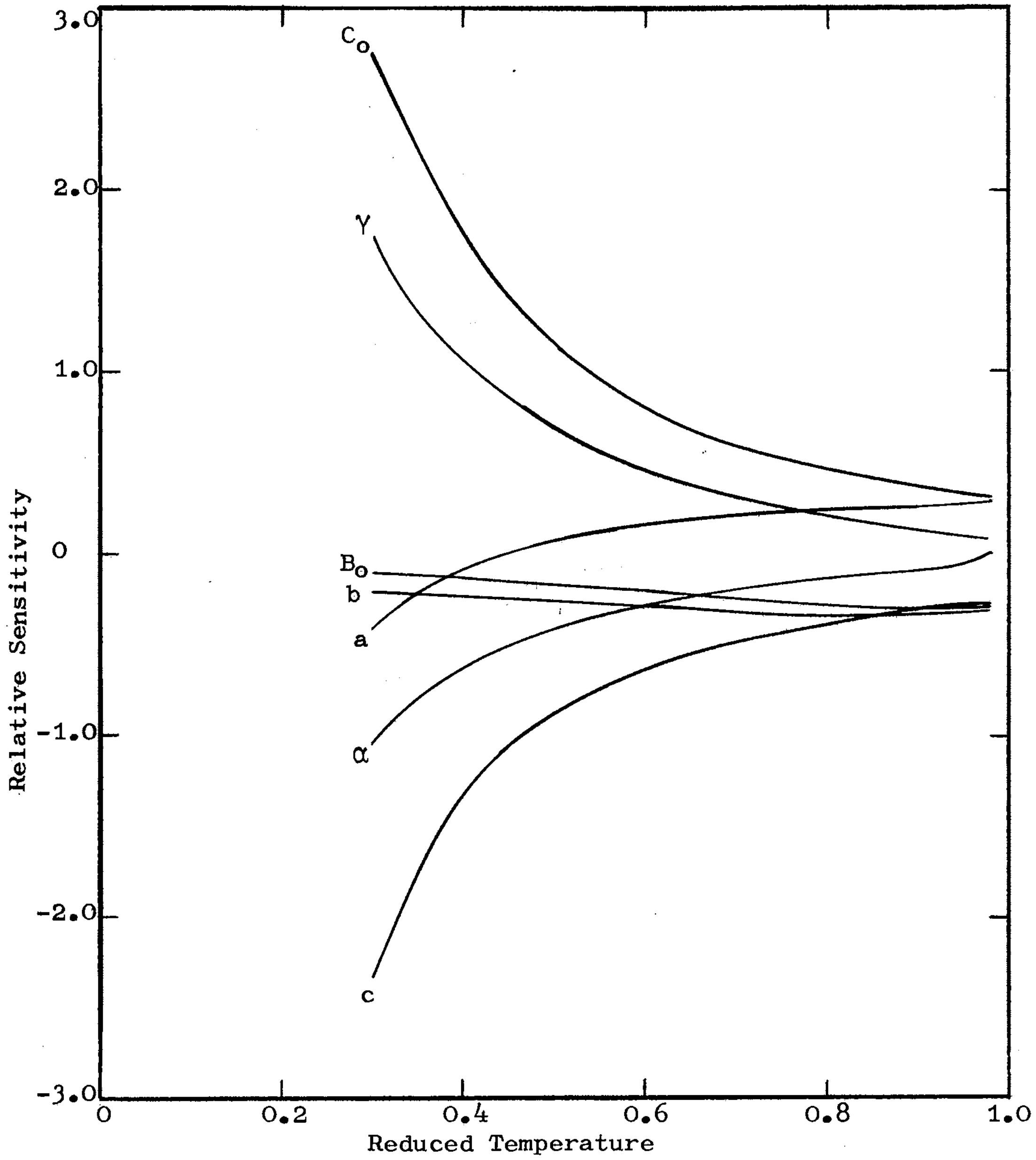


Figure 3. Relative Sensitivities of Saturated Vapor Pressure to BWR Parameters

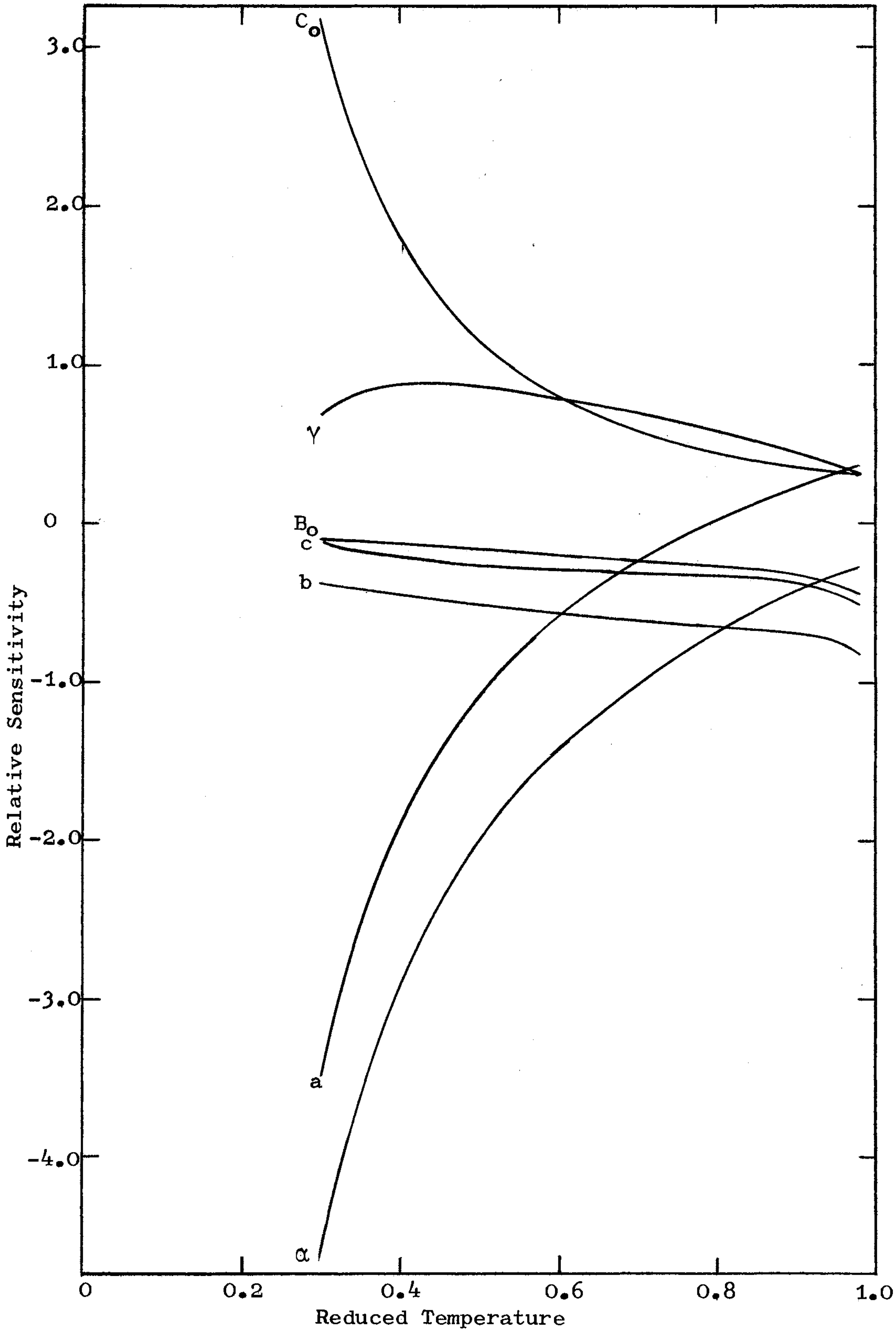


Figure 4. Relative Sensitivities of Saturated Liquid Volume to BWR Parameters

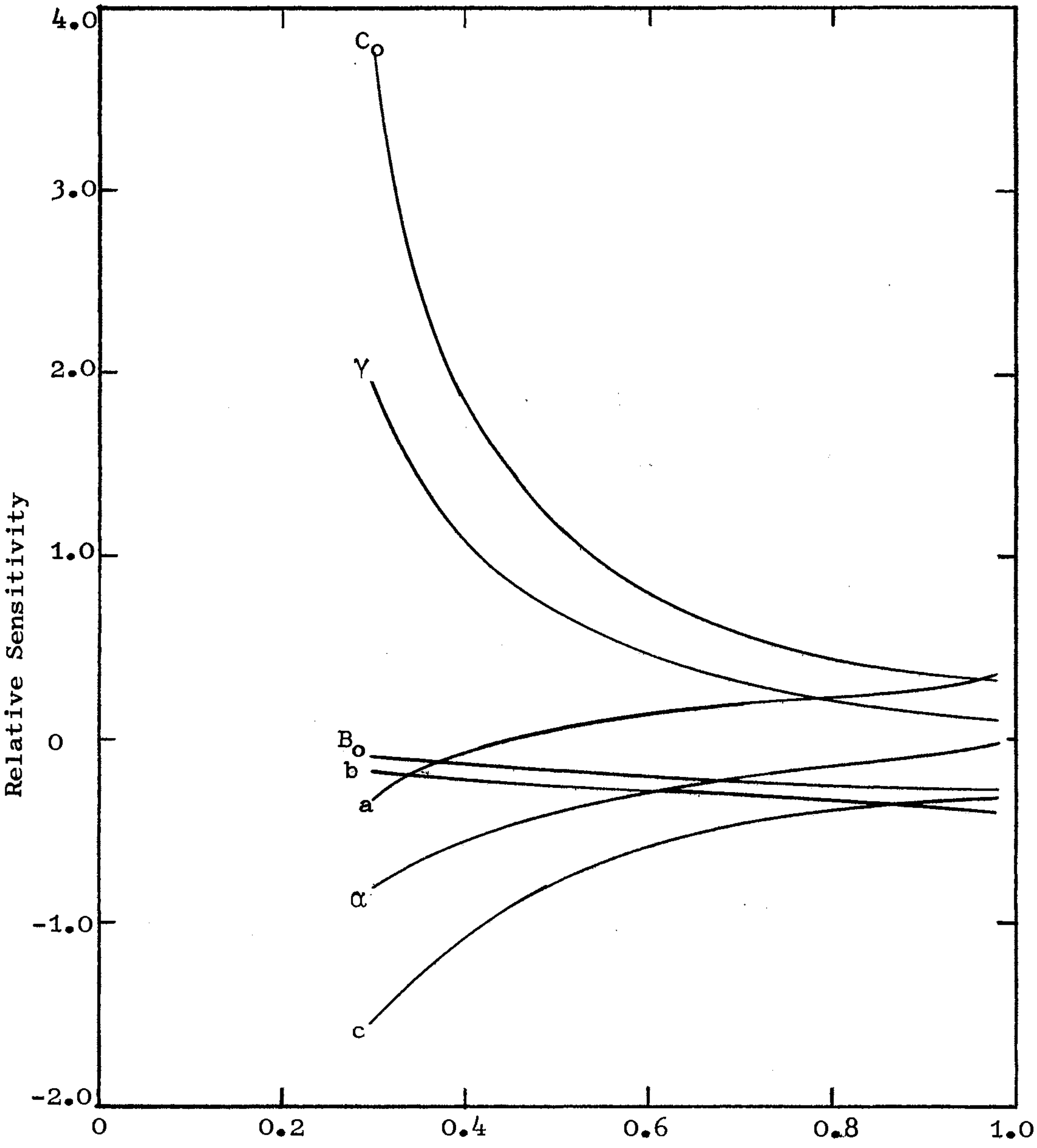


Figure 5. Relative Sensitivities of Saturated Vapor Volume to BWR Parameters

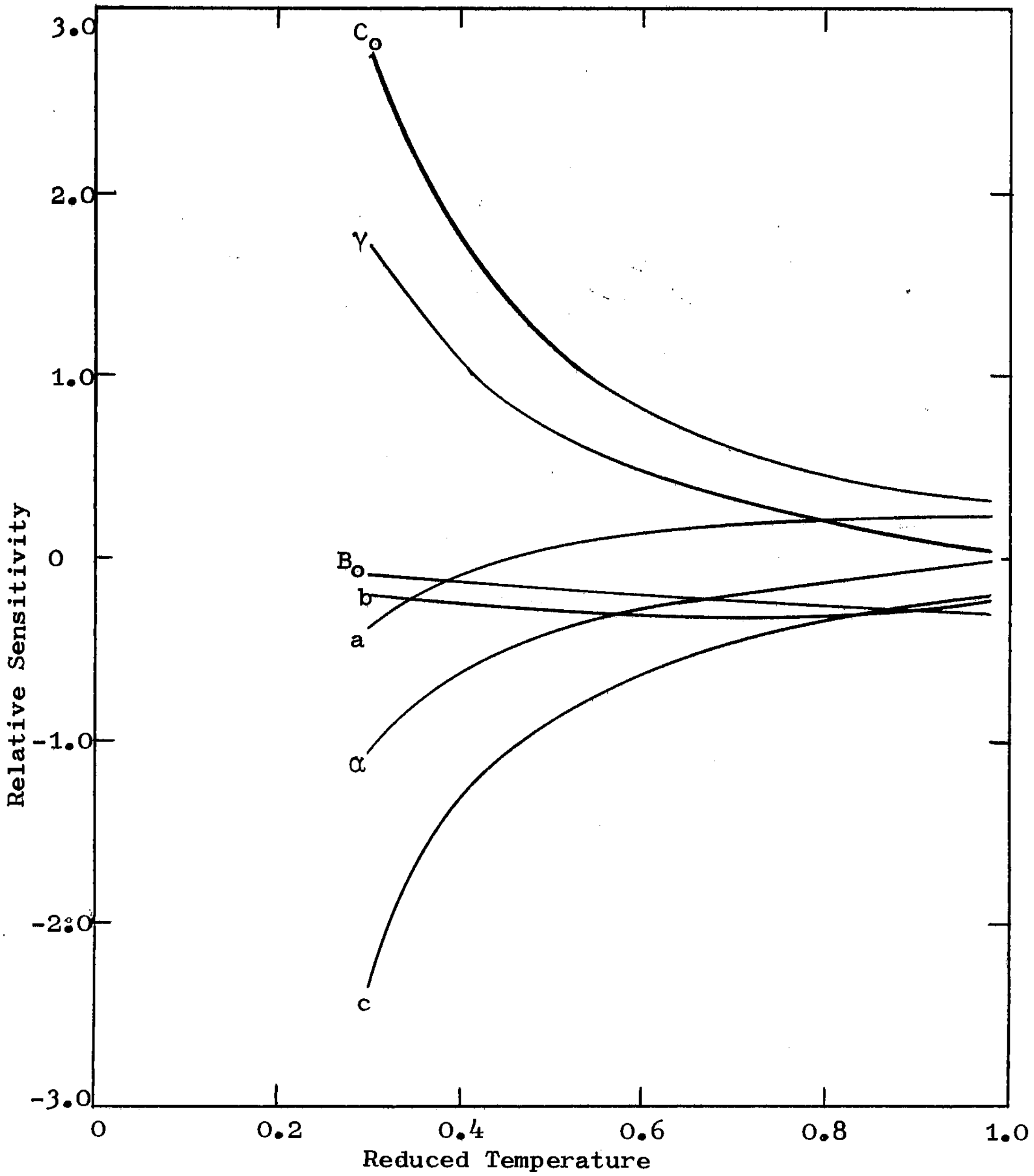


Figure 6. Relative Sensitivities of Saturated Phase Fugacity to BWR Parameters

CHAPTER IV

SIMULTANEOUS MODIFICATION OF PARAMETERS OF REDLICH-KWONG EQUATION TO PREDICT SATURATED PHASE PROPERTIES

The basic Redlich-Kwong equation of state is written as:

$$P = \frac{RT}{V - b} - \frac{a}{T^{1/2}\, V(V + b)} \qquad (4\text{-}1)$$

where

$$a = 0.4278\, \frac{R^2 T_c^{2.5}}{P_c} \qquad (4\text{-}2)$$

and

$$b = 0.0867\, \frac{R\, T_c}{P_c}\,. \qquad (4\text{-}3)$$

In order to predict better p-v-T behavior at saturated phase conditions, Chueh and Prausnitz (11, 12) suggested that the RK parameters were computed from the following equations:

$$a = \frac{\Omega_a R^2 T_c^{2.5}}{P_c} \qquad (4\text{-}4)$$

$$b = \frac{\Omega_b R\, T_c}{P_c}\,. \qquad (4\text{-}5)$$

They evaluated two pairs of constants ${}_g\Omega_a$, ${}_g\Omega_b$, and ${}_\ell\Omega_a$, ${}_\ell\Omega_b$ for vapor and liquid phases by fitting Equation (4-1) to saturated vapor and liquid phase p-v-T data, respectively.

Wilson (39, 40) had earlier proposed to keep the RK constant Ω_b = 0.0867 at all temperatures and to modify Ω_a as a function of temperature by equalizing fugacities along the vapor-pressure curve. Zudkevitch and Joffe (43) have applied experimental vapor pressures and saturated liquid and vapor densities (with the help of a fugacity coefficient correlation for saturated vapors) to obtain simultaneously the constants Ω_a and Ω_b as functions of temperature.

In this study, experimental vapor pressures and saturated liquid volumes were used for adjusting the constants Ω_a and Ω_b simultaneously. Such procedure has been discussed by Zudkevitch and Joffe (43). Constants for several hydrocarbons and non-hydrocarbons were modified. Table II shows the summary of data used in the modifications.

TABLE II

SUMMARY OF DATA FOR MODIFICATION

Substance	Temperature Range (°K)	Reference
Methane	99.83 - 191.05	(24)
Ethane	155.38 - 288.72	(3)
Propane	310.94 - 368.38	(34)
n-Butane	309.91 - 419.29	(15, 34)
n-Pentane	310.94 - 460.94	(34)
Carbon Dioxide	277.92 - 304.16	(34)
Hydrogen Sulfide	283.60 - 373.33	(34)

A detailed procedure for simultaneous modification of RK parameters is given in Appendix B. Results of calculations of the constants are shown in Table III and Figures 7 and 8. The plots of Figures 7 and 8 indicate that the temperature dependence of the RK parameters appears to be of a similar functional form.

Later, in Chapter VI, the results of saturated phase property predictions using the unmodified and modified equations will be compared.

TABLE III

EFFECT OF TEMPERATURE ON RK CONSTANTS

Substance	Temperature °K	Reduced Temp.	Ω_a	Ω_b
Methane	99.83	0.523	0.3968	0.08678
	108.16	0.566	0.4027	0.08652
	116.49	0.610	0.4053	0.08607
	124.83	0.653	0.4078	0.08554
	133.16	0.697	0.4103	0.08503
	141.49	0.741	0.4111	0.08434
	152.60	0.799	0.4111	0.08327
	163.72	0.857	0.4094	0.08194
	174.83	0.915	0.4054	0.08040
	185.94	0.973	0.4034	0.07946
	188.72	0.988	0.4049	0.07993
	191.05	1.000	0.4278	0.0866
Ethane	155.38	0.509	0.4165	0.08494
	177.60	0.582	0.4216	0.08452
	194.27	0.636	0.4226	0.08392
	205.38	0.672	0.4227	0.08352
	222.05	0.727	0.4215	0.08277
	238.72	0.782	0.4181	0.08170
	255.38	0.836	0.4137	0.08052
	263.72	0.863	0.4111	0.07988
	272.05	0.891	0.4087	0.07930
	288.72	0.945	0.4039	0.07828
Propane	310.94	0.840	0.4159	0.08004
	313.49	0.847	0.4156	0.07999
	327.60	0.885	0.4109	0.07921
	332.05	0.897	0.4094	0.07896
	344.27	0.931	0.4048	0.07827
	346.44	0.936	0.4040	0.07812
	358.27	0.968	0.4008	0.07792
	360.94	0.976	0.4006	0.07801
	368.38	0.996	0.4029	0.07924
n-Butane	309.91	0.729	0.4294	0.08070
	316.38	0.744	0.4280	0.08053
	327.60	0.771	0.4255	0.08021
	336.25	0.791	0.4234	0.08000
	344.27	0.810	0.4216	0.07978
	367.96	0.865	0.4160	0.07925
	377.60	0.888	0.4110	0.07834
	389.26	0.916	0.4066	0.07781
	405.84	0.955	0.4012	0.07726
	410.94	0.967	0.4002	0.07735
	419.29	0.986	0.4043	0.07917

TABLE III (Continued)

Substance	Temperature °K	Reduced Temp.	Ω_a	Ω_b
n-Pentane	310.94	0.661	0.4379	0.08015
	327.60	0.696	0.4396	0.08038
	344.27	0.732	0.4344	0.08017
	357.88	0.761	0.4317	0.07993
	370.10	0.786	0.4287	0.07962
	380.10	0.808	0.4260	0.07942
	390.49	0.830	0.4224	0.07912
	410.94	0.873	0.4153	0.07830
	427.60	0.909	0.4084	0.07750
	444.27	0.944	0.4027	0.07704
	460.94	0.980	0.3998	0.07752
Carbon Dioxide	279.92	0.920	0.4067	0.07773
	283.04	0.931	0.4048	0.07752
	285.92	0.940	0.4030	0.07739
	288.64	0.949	0.4012	0.07725
	291.23	0.958	0.3993	0.07708
	293.72	0.966	0.3979	0.07701
	296.12	0.974	0.3969	0.07702
	298.50	0.981	0.3968	0.07726
	300.83	0.989	0.3988	0.07804
	304.16	1.000	0.4278	0.08645
Hydrogen Sulfide	283.60	0.760	0.4217	0.08284
	299.33	0.802	0.4187	0.08206
	311.60	0.835	0.4171	0.08170
	321.88	0.862	0.4164	0.08156
	330.77	0.886	0.4142	0.08106
	338.66	0.907	0.4119	0.08054
	345.72	0.926	0.4098	0.08011
	352.05	0.943	0.4083	0.07993
	363.60	0.794	0.4074	0.07996
	373.33	1.000	0.4278	0.08656

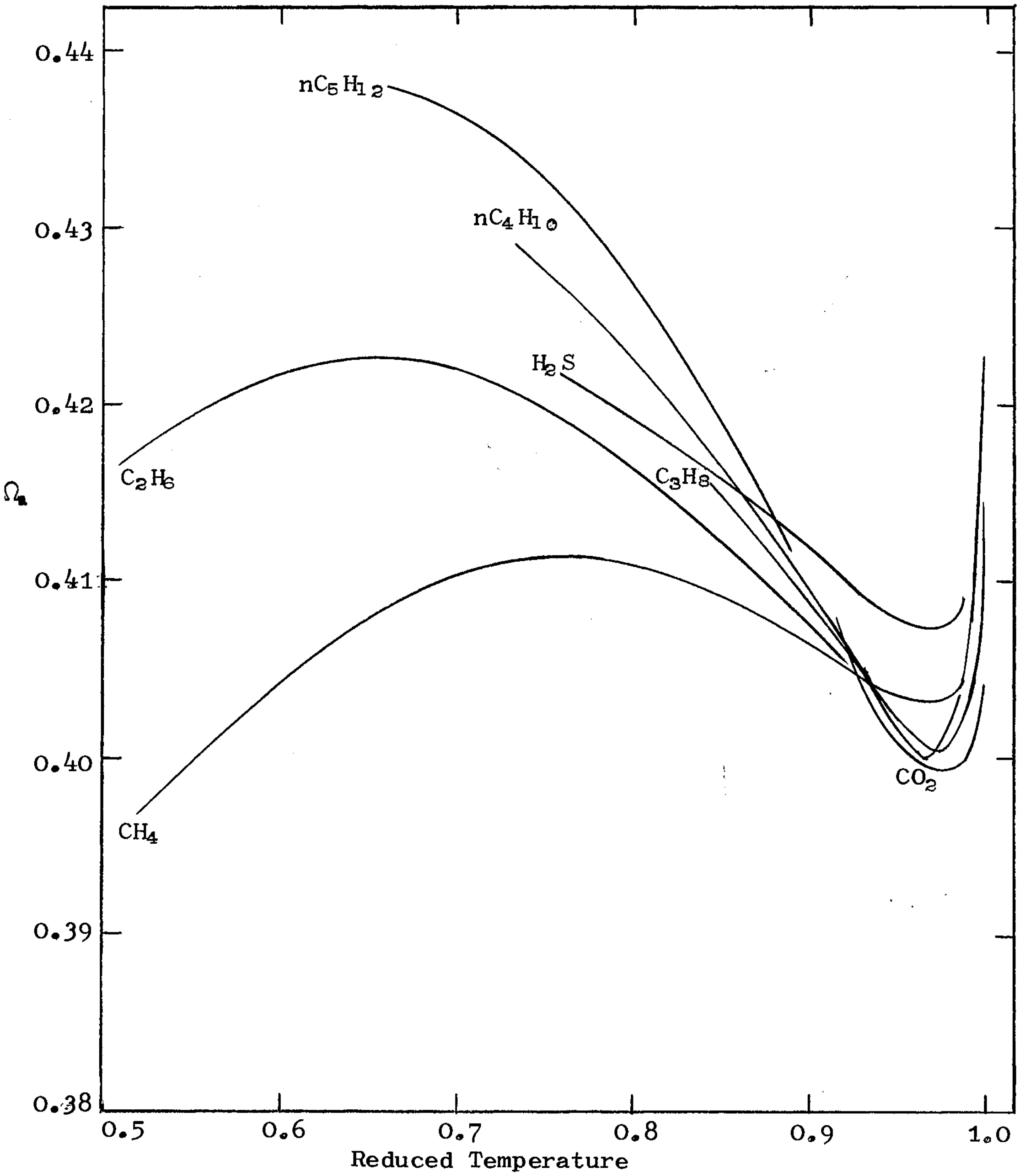


Figure 7. Temperature Dependence of Ω_a of RK Equation

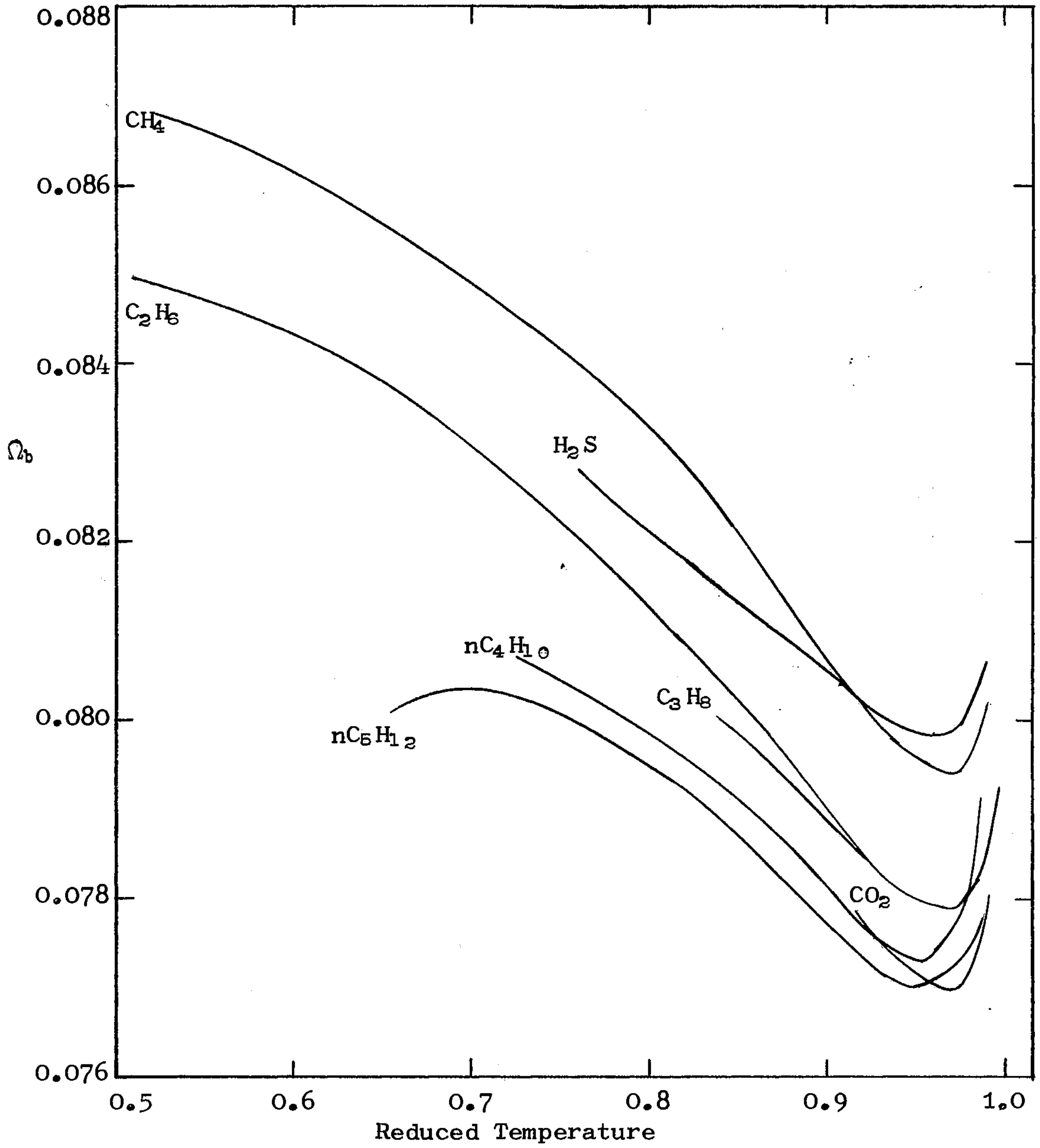


Figure 8. Temperature Dependence of Ω_b of RK Equation

CHAPTER V

SIMULTANEOUS MODIFICATION OF PARAMETERS OF BENEDICT-WEBB-RUBIN EQUATION TO PREDICT SATURATED PHASE PROPERTIES

The BWR equation of state was originally developed in 1940 to correlate and predict thermodynamic properties of light hydrocarbons and their mixtures. Since that time, many efforts have been extended towards the investigation of the applicability of this equation to other components. Some investigators (27) pointed out that the BWR equation was not suitable for extrapolation, and remarkable deviations were introduced when it was applied to conditions other than where the constants were fitted, especially at low temperatures.

The present study of simultaneous modifications of multiple parameters of the BWR equation was undertaken for the following reasons:

1. The basic BWR equation is known to be more accurate than the basic RK equation. As the RK equation modified by Zudkevitch and Joffe (43) produced excellent K values for binary systems, the BWR equation (with two parameters modified to fit vapor pressures and liquid volumes) seemed likely to predict more accurate K values.
2. Three BWR parameters could be modified to fit saturated phase properties (vapor pressures, liquid volumes, and vapor volumes) to determine if even further improvement

in vapor-liquid equilibrium calculations results. Thus, the modification of RK parameters described in the previous chapter was done to serve primarily as a basis for evaluating the planned BWR modifications.

The results of the preliminary investigations indicated that parameters C_o, α, and c may be most suitable for modification to predict more correct values of saturated phase properties. Furr (20) chose four pairs of parameters - A_o and γ, C_o and γ, γ and α, c and γ, to be fitted simultaneously to vapor pressures and saturated liquid densities. Starling and Powers (37) chose C_o and "a" for modification using multiproperty analysis. In this study, experimental vapor pressures and saturated liquid volumes were used to modify C_o and α, simultaneously, as functions of temperature. Three parameters, C_o, α, and c, were also simultaneously modified as functions of temperature by using experimental vapor pressures, saturated liquid volumes, and saturated vapor volumes.

Table IV shows the BWR parameters of several hydrocarbons and nonhydrocarbons which were modified.

TABLE IV

BWR PARAMETERS

Parameter \ Substance	Methane	Ethane	Propane	n-Butane	n-Pentane	Hydrogen Sulfide	Carbon Dioxide
$B_0 \times 10^2$	3.89972	6.27724	9.7313	12.4361	15.6751	4.081076	4.6940274
A_0	1.841062	4.15556	6.87225	10.0847	12.1794	3.1210859	2.7208408
$C_0 \times 10^{-5}$	0.1931744	1.79592	5.08256	9.9283	21.2121	2.3417331	1.239768
$b \times 10^3$	4.06537	11.122	22.5	39.9983	66.812	4.2705769	5.2112469
a	0.05767643	0.34516	0.9477	1.88231	4.0748	0.15453004	0.16905040
$\alpha \times 10^4$	0.86380	2.43389	6.07175	11.0132	18.10	0.68584625	0.52223807
$c \times 10^{-4}$	0.21540	3.2767	12.9	31.64	82.417	2.1359052	1.4052363
$\gamma \times 10^3$	5.1	11.8	22.0	34.0	47.5	4.1663636	4.2814994
Reference	(2)	(7)	(7)	(7)	(9)	(26)	(26)

Modification of Parameters C_o and α

In this section, experimental vapor pressures and saturated liquid volumes were used to modify C_o and α, simultaneously, as functions of temperature. The summary of experimental data for several hydrocarbons and non-hydrocarbons is shown in Table II. The procedure for modification used in this section is explained in Appendix C.

Results of the effects of temperature on the parameters were shown in Table V and Figures 9 through 15. The simultaneous fit of two parameters to vapor pressures and liquid volumes reveal a temperature dependence of the parameters which is not of a simple functional form. There is no apparent generality in the behavior of the temperature dependence of the parameters for different components. This might be due to the fact that the parameters for each component were fitted at different range of condition.

The predicted saturated phase properties using unmodified and modified parameters will be compared in Chapter VI.

TABLE V

EFFECT OF TEMPERATURE ON BWR PARAMETERS C_o and α

Substance	Temperature ^oK	Reduced Temp.	$C_o \times 10^{-6}$	$\alpha \times 10^3$
Methane	99.83	0.523	0.018629838	0.095733743
	108.16	0.566	0.018871921	0.093229870
	116.49	0.610	0.018954771	0.090992737
	124.83	0.653	0.019065888	0.089255934
	133.16	0.697	0.019226627	0.088270028
	141.49	0.741	0.019311596	0.087370192
	152.60	0.800	0.019408612	0.086477255
	163.72	0.857	0.019488122	0.085883465
	174.83	0.915	0.019392080	0.084903932
	185.94	0.973	0.019338906	0.084315830
Ethane	155.38	0.509	0.17080852	0.25364994
	177.60	0.582	0.17264344	0.24116822
	194.27	0.636	0.17340757	0.23415775
	205.38	0.672	0.17400370	0.23136624
	222.05	0.727	0.17483306	0.22891665
	238.72	0.782	0.17556429	0.22791916
	255.38	0.836	0.17660842	0.22934433
	263.72	0.863	0.17714482	0.23049289
	272.05	0.891	0.17790187	0.23254790
	288.72	0.945	0.17937783	0.23740566
Propane	310.94	0.840	0.50389128	0.58452603
	313.49	0.847	0.50495628	0.58763209
	327.60	0.885	0.50705884	0.59669319
	332.05	0.897	0.50782396	0.59963437
	344.27	0.931	0.50903279	0.60762316
	346.44	0.9363	0.50925690	0.60824035
n-Butane	309.91	0.729	0.98786801	1.0745935
	316.38	0.744	0.98803948	1.0730252
	327.60	0.771	0.98970430	1.0737846
	336.25	0.791	0.99133453	1.0794143
	344.27	0.810	0.99345358	1.0850117
	367.96	0.865	1.0007853	1.1143115
	377.60	0.888	0.99818043	1.1040867
	389.26	0.916	0.99799358	1.1115632
	405.84	0.955	0.99811035	1.1178867

TABLE V (Continued)

Substance	Temperature ^{o}K	Reduced Temp.	$C_{\theta} \times 10^{-6}$	$\alpha \times 10^{3}$
n-Pentane	310.94	0.661	2.0862834	1.7535447
	327.60	0.696	2.1077859	1.7671245
	344.27	0.732	2.1017159	1.7662296
	357.88	0.761	2.1060317	1.7697781
	370.10	0.786	2.1092985	1.7748225
	380.10	0.808	2.1114945	1.7829967
	390.49	0.830	2.1118856	1.7943483
	410.94	0.873	2.1145487	1.8086742
	427.60	0.909	2.1131639	1.8157965
	444.27	0.944	2.1134883	1.8283396
Carbon Dioxide	279.92	0.920	0.12536919	0.052273977
	283.04	0.931	0.12510016	0.052257598
	285.92	0.940	0.12470702	0.052223785
	288.64	0.949	0.12427721	0.052076347
	291.23	0.958	0.12382305	0.051802934
	293.72	0.966	0.12341964	0.051506567
	296.12	0.974	0.12306399	0.051170356
	298.50	0.981	0.12286560	0.050926405
	300.83	0.989	0.12280848	0.050858408
	304.16	1.000	0.12297990	0.051761364
Hydrogen Sulfide	283.60	0.760	0.22108017	0.065597474
	299.30	0.802	0.22197369	0.064791331
	311.60	0.835	0.22302692	0.064829645
	321.88	0.862	0.22319848	0.065357883
	330.77	0.886	0.22453275	0.064962721
	338.66	0.907	0.22471689	0.064472782
	345.72	0.926	0.22471689	0.063955644
	352.05	0.943	0.22453857	0.063697724
	363.60	0.974	0.22469592	0.063129483
	373.33	1.000	0.22429592	0.07328204

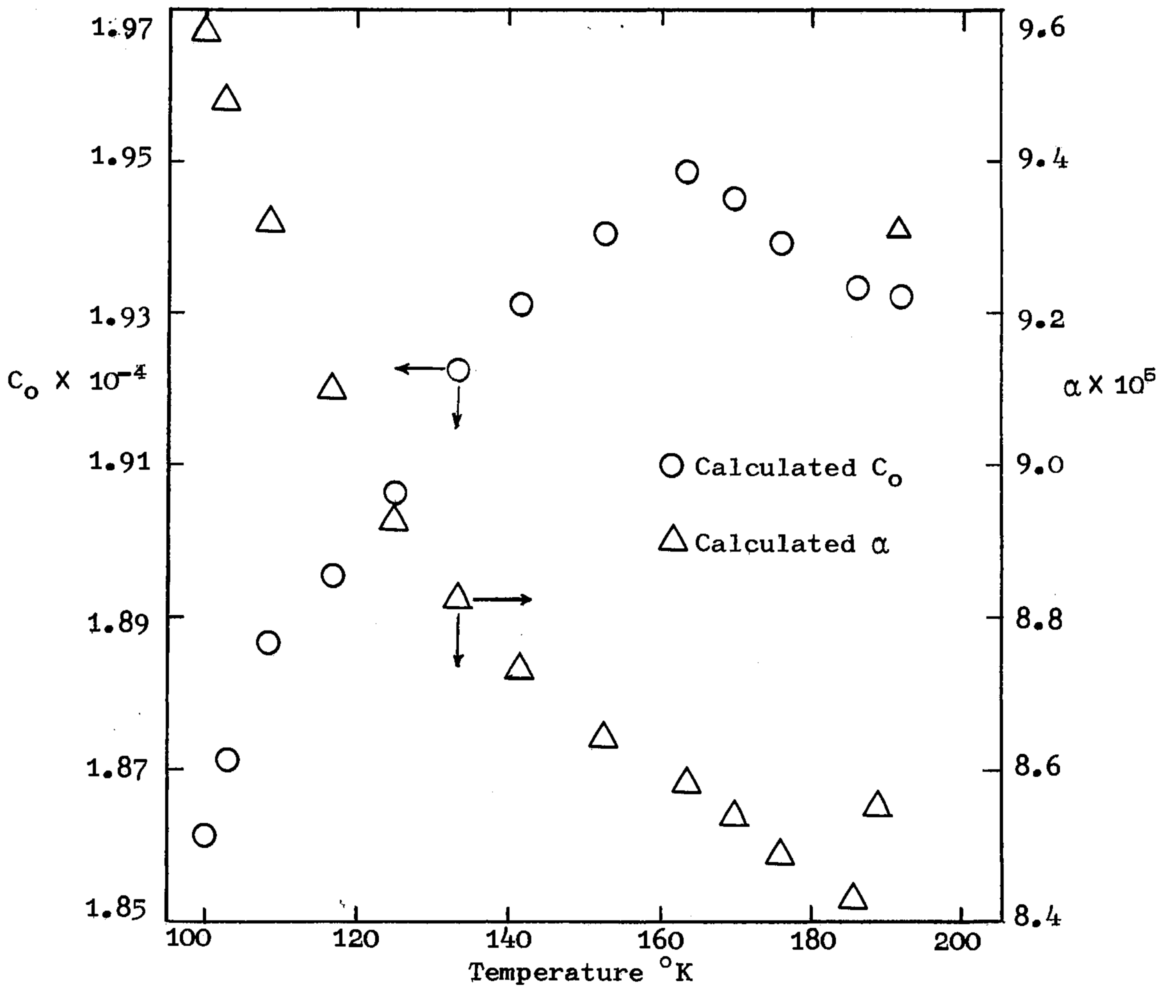


Figure 9. Temperature Dependence of C_o and α of Methane Simultaneously Modified to Fit Vapor Pressures and Liquid Volumes

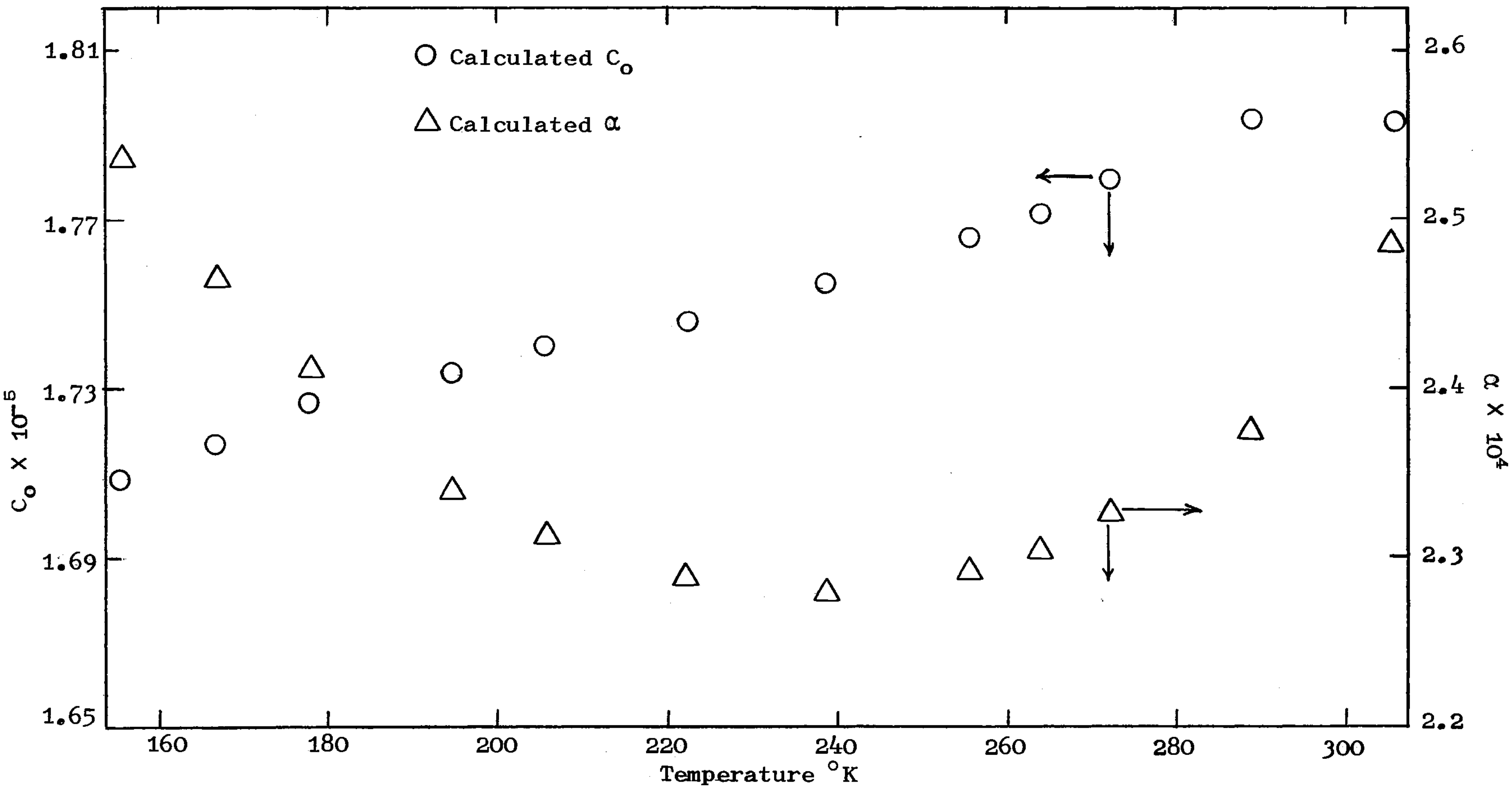


Figure 10. Temperature Dependence of C_o and α of Ethane Simultaneously Modified to Fit Vapor Pressures and Liquid Volumes

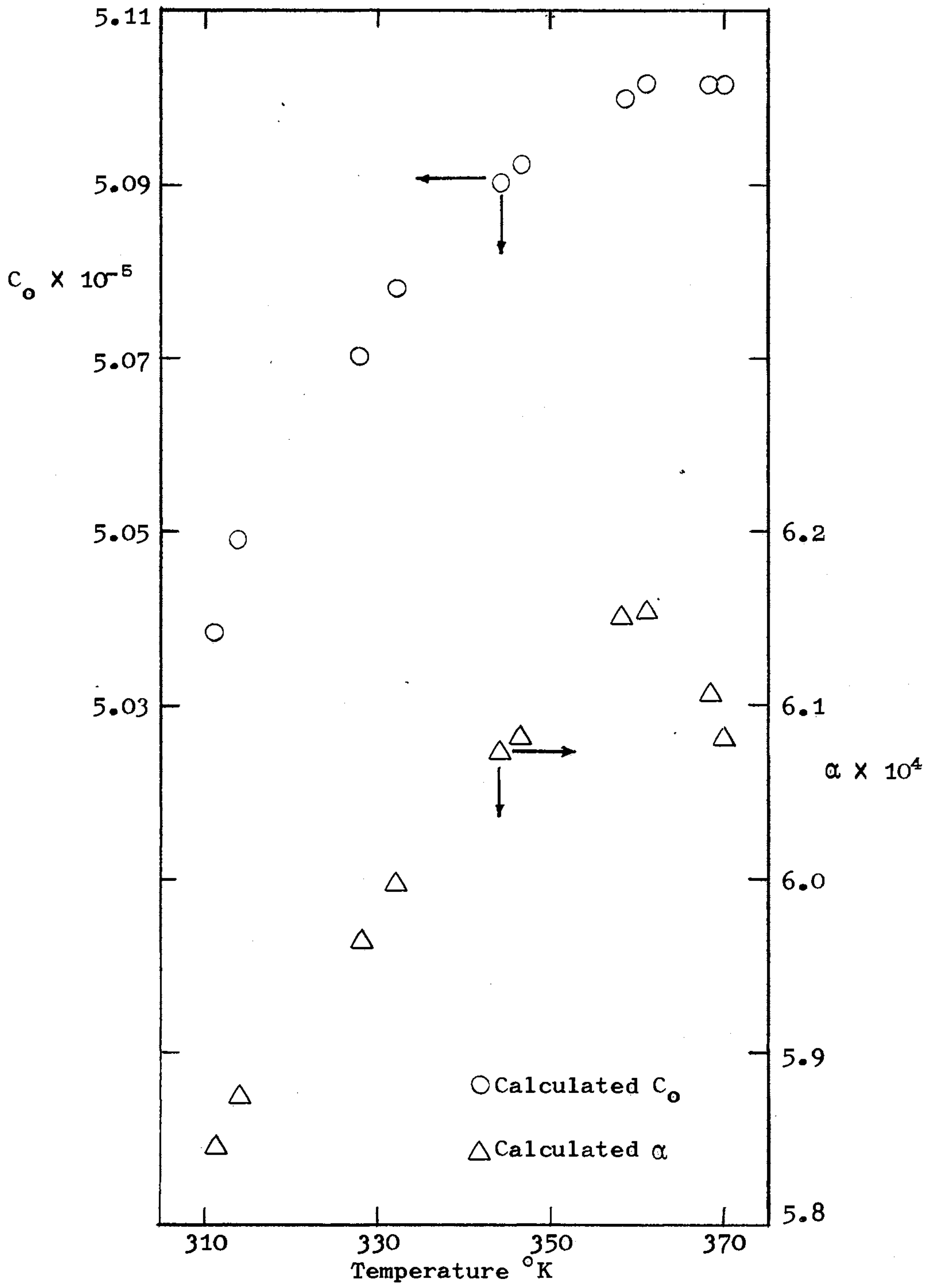


Figure 11. Temperature Dependence of C_o and α of Propane Simultaneously Modified to Fit Vapor Pressures and Liquid Volumes

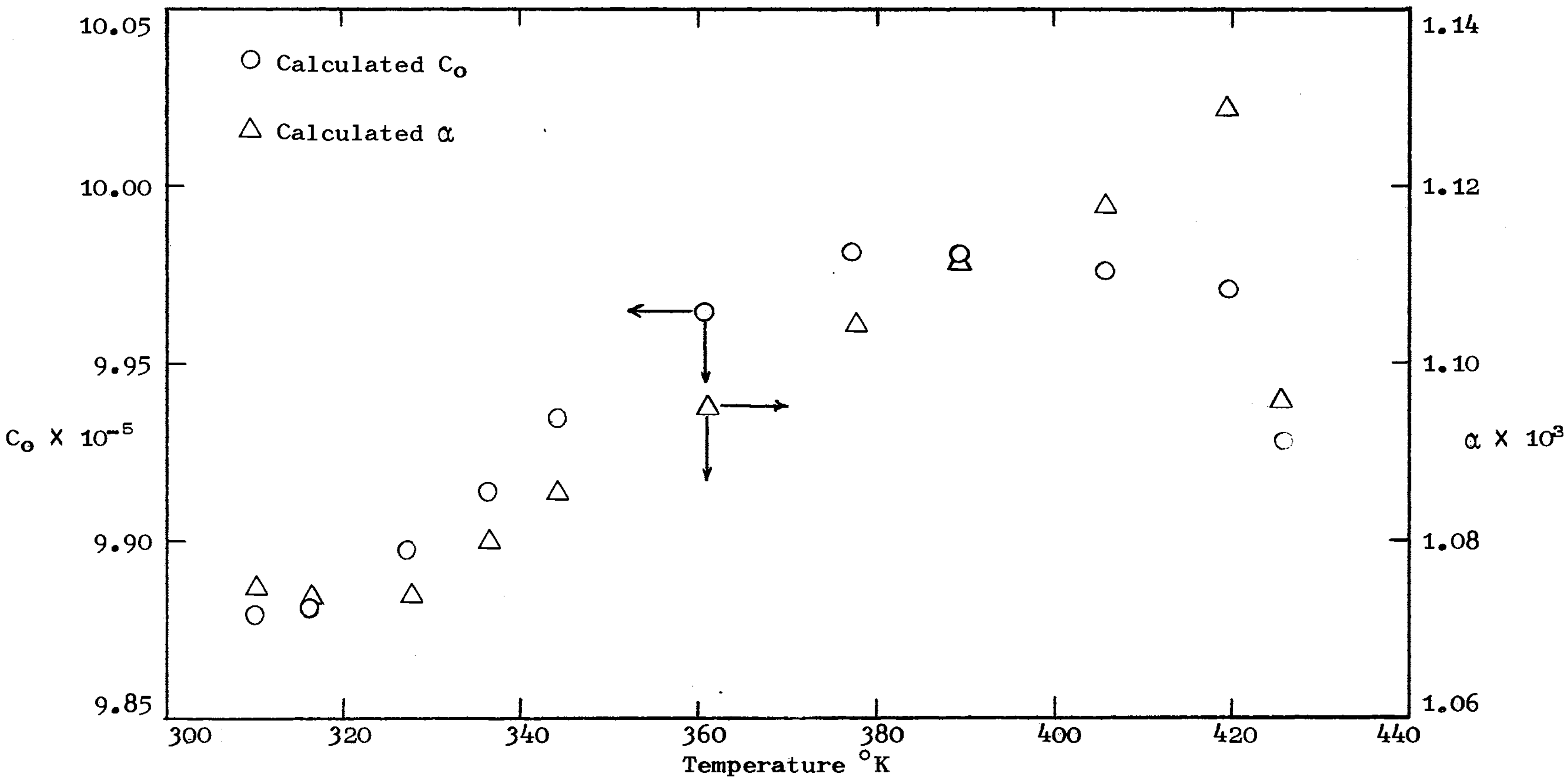


Figure 12. Temperature Dependence of C_o and α of n-Butane Simultaneously Modified to Fit Vapor Pressures and Liquid Volumes

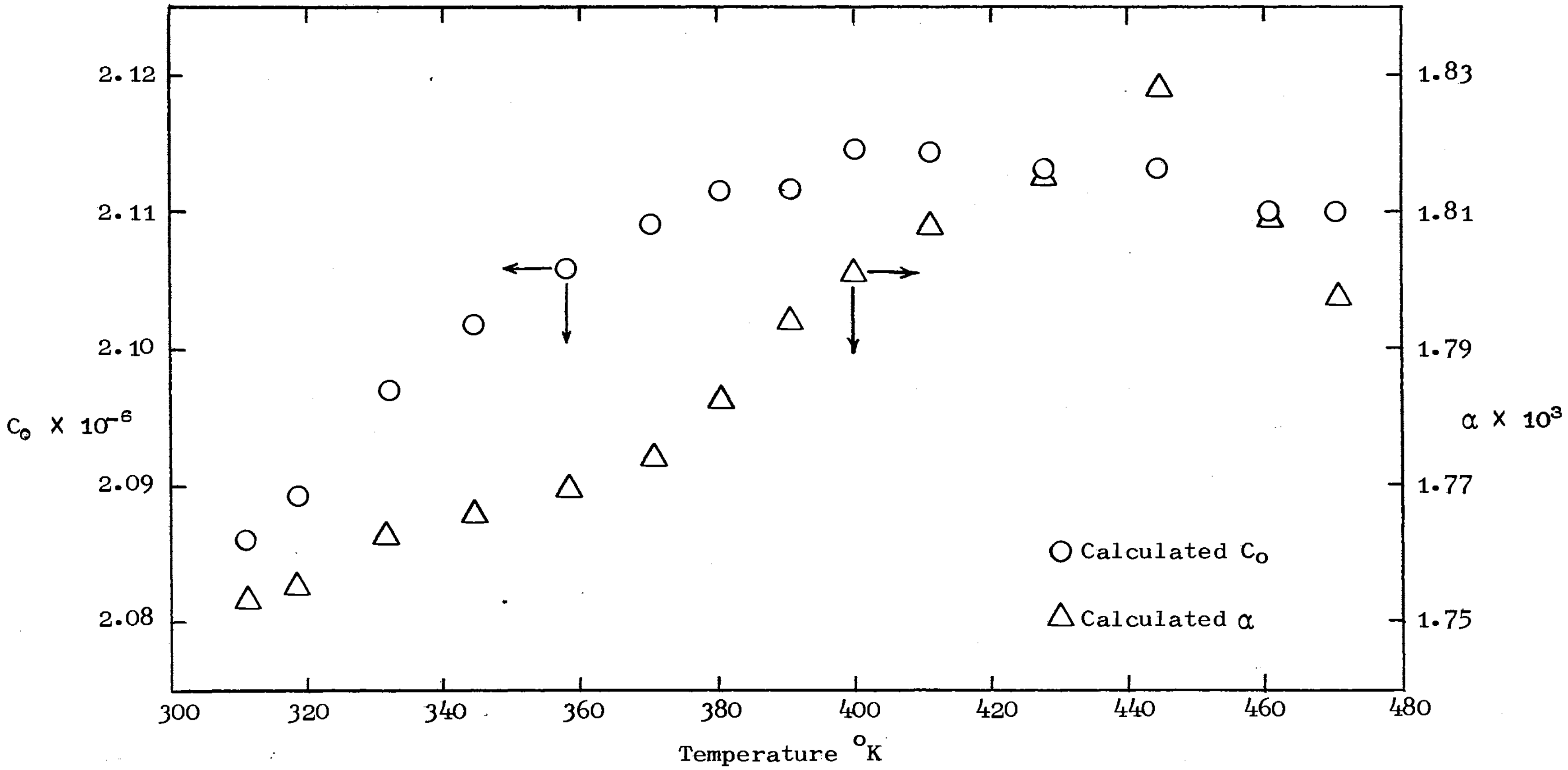


Figure 13. Temperature Dependence of C_o and α of n-Pentane Simultaneously Modified to Fit Vapor Pressures and Liquid Volumes

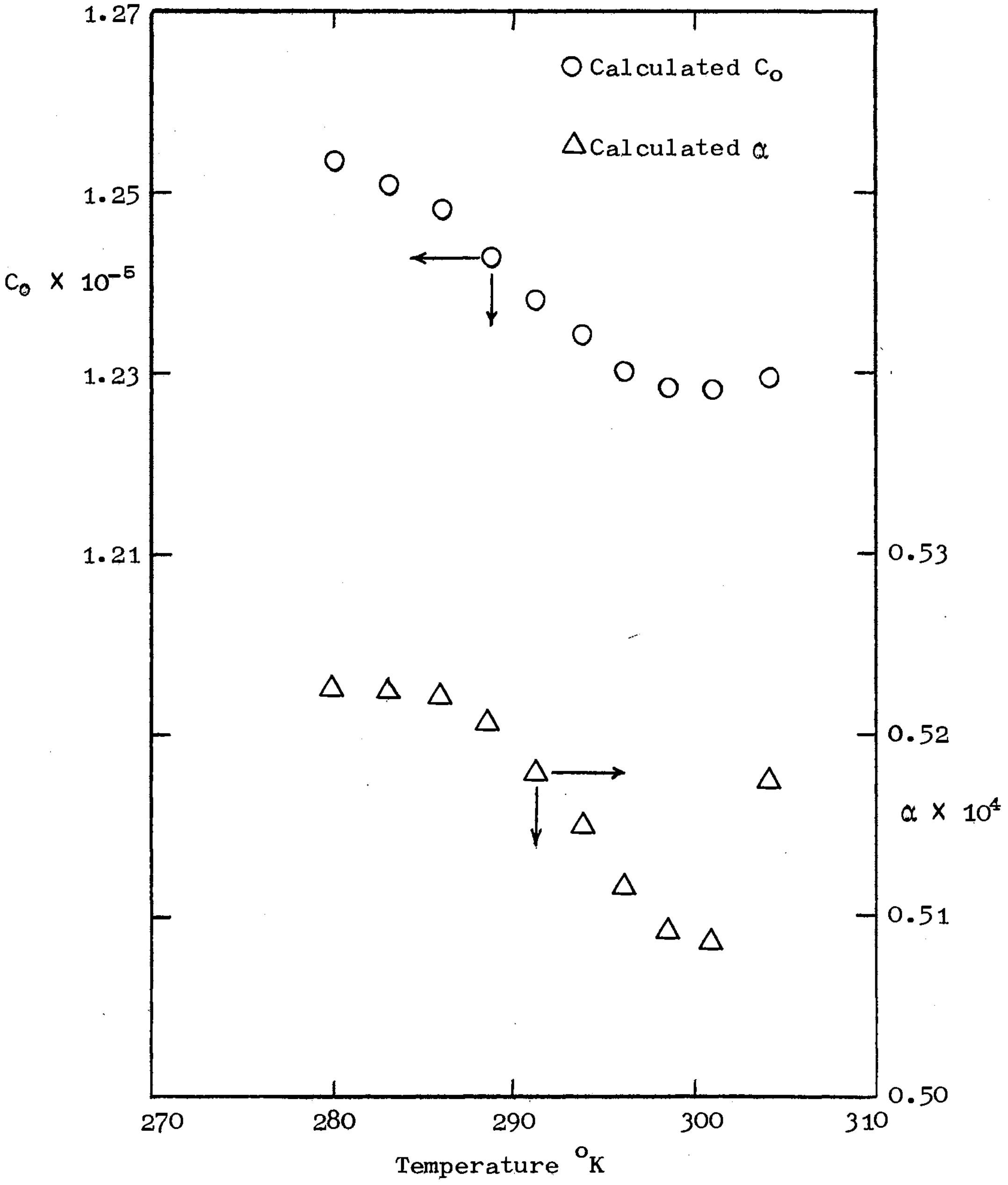


Figure 14. Temperature Dependence of C_o and α of Carbon Dioxide Simultaneously Modified to Fit Vapor Pressures and Liquid Volumes

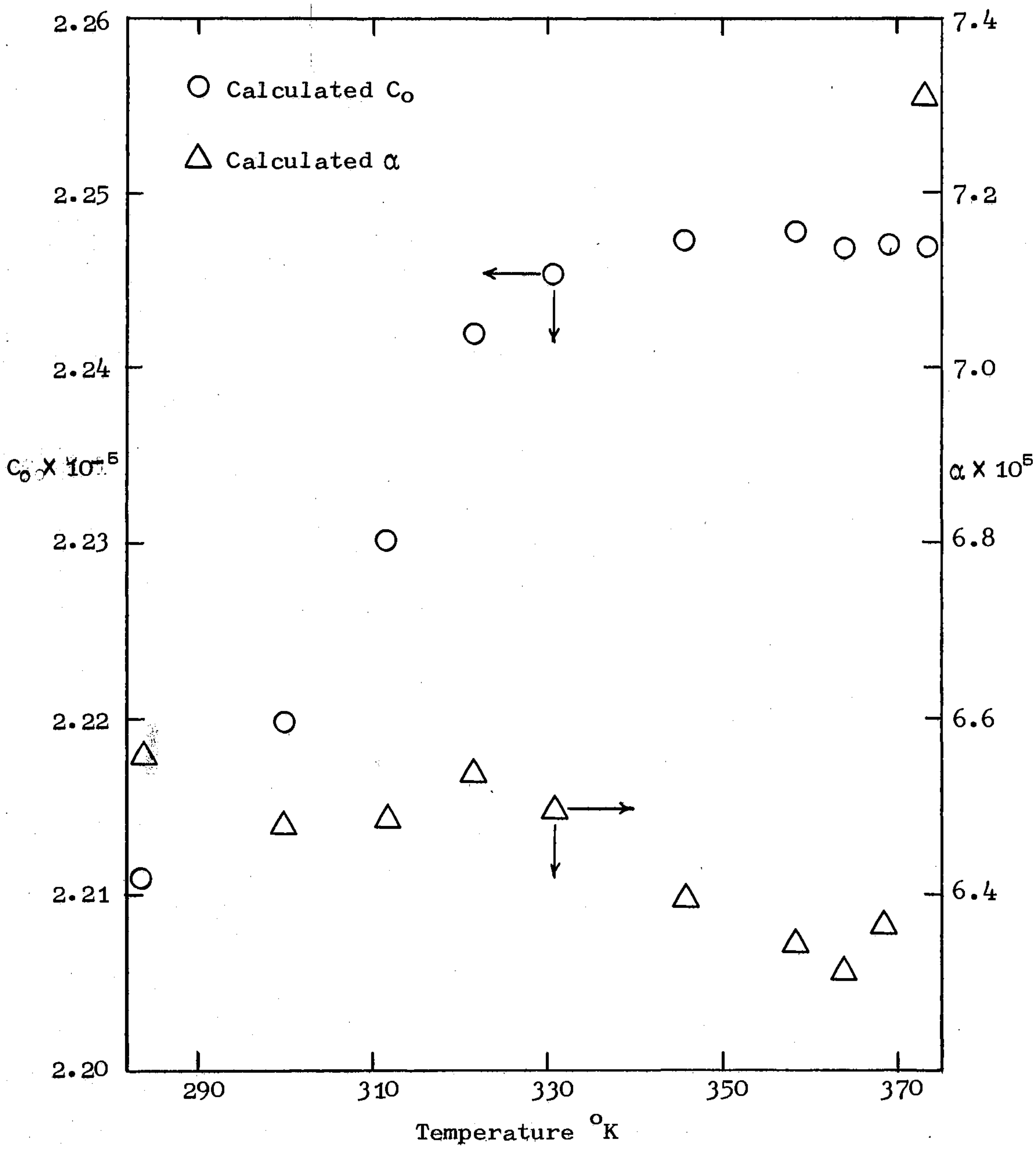


Figure 15. Temperature Dependence of C_o and α of Hydrogen Sulfide Simultaneously Modified to Fit Vapor Pressures and Liquid Volumes

Modification of Parameters C_o, α, and c

The parameters C_o, α, and c were modified as functions of temperature by using experimental vapor pressures, liquid volumes, and vapor volumes. A detailed procedure for simultaneously modifying the parameters at a given temperature is shown in Appendix C.

Table VI and Figures 16 through 22 show the results of calculations. The temperature dependence of the parameters is not of a simple functional form. There is no generality in behavior of temperature dependence of the parameters for different components.

TABLE VI

EFFECT OF TEMPERATURE ON BWR PARAMETERS C_0, α, and c

Substance	Temp. ^{o}K	Reduced Temp.	$C_0 \times 10^{-6}$	$\alpha \times 10^{3}$	$c \times 10^{-5}$
Methane	99.83	0.523	0.025567817	0.10907949	0.030585248
	108.16	0.566	0.023488357	0.10098335	0.027526722
	116.49	0.610	0.021461099	0.094672429	0.024774050
	124.83	0.653	0.020865996	0.091554039	0.023851604
	133.16	0.697	0.020774943	0.089961554	0.023518972
	141.49	0.741	0.019464090	0.087508991	0.021733338
	152.60	0.800	0.019832978	0.086735847	0.022078156
	163.72	0.857	0.020692966	0.086164344	0.023050957
	174.83	0.915	0.020376101	0.084479044	0.022768072
	185.94	0.973	0.020990775	0.080841195	0.023596918
Ethane	155.38	0.509	0.17080841	0.25364945	0.32767000
	177.60	0.582	0.22088971	0.26684287	0.42352643
	194.27	0.636	0.18948914	0.24160213	0.35931880
	205.38	0.672	0.18487600	0.23596075	0.34891699
	222.05	0.727	0.17778030	0.22999428	0.33336332
	238.72	0.782	0.18092664	0.22956313	0.33791075
	255.38	0.836	0.17673895	0.22937471	0.32791601
	263.72	0.863	0.17535105	0.23016374	0.32429585
	272.05	0.891	0.17489460	0.23217724	0.32206788
	288.72	0.945	0.18234156	0.23720669	0.33299897
Propane	310.94	0.840	0.49962767	0.58374850	1.2790000
	313.49	0.847	0.50457499	0.58756910	1.2890110
	327.60	0.885	0.50667412	0.59666049	1.2890110
	332.50	0.897	0.50566999	0.59951817	1.2844880
	344.27	0.931	0.50238749	0.60812560	1.2730789
	346.44	0.936	0.50137503	0.60904032	1.2699878
n-Butane	309.91	0.729	0.90516313	1.0514865	2.8907092
	316.38	0.744	0.90518216	1.0510981	2.8907092
	327.60	0.771	0.92735512	1.0589764	2.9590382
	336.25	0.791	0.93884204	1.0682361	2.9916852
	344.27	0.810	0.94080697	1.0750855	2.9916852
	367.96	0.865	0.96941452	1.1117337	3.0617079
	377.60	0.888	0.97619576	1.1032021	3.0927396
	389.26	0.916	0.97591242	1.1126908	3.0927396
	405.84	0.955	0.98011265	1.1229284	3.1061470

TABLE VI (Continued)

Substance	Temp. °K	Reduced Temp.	$C_0 \times 10^{-6}$	$\alpha \times 10^{3}$	$C \times 10^{-5}$
n-Pentane	310.94	0.661	1.6602581	1.6459707	6.5615712
	327.60	0.696	1.8476877	1.7089035	7.2177246
	344.27	0.732	1.8127316	1.7102368	7.1059002
	357.88	0.761	1.8905134	1.7337277	7.3952650
	370.10	0.786	1.9255921	1.7488648	7.5212736
	380.10	0.808	1.9277212	1.7616343	7.5212736
	390.49	0.830	1.9497166	1.7806139	7.6056430
	410.94	0.873	2.0117660	1.8075728	7.8397538
	427.60	0.909	2.0399354	1.8216067	7.9556694
	444.27	0.944	2.0542289	1.8426827	8.0106793
Carbon Dioxide	279.92	0.920	0.13311404	0.051786147	0.14961016
	281.50	0.926	0.13299586	0.051731735	0.14961016
	283.04	0.931	0.13283211	0.051594168	0.14961016
	284.47	0.935	0.13258843	0.051485964	0.14961016
	285.92	0.940	0.13243304	0.051361324	0.14961016
	287.29	0.945	0.13221837	0.051181110	0.14961016
	288.64	0.949	0.13201218	0.051002714	0.14961016
Hydrogen Sulfide	283.60	0.760	0.26146767	0.066703639	0.26152731
	299.33	0.802	0.25138310	0.064941851	0.24859181
	311.60	0.835	0.24759185	0.064343586	0.24297081
	321.88	0.862	0.24606488	0.064268060	0.23992234
	330.77	0.886	0.24631423	0.063276267	0.23992234
	338.66	0.907	0.24645423	0.062131193	0.23992234
	345.72	0.926	0.24639875	0.060867777	0.23992234
	352.05	0.943	0.24713164	0.059401871	0.24115209

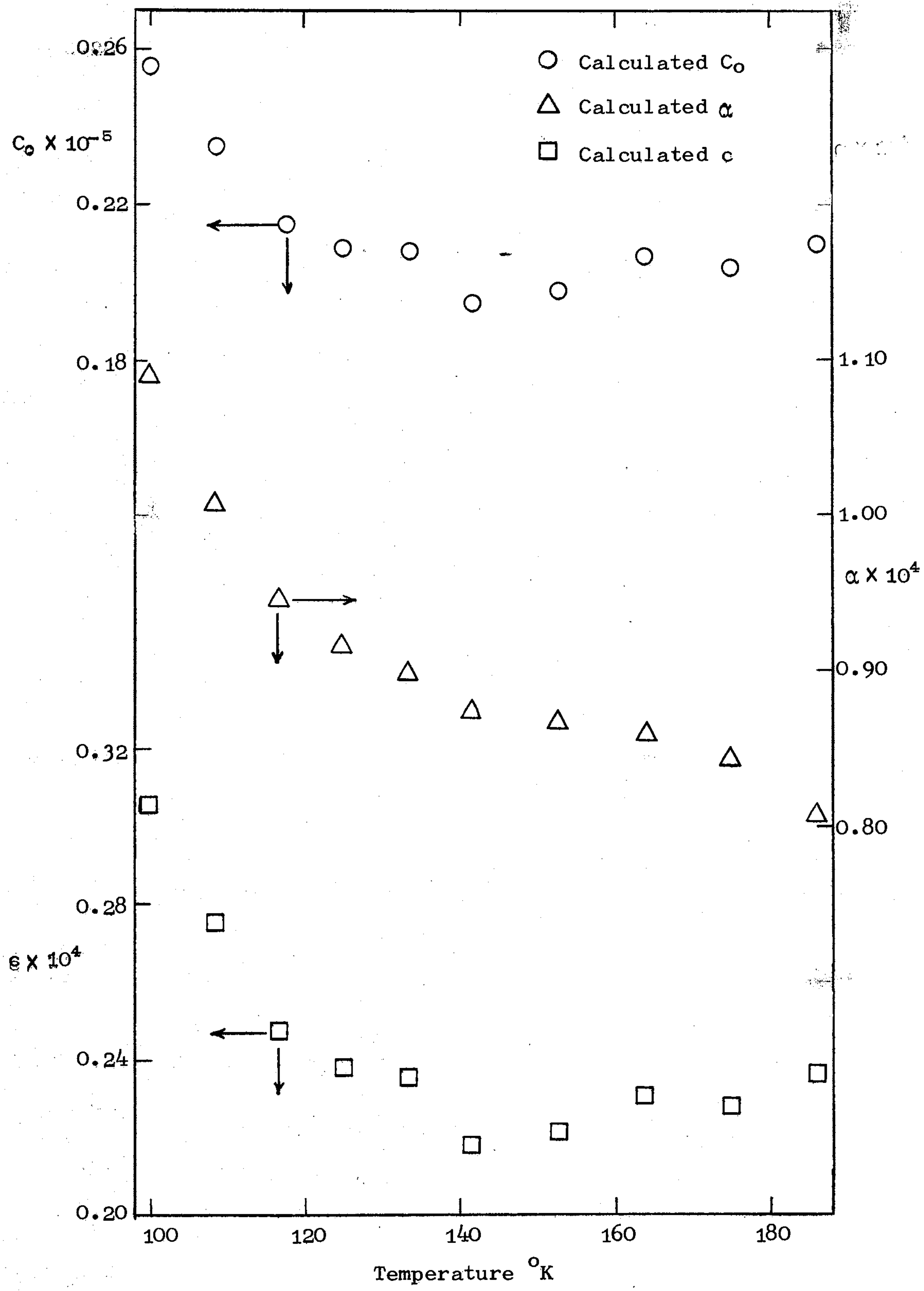


Figure 16. Temperature Dependence of C_o, α, and c for Methane

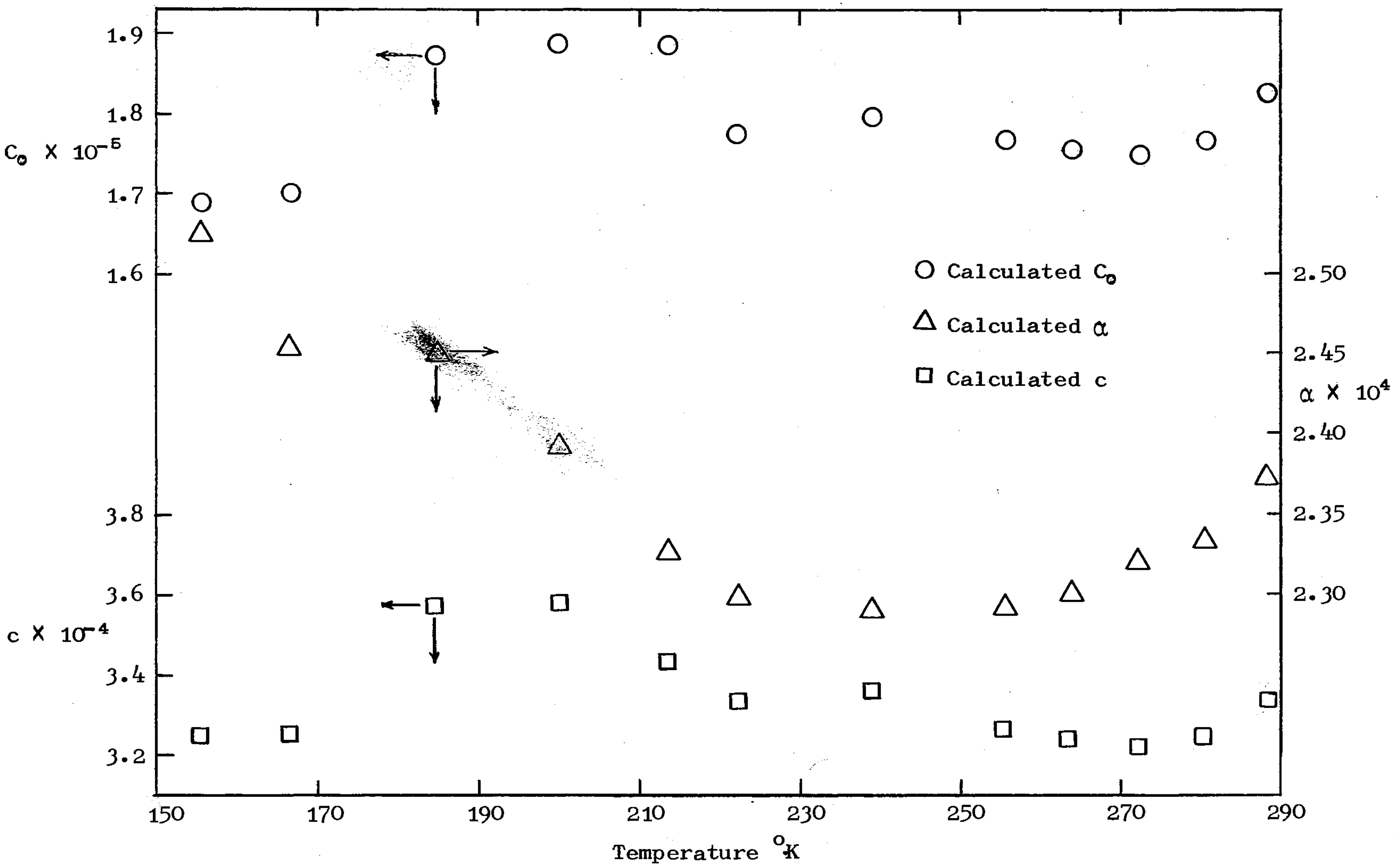


Figure 17. Temperature Dependence of C_o, α, and c for Ethane

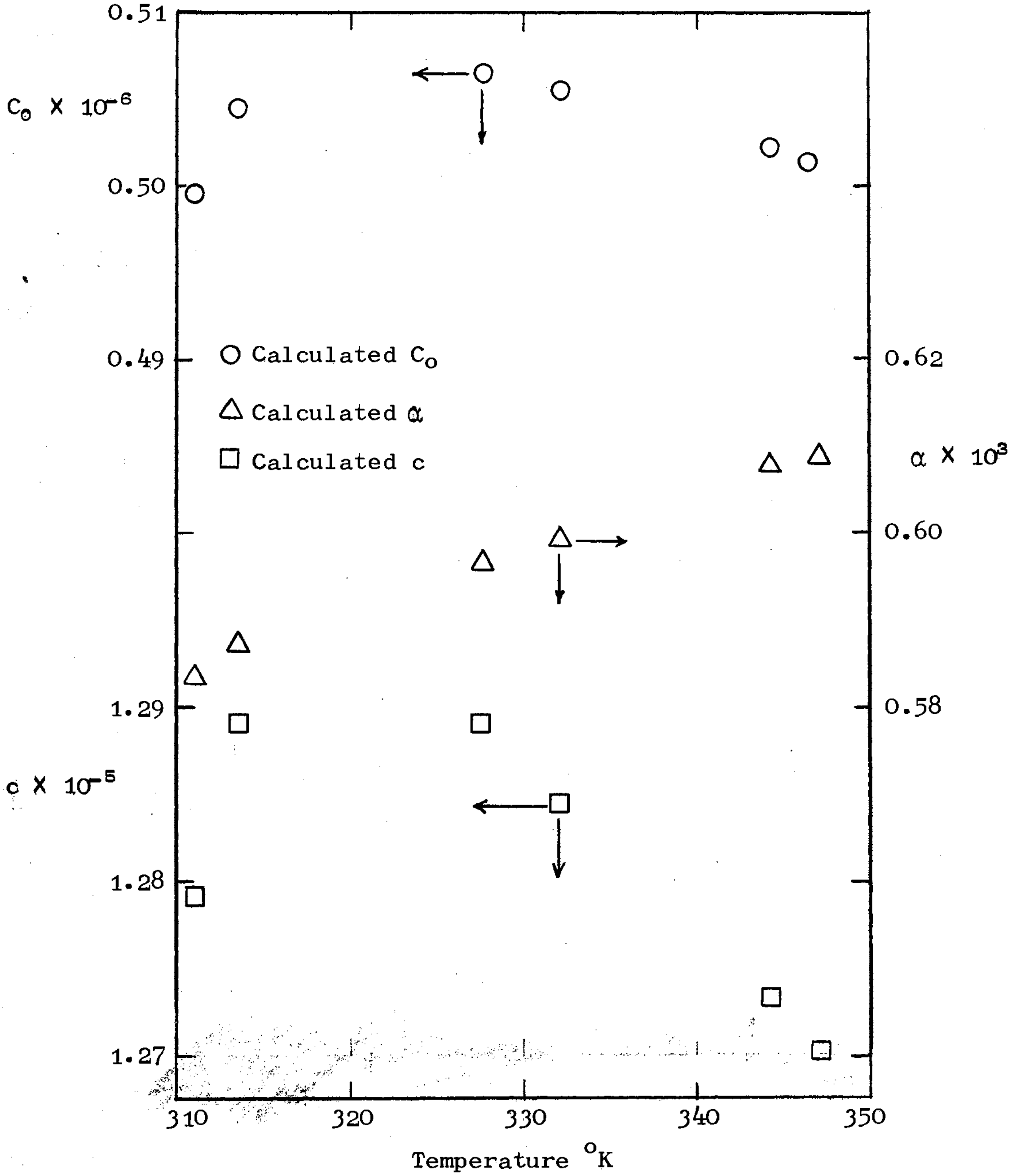


Figure 18. Temperature Dependence of C_o, α, and c for Propane

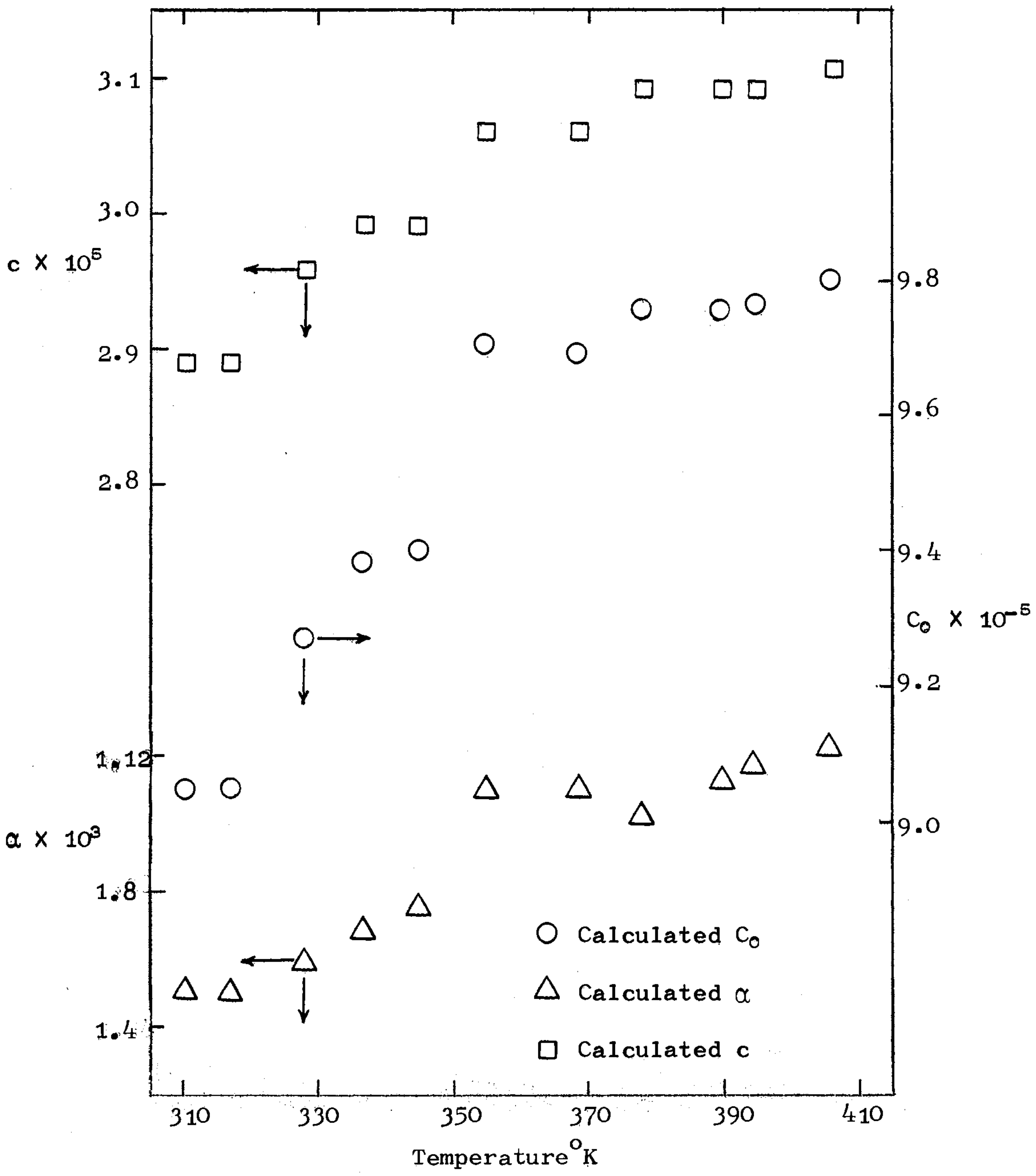


Figure 19. Temperature Dependence of C_0, α, and c for n-Butane

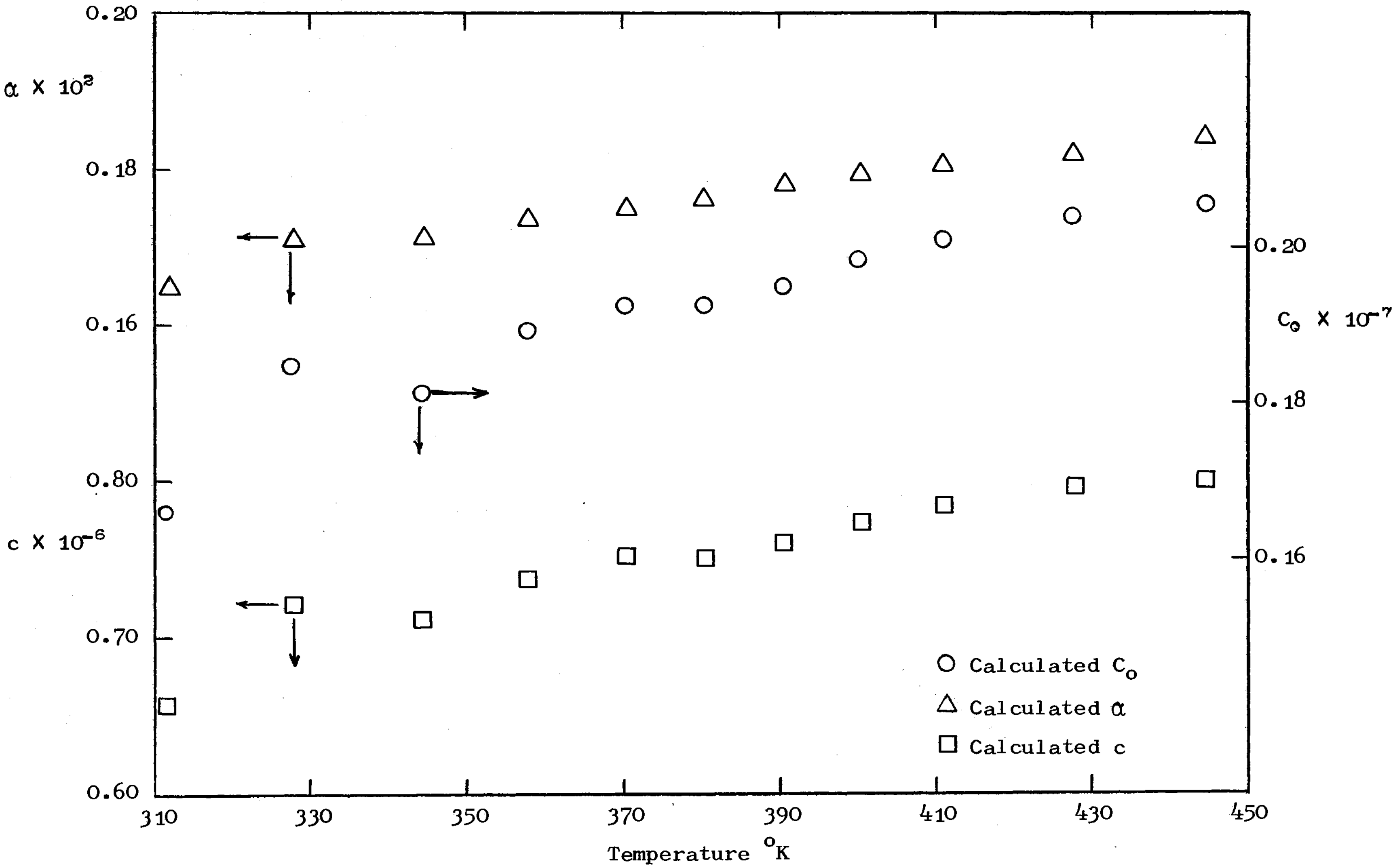


Figure 20. Temperature Dependence of C_o, α, and c for n-Pentane

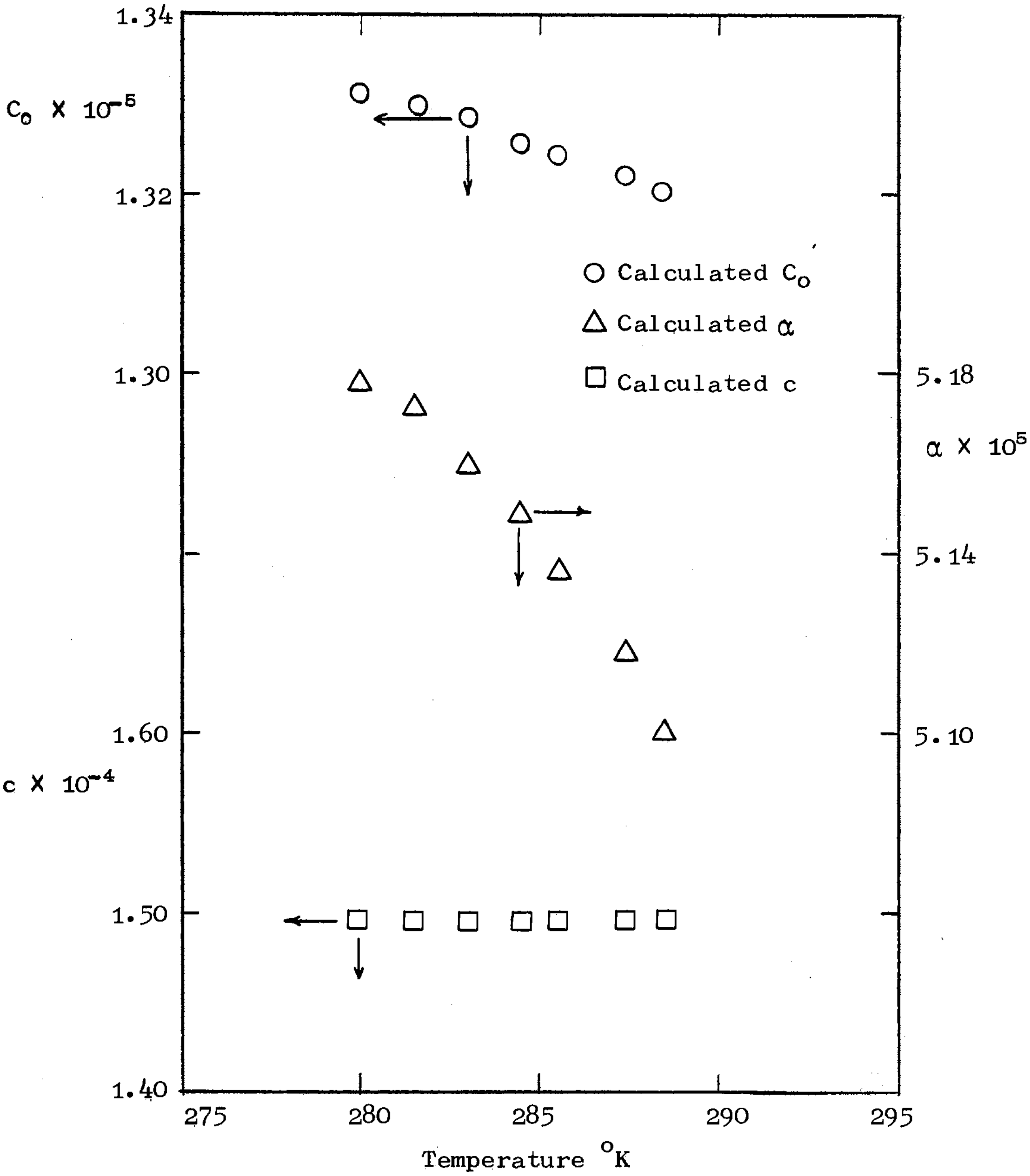


Figure 21. Temperature Dependence of C_o, α, and c for Carbon Dioxide

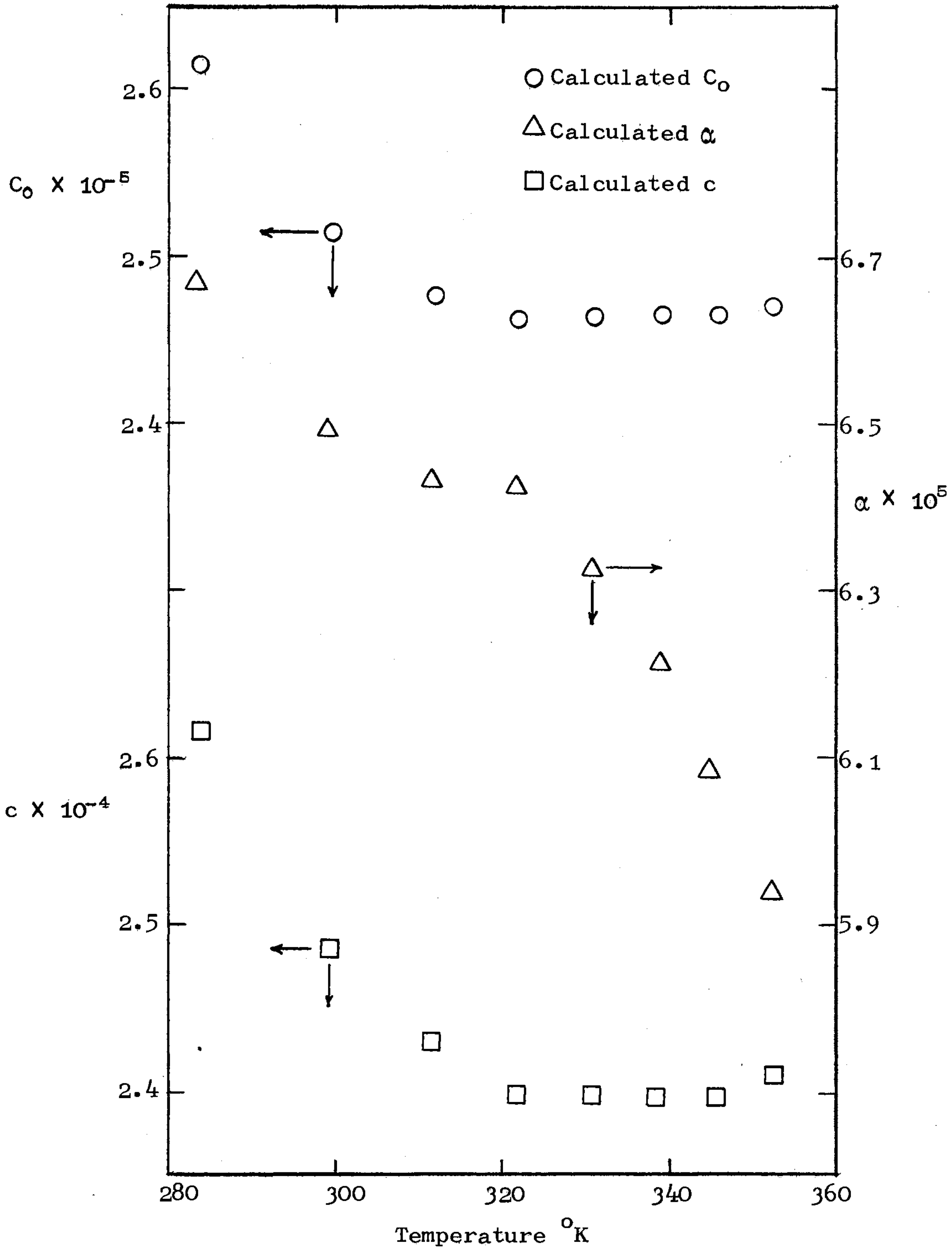


Figure 22. Temperature Dependence of C_o, α, and c for Hydrogen Sulfide

CHAPTER VI

COMPARISON OF THE RESULTS OF PREDICTED SATURATED PHASE PROPERTIES BY USING BASIC AND MODIFIED EQUATIONS OF STATE

Deviations of calculated saturated phase properties from experimental data were compared. The saturated phase properties were first predicted using the basic equations of state, and then predicted by using the modified equations. Tables VII through XIII give the over-all comparisons for several hydrocarbons and non-hydrocarbons which have been studied.

As shown by previous investigations, the BWR equation gives better results than the RK equation. In predicting the saturated liquid volume, the unmodified RK equation showed considerable errors, especially in the critical region. In predicting the saturated phase properties, other than liquid volume, the unmodified RK equation also gave large deviations for methane, n-butane, and n-pentane.

Equations simultaneously modified from vapor pressures and liquid volumes predict more accurate vapor volumes and fugacities than the unmodified equations. Of course, the BWR equation with three modified parameters predicts more accurate vapor volumes than the BWR equation with two modified parameters; it also predicts better fugacities.

The errors shown in the following tables for properties which have been fitted to are results of tolerance limits set for conversion in the computer program (a tolerance of 0.1 per cent deviation between the calculated and experimental phase properties was used).

TABLE VII

DEVIATIONS OF CALCULATED SATURATED PHASE PROPERTIES FROM EXPERIMENTAL DATA (24) FOR METHANE

Temperature °K	Unmod. RK	Mod. RK	Unmod. BWR	Mod. BWR-1*	Mod. BWR-2**
		Vapor Pressure Per Cent Deviations			
99.83	-44.086	-0.060	-37.801	-0.003	0.001
108.16	-32.733	-0.030	-22.660	-0.000	-0.000
116.49	-25.035	0.037	-14.048	0.004	0.004
124.83	-18.102	0.031	-7.748	-0.004	-0.003
133.16	-12.117	0.050	-3.221	0.005	0.005
141.49	-7.930	0.029	-0.906	0.006	0.001
152.60	-3.786	-0.046	0.788	-0.003	0.009
163.72	-0.955	0.025	1.578	0.019	0.019
174.83	-0.081	0.024	0.975	0.006	0.020
185.94	0.304	-0.067	0.532	0.002	0.054
Maximum	-44.086	-0.067	-37.801	0.019	0.054
Average	14.513	0.040	9.026	0.005	0.012
		Saturated Liquid Volume Per Cent Deviations			
99.83	-1.863	0.052	-4.334	0.000	0.000
108.16	-1.490	-0.022	-3.241	-0.000	-0.000
116.49	-0.954	-0.066	-2.349	0.000	0.000
124.83	-0.166	-0.078	-1.559	0.000	0.000
133.16	0.769	-0.056	-0.981	-0.000	-0.000
141.49	2.000	-0.030	-0.487	-0.000	-0.000
152.60	4.229	0.061	0.089	-0.001	-0.001
163.72	7.375	0.055	0.615	-0.002	-0.002
174.83	12.043	0.091	1.207	-0.006	-0.007
185.94	20.552	-0.006	1.982	-0.046	-0.088
Maximum	20.552	0.091	-4.334	-0.046	-0.088
Average	5.144	0.052	1.684	0.006	0.010
		Saturated Vapor Volume Per Cent Deviations			
99.83	81.140	0.795	62.413	0.378	0.009
108.16	51.236	1.025	30.818	0.490	0.087
116.49	36.044	1.013	17.614	0.387	0.046
124.83	24.643	1.043	9.358	0.300	-0.057
133.16	16.235	1.194	4.118	0.390	-0.033
141.49	10.371	0.927	1.132	0.041	-0.009
152.60	5.127	1.236	-0.734	0.235	-0.007
163.72	1.594	2.026	-1.216	0.911	-0.043

TABLE VII (Continued)

Temperature °K	Unmod. RK	Mod. RK	Unmod. BWR	Mod. BWR-1*	Mod. BWR-2**
174.83	-0.706	3.039	-0.445	1.241	-0.012
185.94	-2.619	8.197	2.372	4.042	-0.246
Maximum	81.140	8.197	62.413	4.042	-0.246
Average	22.971	2.049	13.022	0.842	0.055
Saturated Fugacity Per Cent Deviations					
99.83	-44.037	-0.505	-37.901	-0.791	-1.137
108.16	-32.767	-0.770	-23.109	-1.217	-1.593
116.49	-25.354	-1.240	-15.110	-1.864	-2.169
124.83	-18.650	-1.503	-9.321	-2.207	-2.510
133.16	-13.147	-1.864	-5.454	-2.596	-2.934
141.49	-9.481	-2.154	-3.626	-2.853	-2.898
152.60	-5.397	-1.691	-1.614	-2.281	-2.422
163.72	-2.767	-1.024	-0.407	-1.633	-2.166
174.83	-2.236	-0.560	-0.609	-1.283	-1.803
185.94	-1.860	0.136	-0.365	-0.657	-1.699
Maximum	-44.037	-2.154	-37.901	-2.853	-2.934
Average	15.570	1.145	9.752	1.738	2.133

*Modified BWR-1 = Two parameters C_0 and α were modified as functions of temperature.

**Modified BWR-2 = Three parameters C_0, α, and c were modified as functions of temperature.

TABLE VIII

DEVIATIONS OF CALCULATED SATURATED PHASE PROPERTIES FROM EXPERIMENTAL DATA (3) FOR ETHANE

Temperature $^{\circ}$K	Unmod. RK	Mod. RK	Unmod. BWR	Mod. BWR-1	Mod. BWR-2
Vapor Pressure Per Cent Deviations					
155.38	-6.998	-0.005	-51.012	-0.000	-0.000
177.60	4.855	-0.005	-23.121	-0.003	-0.001
194.27	9.007	0.018	-11.109	-0.003	0.005
205.38	10.386	0.046	-6.248	0.003	0.002
222.05	10.862	-0.060	-2.178	0.000	-0.004
238.72	10.130	-0.040	-0.415	-0.002	-0.002
255.38	8.733	-0.031	0.246	-0.005	-0.005
263.72	7.854	-0.004	0.372	-0.005	-0.018
272.05	6.960	0.008	0.527	0.000	-0.011
288.72	4.791	0.020	0.747	-0.002	-0.033
Maximum	10.862	-0.060	-51.012	-0.005	-0.033
Average	8.058	0.024	9.597	0.002	0.008
Saturated Liquid Volume Per Cent Deviations					
155.38	2.019	0.083	-2.535	0.000	0.000
177.60	2.879	-0.025	-0.521	0.000	0.000
194.27	4.047	-0.038	0.756	0.000	0.000
205.38	4.953	0.012	1.374	0.000	0.000
222.05	6.661	0.089	2.062	0.000	0.000
238.72	8.979	0.078	2.549	0.000	0.000
255.38	11.933	0.046	2.664	0.001	0.001
263.72	13.847	0.069	2.663	0.002	0.002
272.05	16.034	0.093	2.513	0.003	0.003
288.72	22.208	0.078	2.163	0.008	0.012
Maximum	22.208	0.093	2.664	0.008	0.012
Average	9.356	0.061	1.980	0.001	0.002
Saturated Vapor Volume Per Cent Deviations					
155.38	7.888	0.315	105.087	-0.016	-0.016
177.60	-3.539	1.289	31.580	0.521	-0.014
194.27	-7.363	1.419	13.376	0.262	-0.067
205.38	-8.417	1.826	7.480	0.383	0.080
222.05	-9.190	2.181	2.444	0.117	-0.007
238.72	-8.740	2.956	0.482	0.269	-0.089
255.38	-8.255	3.597	-0.722	-0.011	-0.024
263.72	-7.970	4.031	-1.200	-0.248	-0.008

TABLE VIII (Continued)

Temperature °K	Unmod. RK	Mod. RK	Unmod. BWR	Mod. BWR-1	Mod. BWR-2
272.05	-7.709	4.724	-1.729	-0.493	-0.010
288.72	-4.907	10.079	-1.009	0.918	0.130
Maximum	-9.190	10.079	105.087	0.918	0.130
Average	7.398	3.242	16.511	0.324	0.045
Saturated Fugacity Per Cent Deviations					
155.38	-6.823	0.154	-50.857	-0.161	-0.161
177.60	5.392	0.642	-22.715	-0.080	-0.578
194.27	10.081	1.425	-10.387	0.322	0.041
205.38	11.465	1.711	-5.606	0.351	0.088
222.05	11.810	1.971	-1.728	0.381	0.274
238.72	11.010	2.513	0.027	0.576	0.319
255.38	9.484	3.052	0.725	0.735	0.727
263.72	8.460	3.266	0.801	0.720	0.836
272.05	7.355	3.399	0.813	0.605	0.832
288.72	4.811	3.578	0.587	0.180	-0.126
Maximum	11.810	3.578	-50.857	0.735	0.836
Average	8.669	2.171	9.425	0.411	0.398

TABLE IX

DEVIATIONS OF CALCULATED SATURATED PHASE PROPERTIES FROM EXPERIMENTAL DATA (34) FOR PROPANE

Temperature °K	Unmod. RK	Mod. RK	Unmod. BWR	Mod. BWR-1	Mod. BWR-2
		Vapor Pressure Per Cent Deviation			
310.94	12.968	0.030	0.694	-0.009	0.001
313.49	12.573	0.005	0.800	-0.004	-0.005
327.60	9.517	-0.038	0.538	-0.015	-0.015
332.05	8.659	-0.021	0.540	-0.004	-0.003
344.27	5.943	0.012	0.301	-0.007	0.007
346.44	5.538	-0.032	0.345	-0.010	-0.010
Maximum	12.968	-0.038	0.800	-0.015	-0.015
Average	9.200	0.023	0.536	0.008	0.007
		Saturated Liquid Volume Per Cent Deviation			
310.94	13.913	0.096	1.896	0.001	0.001
313.49	14.187	0.076	1.697	0.001	0.001
327.60	16.745	0.050	1.070	0.003	0.003
332.05	17.747	0.063	0.855	0.003	0.003
344.27	20.988	0.075	0.067	0.006	0.007
346.44	21.814	0.050	0.022	0.007	0.006
Maximum	21.814	0.096	1.896	0.007	0.007
Average	17.566	0.068	0.934	0.003	0.003
		Saturated Vapor Volume Per Cent Deviation			
310.94	-12.406	3.817	-1.317	-0.142	0.012
313.49	-12.043	4.138	-1.324	-0.027	-0.011
327.60	-9.743	5.462	-1.051	-0.067	-0.044
332.05	-9.121	5.941	-1.107	-0.143	-0.003
344.27	-6.962	7.761	-1.127	-0.599	-0.000
346.44	-6.752	8.210	-1.390	-0.779	0.019
Maximum	-12.406	8.210	-1.390	-0.779	-0.044
Average	9.505	5.888	1.219	0.293	0.015

TABLE IX (Continued)

Temperature °K	Unmod. RK	Mod. RK	Unmod. BWR	Mod. BWR-1	Mod. BWR-2
		Saturated Fugacity Per Cent Deviation			
310.94	11.431	1.676	-0.505	-0.924	-0.814
313.49	10.882	1.569	-0.536	-1.048	-1.039
327.60	7.777	1.710	-0.868	-1.206	-1.195
332.05	7.762	2.608	-0.107	-0.467	-0.399
344.27	5.163	2.845	-0.411	-0.633	-0.396
346.44	5.139	3.217	-0.055	-0.314	-0.022
Maximum	11.431	3.217	-0.868	-1.206	-1.195
Average	8.026	2.271	0.414	0.765	0.644

TABLE X

DEVIATIONS OF CALCULATED SATURATED PHASE PROPERTIES FROM EXPERIMENTAL DATA (15, 34) FOR n-BUTANE

Temperature ^{o}K	Unmod. RK	Mod. RK	Unmod. RK	Mod. BWR-1	Mod. BWR-2
Vapor Pressure Per Cent Deviation					
309.91	34.146	-0.022	1.408	-0.006	-0.005
316.38	31.586	-0.049	1.562	0.002	-0.001
327.60	27.736	0.006	1.854	-0.027	-0.017
336.25	24.613	0.025	1.657	-0.001	-0.014
344.27	22.184	-0.027	1.667	0.007	-0.004
354.13	19.340	-0.055	1.606	-0.002	-0.009
367.96	15.395	0.026	1.291	-0.001	-0.001
377.60	12.913	-0.001	1.181	-0.014	-0.015
389.26	9.609	-0.001	0.705	-0.024	-0.020
405.84	5.433	-0.012	0.518	-0.039	-0.041
Maximum	34.146	-0.055	1.854	-0.039	-0.041
Average	20.295	0.022	1.345	0.012	0.013
Saturated Liquid Volume Per Cent Deviation					
309.91	11.732	-0.036	1.024	0.000	0.000
316.38	12.290	0.023	1.122	0.000	0.000
327.60	13.310	0.077	1.185	-0.001	0.000
336.25	14.001	0.080	1.008	0.000	0.000
344.27	14.773	0.075	0.840	0.006	0.000
354.13	14.807	-0.024	-0.334	0.001	0.001
367.96	17.141	0.066	-0.363	0.001	0.001
377.60	19.753	0.069	0.126	0.002	0.002
389.26	22.147	0.093	-0.359	0.006	0.005
405.84	26.918	0.101	-0.949	0.017	0.016
Maximum	26.918	0.101	1.185	0.017	0.016
Average	16.687	0.064	0.731	0.003	0.003
Saturated Vapor Volume Per Cent Deviation					
309.91	-26.889	1.300	-2.162	-0.575	0.011
316.38	-25.596	1.468	-2.395	-0.615	0.061
327.60	-23.578	1.719	-2.792	-0.593	0.030
336.25	-21.805	1.979	-2.636	-0.641	0.010
344.27	-20.423	2.323	-2.707	-0.670	0.087
354.13	-18.536	2.905	-2.462	-0.548	-0.001
367.96	-16.161	3.453	-2.349	-0.729	-0.011
377.60	-14.477	4.470	-2.241	-0.579	0.042

TABLE X (Continued)

Temperature °K	Unmod. RK	Mod. RK	Unmod. BWR	Mod. BWR-1	Mod. BWR-2
389.26	-12.081	5.702	-1.848	-0.820	0.004
405.84	-8.347	9.436	-1.813	-1.014	0.135
Maximum	-26.889	9.436	-2.792	-1.014	0.135
Average	18.789	3.476	2.340	0.678	0.039
		Saturated Fugacity Per Cent Deviation			
309.91	31.842	0.906	0.594	-0.639	-0.152
316.38	29.128	0.906	0.628	-0.713	-0.172
327.60	25.391	1.303	1.015	-0.570	-0.074
336.25	21.503	0.829	0.184	-1.177	-0.725
344.27	19.661	1.409	0.671	-0.684	-0.173
354.13	16.540	1.204	0.352	-1.012	-0.669
367.96	12.897	1.705	0.225	-0.846	-0.432
377.60	11.224	2.606	0.746	-0.189	0.136
389.26	8.471	3.120	0.578	0.000	0.375
405.84	5.255	3.919	0.750	0.293	0.657
Maximum	31.842	3.919	1.015	-1.177	-0.725
Average	18.191	1.791	0.574	0.612	0.357

TABLE XI

DEVIATIONS OF CALCULATED SATURATED PHASE PROPERTIES FROM EXPERIMENTAL DATA (34) FOR n-PENTANE

Temperature °K	Unmod. RK	Mod. RK	Unmod. BWR	Mod. BWR-1	Mod. BWR-2
		Vapor Pressure Per Cent Deviation			
310.94	65.591	-0.091	-4.529	-0.002	-0.002
327.60	59.654	0.045	0.909	0.001	-0.002
344.27	45.787	-0.019	-0.821	0.000	-0.012
357.88	39.537	0.025	-0.116	0.005	-0.013
370.10	34.245	-0.048	0.084	-0.016	-0.010
380.10	29.932	0.031	-0.120	-0.017	-0.010
390.49	25.265	0.022	-0.771	-0.002	-0.012
410.94	18.228	-0.048	-1.021	-0.020	-0.009
427.60	12.780	0.008	-1.411	-0.019	-0.026
444.27	7.765	-0.057	-1.602	-0.008	-0.022
Maximum	65.591	-0.091	-4.529	-0.020	-0.026
Average	33.878	0.040	1.138	0.009	0.012
		Saturated Liquid Volume Per Cent Deviation			
310.94	12.381	-0.039	1.042	0.000	0.000
327.60	12.808	-0.051	1.017	0.000	0.000
344.27	13.600	0.046	1.002	0.000	0.000
357.88	14.556	0.057	1.007	0.000	0.000
370.10	15.585	0.025	0.944	0.000	0.000
380.10	16.447	0.097	0.741	0.000	0.000
390.49	17.357	0.057	0.364	0.001	0.001
410.94	20.174	0.023	-0.138	0.002	0.001
427.60	23.354	0.095	-0.608	0.004	0.004
444.27	26.861	0.030	-1.733	0.012	0.013
Maximum	26.861	0.097	-1.733	0.012	0.013
Average	17.312	0.052	0.860	0.002	0.002
		Saturated Vapor Volume Per Cent Deviation			
310.94	-40.628	0.819	4.113	-0.790	0.029
327.60	-38.627	1.203	-1.681	-0.678	0.034
344.27	-33.079	1.503	-0.233	-1.070	0.087
357.88	-30.279	1.914	-1.062	-1.117	0.016
370.10	-27.726	2.442	-1.380	-1.175	0.013
380.10	-25.529	2.665	-1.302	-1.344	0.090
390.49	-22.873	3.118	-0.656	-1.562	0.013
410.94	-18.225	4.928	-0.062	-1.449	0.031

TABLE XI (Continued)

Temperature °K	Unmod. RK	Mod. RK	Unmod. BWR	Mod. BWR-1	Mod. BWR-2
427.60	-14.067	6.896	0.644	-1.608	-0.030
444.27	-9.258	10.557	1.235	-2.143	-0.042
Maximum	-40.628	10.557	4.113	-2.143	0.090
Average	26.029	3.604	1.237	1.294	0.039
Saturated Fugacity Per Cent Deviation					
310.94	62.352	0.144	-5.463	-1.158	-0.411
327.60	55.873	0.511	-0.436	-1.234	-0.621
344.27	42.203	0.756	-2.166	-1.373	-0.438
357.88	34.416	-0.042	-2.650	-2.476	-1.633
370.10	31.302	1.746	-0.925	-0.949	-0.058
380.10	26.036	1.173	-1.923	-1.783	-0.773
390.49	21.573	1.338	-2.519	-1.858	-0.851
410.94	15.723	2.402	-2.026	-1.245	-0.414
427.60	10.639	2.735	-2.408	-1.404	-0.706
444.27	6.462	3.220	-2.376	-1.348	-0.670
Maximum	62.352	3.220	-5.463	-2.476	-1.633
Average	30.658	1.407	2.289	1.483	0.657

TABLE XII

DEVIATIONS OF CALCULATED SATURATED PHASE PROPERTIES FROM EXPERIMENTAL DATA (34) FOR CARBON DIOXIDE

Temperature °K	Unmod. RK	Mod. RK	Unmod. BWR	Mod. BWR-1	Mod. BWR-2
Vapor Pressure Per Cent Deviation					
279.92	9.886	0.034	2.361	-0.009	-0.036
281.50	9.165	-0.021	2.100	-0.057	-0.038
283.04	8.466	-0.032	1.823	-0.022	-0.035
284.47	7.628	-0.046	1.419	-0.025	-0.026
285.92	6.972	-0.042	1.159	-0.013	-0.016
287.29	6.266	0.006	0.848	-0.008	-0.023
288.64	5.564	-0.039	0.542	-0.033	-0.009
Maximum	9.886	-0.046	2.361	-0.057	-0.038
Average	7.707	0.031	1.465	0.024	0.026
Saturated Liquid Volume Per Cent Deviation					
279.92	22.987	0.118	0.815	0.006	0.008
281.50	23.441	0.040	0.741	-0.051	0.010
283.04	24.014	0.049	0.765	0.009	0.012
284.47	24.396	0.045	0.655	0.011	0.013
285.92	24.892	0.050	0.617	0.012	0.014
287.29	25.417	0.089	0.615	0.013	0.018
288.64	25.917	0.061	0.585	0.015	0.019
Maximum	25.917	0.118	0.815	-0.051	0.019
Average	24.438	0.065	0.685	0.017	0.013
Saturated Vapor Volume Per Cent Deviation					
279.92	-11.390	7.381	-1.407	2.328	0.095
281.50	-10.729	7.893	-0.969	2.529	0.062
283.04	-10.000	8.458	-0.416	2.669	0.100
284.47	-9.010	9.071	0.386	2.885	0.105
285.92	-8.298	9.607	0.921	3.029	0.039
287.29	-7.394	10.217	1.649	3.279	0.084
288.64	06.488	10.953	2.346	3.500	0.001
Maximum	-11.390	10.953	2.346	3.500	0.105
Average	9.044	9.083	1.156	2.888	0.069

TABLE XIII

DEVIATIONS OF CALCULATED SATURATED PHASE PROPERTIES FROM EXPERIMENTAL DATA (34) FOR HYDROGEN SULFIDE

Temperature °K	Unmod. RK	Mod. RK	Unmod. BWR	Mod. BWR-1	Mod. BWR-2
Vapor Pressure Per Cent Deviation					
283.60	9.740	-0.044	-14.426	-0.006	0.000
299.33	8.669	-0.011	-10.931	-0.006	-0.017
311.60	7.664	0.022	-8.976	0.004	-0.006
321.88	6.834	-0.018	-7.654	0.000	-0.012
330.77	6.036	-0.010	-6.771	0.004	0.006
338.66	5.290	0.003	-6.143	0.010	-0.009
345.72	4.466	-0.005	-5.798	-0.030	-0.028
352.05	3.492	0.041	-5.776	-0.036	-0.026
Maximum	9.740	-0.044	-14.426	-0.036	-0.028
Average	6.542	0.019	8.309	0.012	0.013
Saturated Liquid Volume Per Cent Deviation					
283.60	6.825	0.057	-0.134	0.000	0.000
299.33	8.542	0.050	0.516	0.001	0.001
311.60	9.714	0.097	0.534	0.001	0.002
321.88	10.525	0.058	0.133	0.003	0.003
330.77	12.117	0.086	0.356	0.004	0.005
338.66	12.878	0.056	0.619	0.006	0.007
345.72	15.712	0.063	0.808	0.010	0.014
352.05	17.176	0.098	0.495	0.018	0.025
Maximum	17.176	0.098	0.808	0.018	0.025
Average	11.811	0.071	0.449	0.005	0.007
Saturated Vapor Volume Per Cent Deviation					
283.60	-7.192	3.708	21.545	1.887	-0.053
299.33	-6.709	3.956	16.861	1.911	-0.005
311.60	-6.159	4.257	14.633	2.039	-0.016
321.88	-5.697	4.697	13.421	2.256	-0.012
330.77	-5.150	5.392	13.000	2.704	-0.081
338.66	-4.617	6.277	13.063	3.265	-0.080
345.72	-3.722	7.616	13.981	4.214	0.116
352.05	-2.343	9.210	15.970	5.388	0.079
Maximum	-7.192	9.210	21.545	5.388	0.116
Average	5.199	5.639	15.309	2.958	0.055

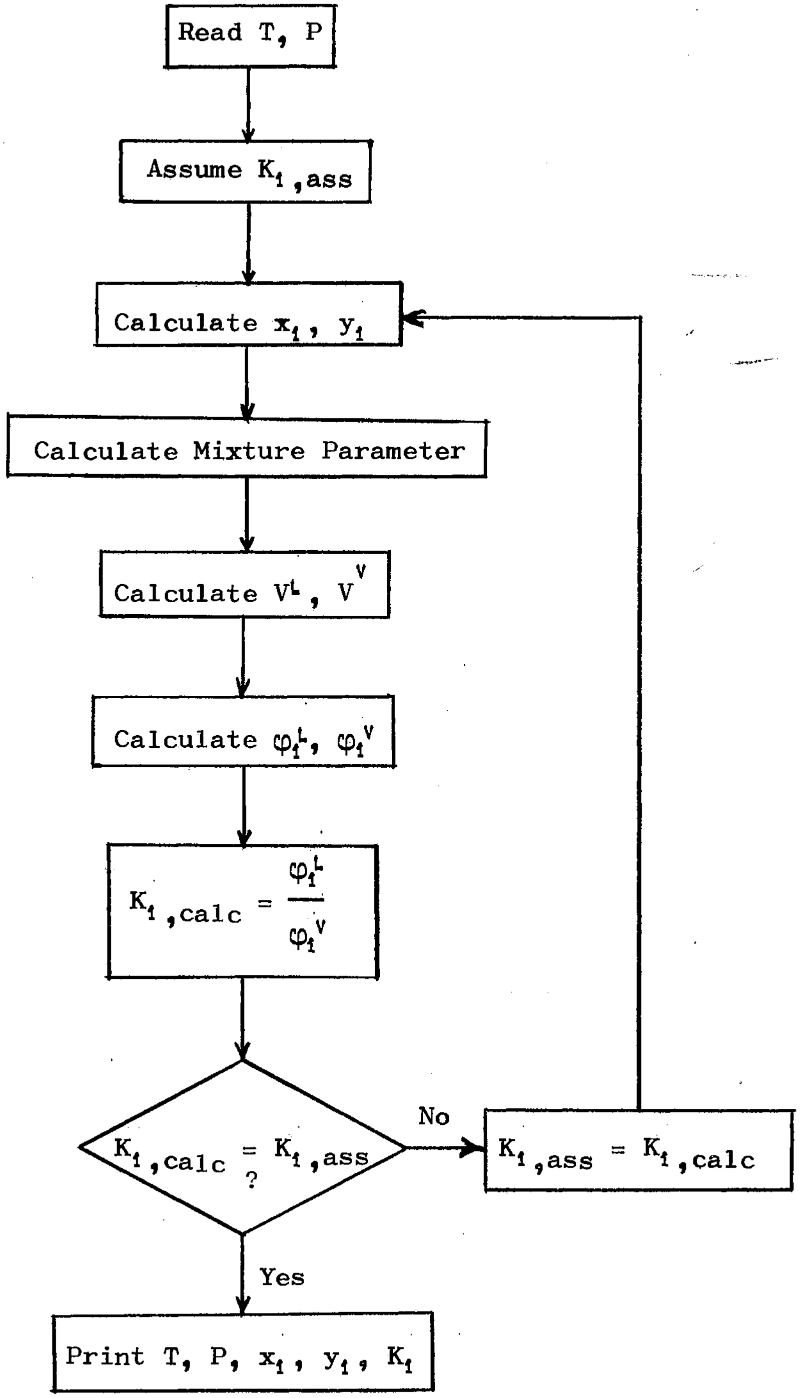
CHAPTER VII

VAPOR-LIQUID EQUILIBRIUM CALCULATIONS FOR BINARY MIXTURES

Vapor-liquid equilibrium calculations are very important in distillation, flash drum, and absorption design work. Both of the RK and BWR equations often give poor results when they are applied to mixtures, especially when the mixtures contain unlike hydrocarbons or mixtures of hydrocarbons with non-hydrocarbons. Hydrogen sulfide is an important component of natural petroleum reservoirs. For this reason, binary systems of methane-hydrogen sulfide and n-pentane-hydrogen sulfide were chosen for vapor-liquid equilibrium calculations. In order to test the results of the modified parameters, the vapor-liquid equilibria were calculated by using original and modified parameters. Also, empirical interaction coefficients have been introduced into the mixing rules of the parameter "a" for RK equation and A_o for BWR equation.

The phase rule shows that two variables are needed to specify vapor-liquid equilibrium calculations for binary mixtures. In this case, temperature and pressure were given.

The following flow diagram shows the procedure used for vapor-liquid equilibrium calculation.



Flow Diagram for Vapor-Liquid Equilibrium Calculations

At each given temperature and pressure, the equilibrium ratios, K_i, were assumed. The liquid and vapor compositions were calculated by solving the following equations simultaneously:

$$K_i = y_i/x_i$$

$$\Sigma x_i = 1$$

$$\Sigma y_i = 1 \, . \qquad (7\text{-}1)$$

Then the mixture parameters were calculated for both liquid and vapor phases from the mixing rules. After calculating liquid and vapor volumes, the liquid and vapor fugacity coefficients for both components were calculated. The calculated equilibrium ratios are equal to liquid fugacity coefficients divided by the vapor fugacity coefficients. If the calculated equilibrium ratios were not equal to the assumed equilibrium ratios, new assumed equilibrium ratios were set equal to the calculated equilibrium ratios. The process of trial and error was repeated until the agreement of equilibrium ratios was obtained.

Redlich-Kwong Equation of State

When the RK equation (4-1) was applied to mixtures, the mixture parameters must be evaluated from the mixing rules. In this study, the mixing rules suggested by Chueh and Prausnitz (12) were used.

$$a_m = \Sigma \Sigma \, y_i \, y_j \, a_{ij} \qquad (7\text{-}2)$$

$$b_m = \Sigma y_i \, b_i \, . \qquad (7\text{-}3)$$

The above mixing rules are applied to both liquid and vapor phases.

The interaction parameter a_{ij} was calculated from the following equation (43):

$$a_{ij} = (1 - C_{ij})\sqrt{a_i \ a_j} \tag{7-4}$$

when the interaction coefficient C_{ij} is equal to zero, which means no deviation of a_{ij} from the classical geometric mean assumption, Equation (7-2) reduces to the basic mixing rule suggested by the original authors of the RK equation (30).

$$a_m = (\Sigma y_i \ a_i^{1/2})^2 . \tag{7-5}$$

The determination of the coefficient C_{ij} from experimental data is discussed later.

The fugacity coefficient for a component k in a mixture is calculated from the following equation:

$$\ln \varphi_k^V = \ln \frac{f_k^V}{P y_k} = \ln \frac{RT}{P(V - b)} + \frac{b_k}{V - b} - \frac{2\Sigma \ y_i a_{ik}}{RT^{3/2} \ b} \ln \frac{V + b}{V} + \frac{ab_k}{RT^{3/2} \ b^2}\left(\ln \frac{V + b}{V} - \frac{b}{V + b}\right) \tag{7-6}$$

The results of the calculation will be shown later.

Benedict-Webb-Rubin Equation of State

The mixing rules used in this study are listed below. The only difference from the original mixing rules suggested by the authors of the BWR equation (8) was that an empirical interaction coefficient was introduced into the usual mixing rule for A_o.

$$B_o = \Sigma y_i \ B_{oi} \tag{7-7a}$$

$$A_o = \Sigma \Sigma y_i \ y_j \ A_{oij} \tag{7-7b}$$

$$C_o = (\Sigma y_i \ C_{oi}^{1/2})^2 \tag{7-7c}$$

$$b = (\Sigma\, y_i \; b_i^{1/3})^3 \tag{7-7d}$$

$$a = (\Sigma\, y_i \; a_i^{1/3})^3 \tag{7-7e}$$

$$\alpha = (\Sigma\, y_i \; \alpha_i^{1/3})^3 \tag{7-7f}$$

$$c = (\Sigma\, y_i \; c_i^{1/3})^3 \tag{7-7g}$$

$$\gamma = (\Sigma\, y_i \; \gamma_i^{1/2})^2 \tag{7-7h}$$

where

$$A_{0ij} = (1 - k_{ij})\sqrt{A_{0i} \cdot A_{0j}} \; . \tag{7-8}$$

When the interaction coefficient k_{ij} is equal to zero, Equation (7-7b) reduces to

$$A_0 = (\Sigma\, y_i A_{0i}^{1/2})^2$$

which reverts to the original mixing rule.

The following equation was used to calculate the fugacity coefficient for component i in a mixture:

$$\begin{aligned} RT\,\ln\varphi_i^V = RT\,\ln\frac{f_i^V}{Py_i} = RT\,\ln\frac{RT}{PV} &+ \Bigg[(B_0 + B_{0i})RT - 2(y_i \; A_{0i} + y_j \; A_{0ij}) \\ &- \frac{2(C_0 \; C_{0i})^{1/2}}{T^2}\Bigg]\frac{1}{V} + \frac{3}{2}\left[RT(b^2 b_i)^{1/3} - (a^2 a_i)^{1/3}\right]\frac{1}{V^2} + \frac{3}{5}\Big[a(\alpha^2 \alpha_i)^{1/3} \\ &+ \alpha(a^2 a_i)^{1/3}\Big]\frac{1}{V^5} + \frac{3(c^2 c_i)^{1/3}}{T^2 V^2}\left[\frac{V^2}{\gamma} - \left(\frac{V^2}{\gamma} + \frac{1}{2}\right)\exp\left(-\frac{\gamma}{V^2}\right)\right] \\ &- \frac{2c}{T^2 V^2}\left(\frac{\gamma_i}{\gamma}\right)^{1/2}\left[\frac{V^2}{\gamma} - \left(\frac{V^2}{\gamma} + \frac{\gamma}{2V^2} + 1\right)\exp\left(-\frac{\gamma}{V^2}\right)\right] \end{aligned} \tag{7-9}$$

The results of vapor-liquid equilibrium calculactions were presented in the next section.

Results of Vapor-Liquid Equilibrium Calculations

The vapor-liquid equilibria for binary mixtures were initially calculated by using both unmodified and modified equations with the interaction coefficients equal zero. Then the interaction coefficients, C_{12} in Equation (7-4) and k_{12} in Equation (7-8), were found by trial-and-error. In this case, the effect of pressure on the binary interaction coefficients is assumed negligible. The procedure for finding the interaction coefficient C_{12} (k_{12}) is shown as follows:

1. Assume several values of C_{12} (k_{12}) and calculate the equilibrium ratios for both components.
2. Plot the sum of absolute deviations in equilibrium ratios versus the interaction coefficient.
3. The optimal value of C_{12} (k_{12}) is the one that gives the minimum sum of absolute deviation at that temperature.

A typical example of this procedure for finding the optimal value of C_{12} for the methane-hydrogen sulfide system at 310.94°K calculated with modified RK equation was shown in Figure 23.

The equilibrium calculations were made isothermally at 310.94 and 344.27 degrees Kelvin for both systems. Since the temperatures were above the critical temperature of methane, the effects of temperature on parameters for pure methane were not considered. For the modified equations, the temperature dependent parameters were used for n-pentane and hydrogen sulfide.

Figures 24 through 43 show the results of calculations for equilibrium ratios. The summaries of results are shown in Tables XIV and XV.

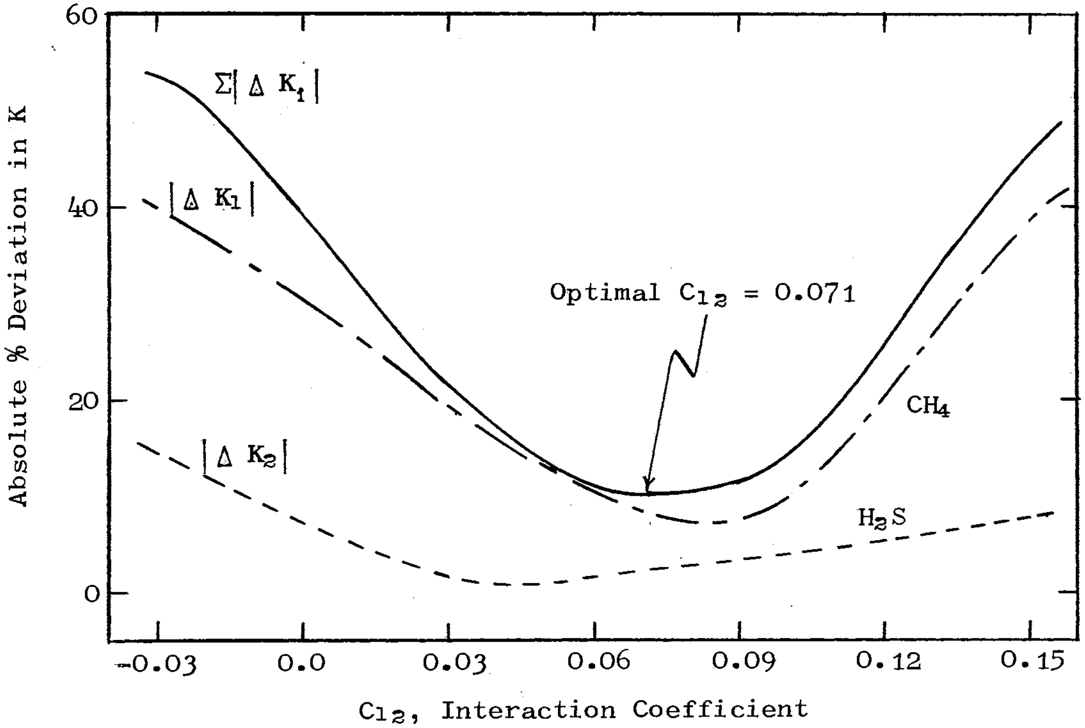


Figure 23. Example: Evaluating C_{12} for Methane - Hydrogen Sulfide System at 310.94 °K Calculated With Modified RK Equation

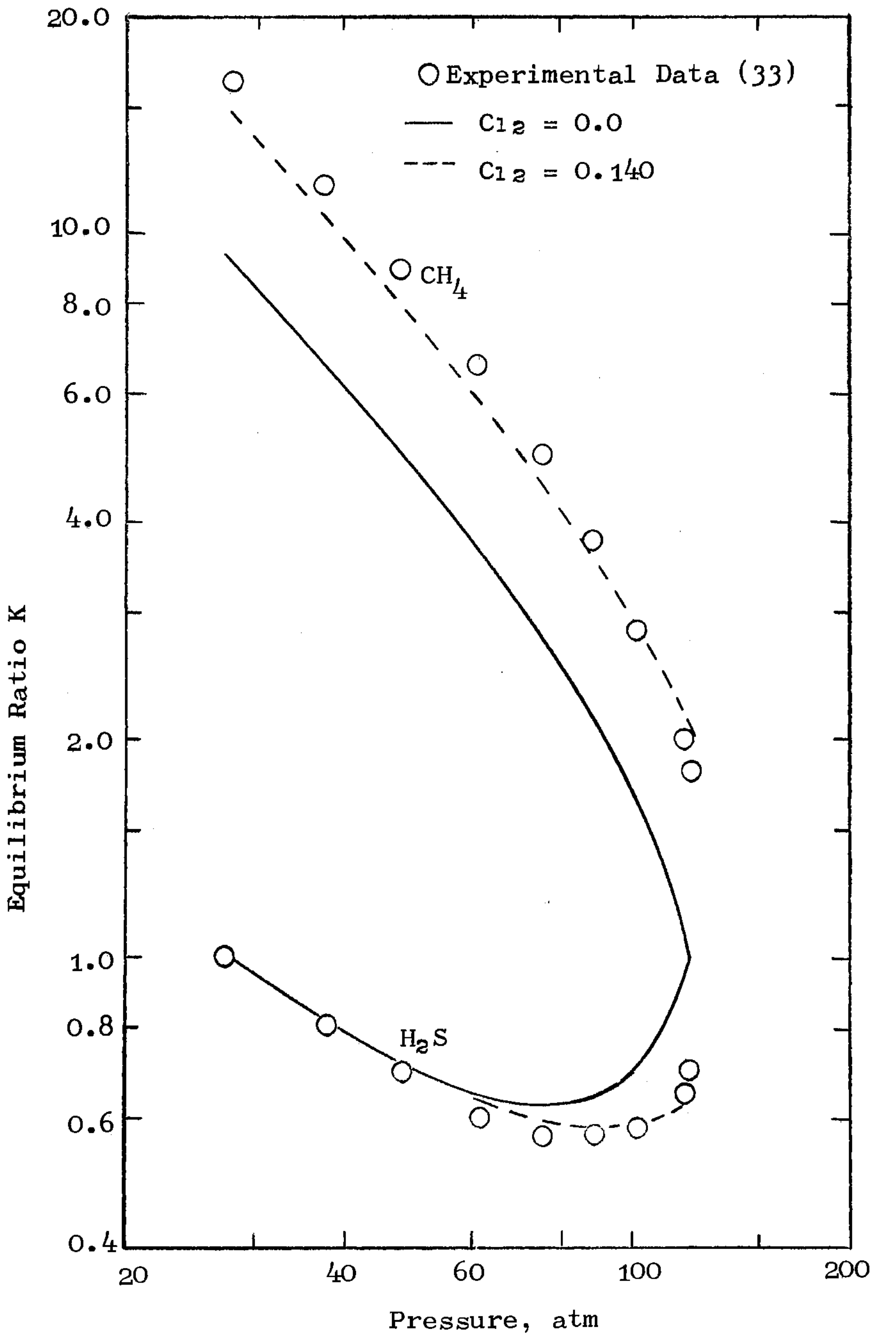


Figure 24. Equilibrium Ratios of Methane-Hydrogen Sulfide System at 310.94°K Calculated With Unmodified RK Equation

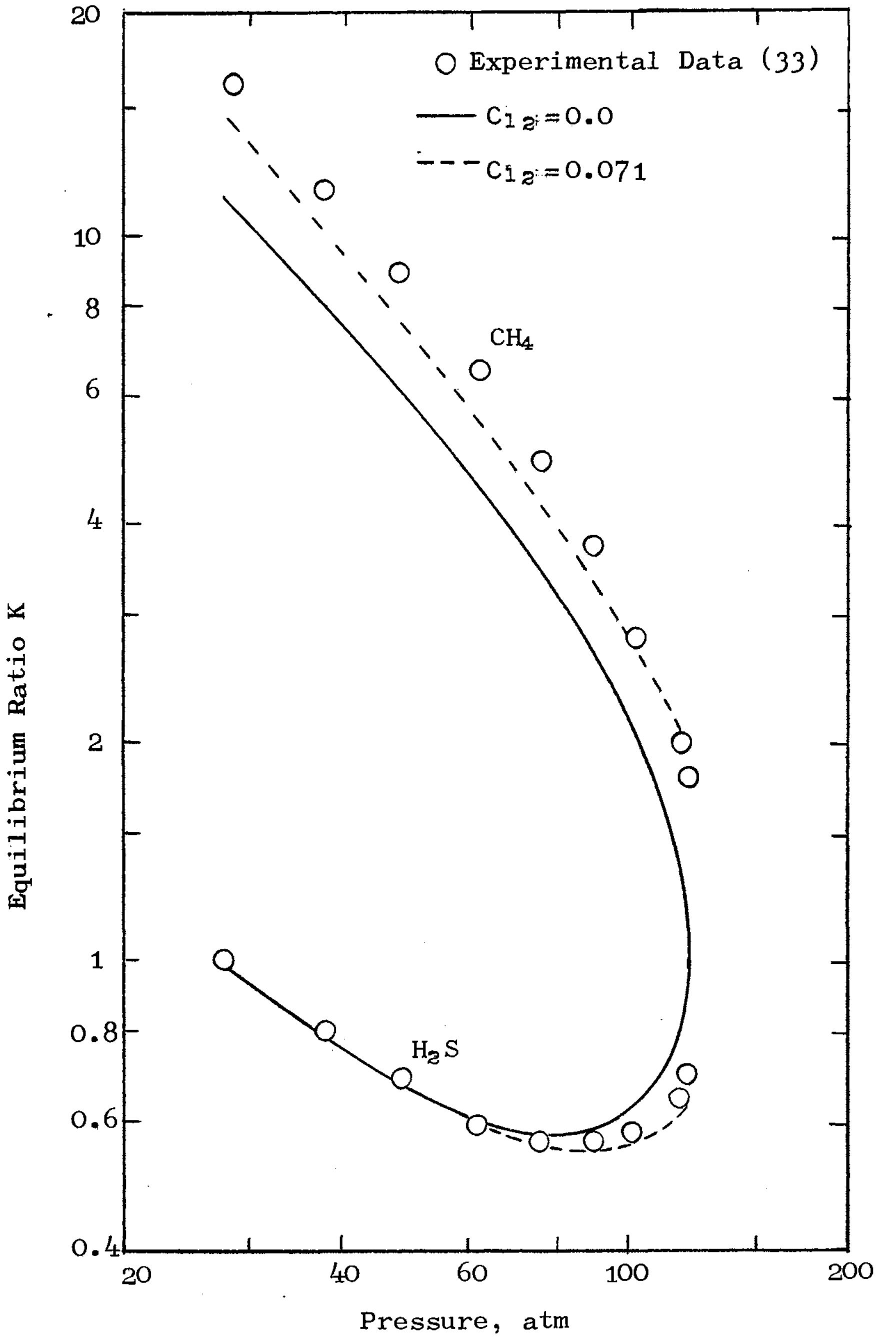


Figure 25. Equilibrium Ratios of Methane-Hydrogen Sulfide System at 310.94°K Calculated With Modified RK Equation

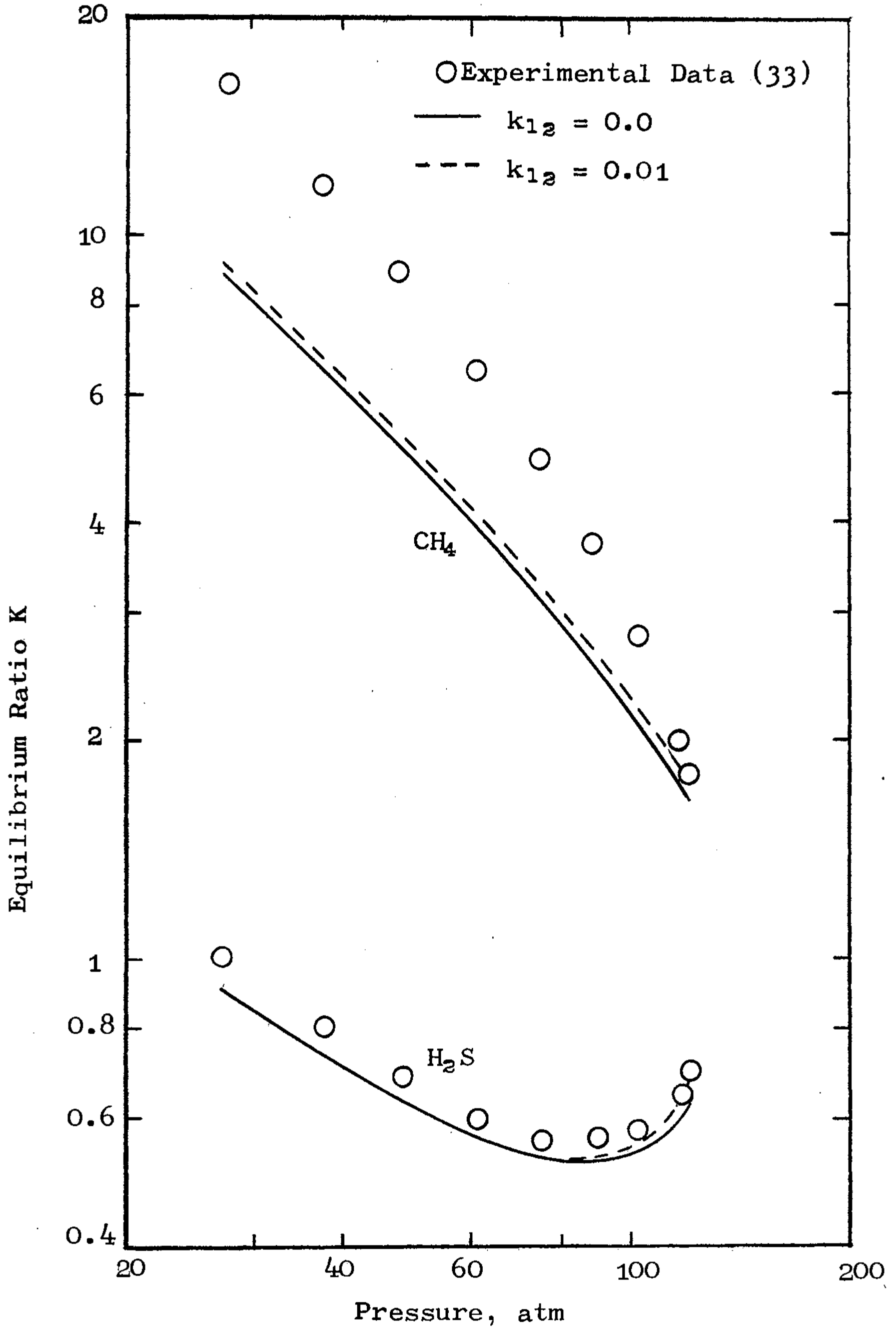


Figure 26. Equilibrium Ratios of Methane-Hydrogen Sulfide System at 310.94°K Calculated With Unmodified BWR Equation

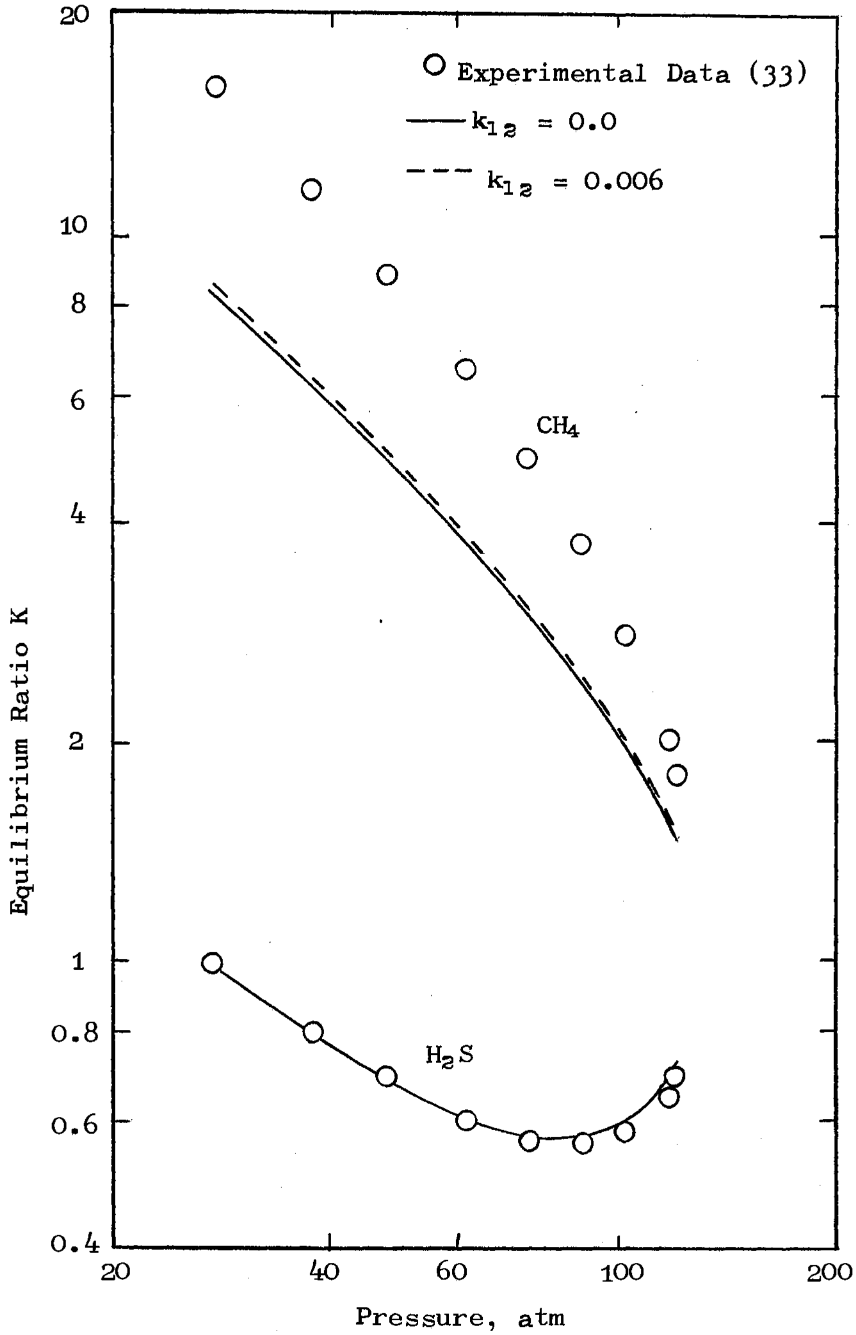


Figure 27. Equilibrium Ratios of Methane-Hydrogen Sulfide System at 310.94°K Calculated With Modified BWR Equation (C_o, α)

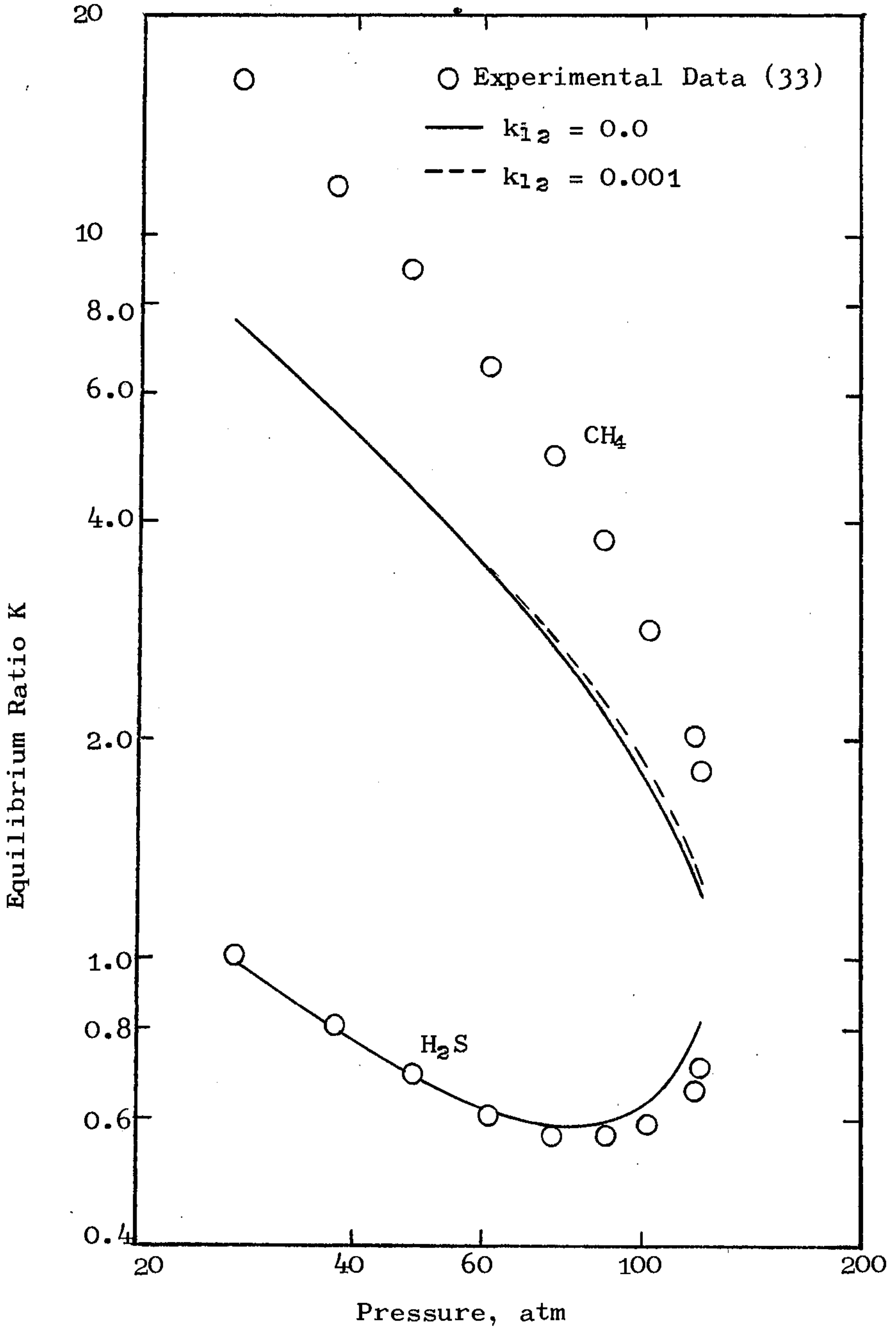


Figure 28. Equilibrium Ratios of Methane-Hydrogen Sulfide System at 310.94°K Calculated With Modified BWR Equation (C_o, α, c)

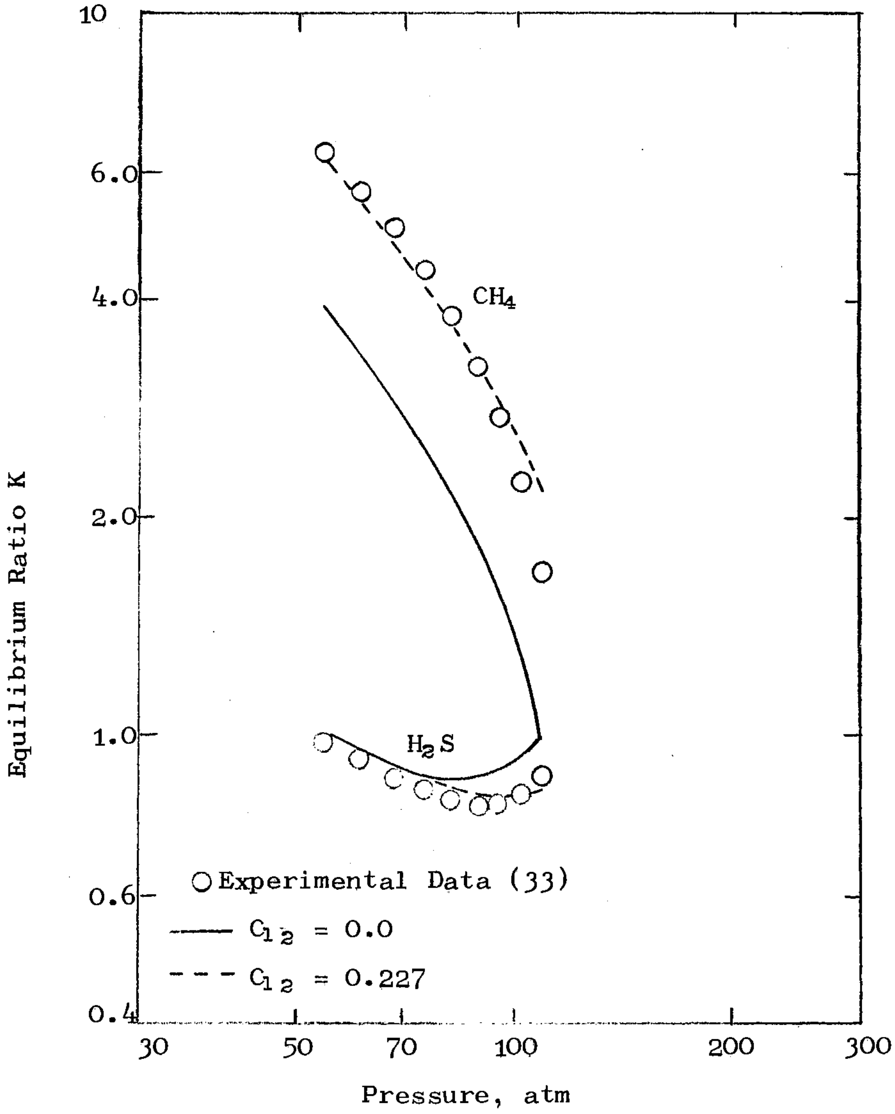


Figure 29. Equilibrium Ratios of Methane-Hydrogen Sulfide System at 344.27°K Calculated With Unmodified RK Equation

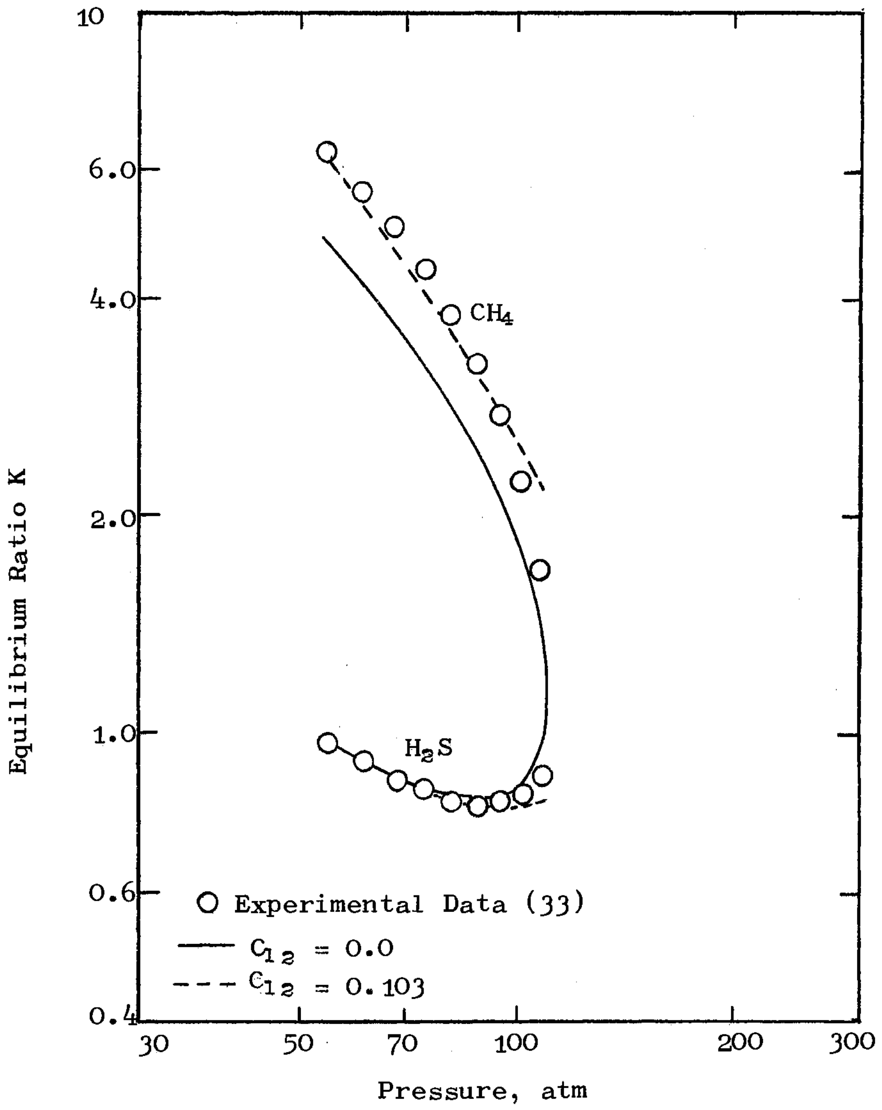


Figure 30. Equilibrium Ratios of Methane-Hydrogen Sulfide System at 344.27°K Calculated With Modified RK Equation

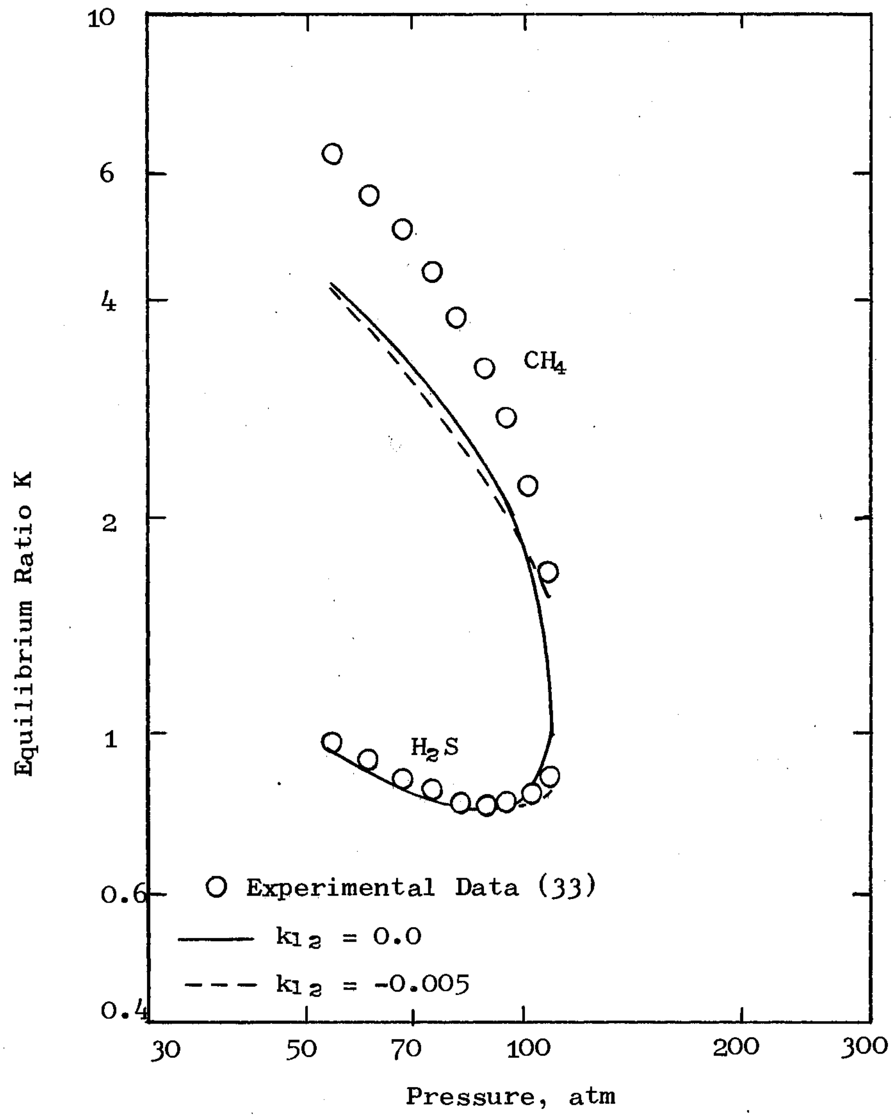


Figure 31. Equilibrium Ratios of Methane-Hydrogen Sulfide System at 344.27°K Calculated With Unmodified BWR Equation

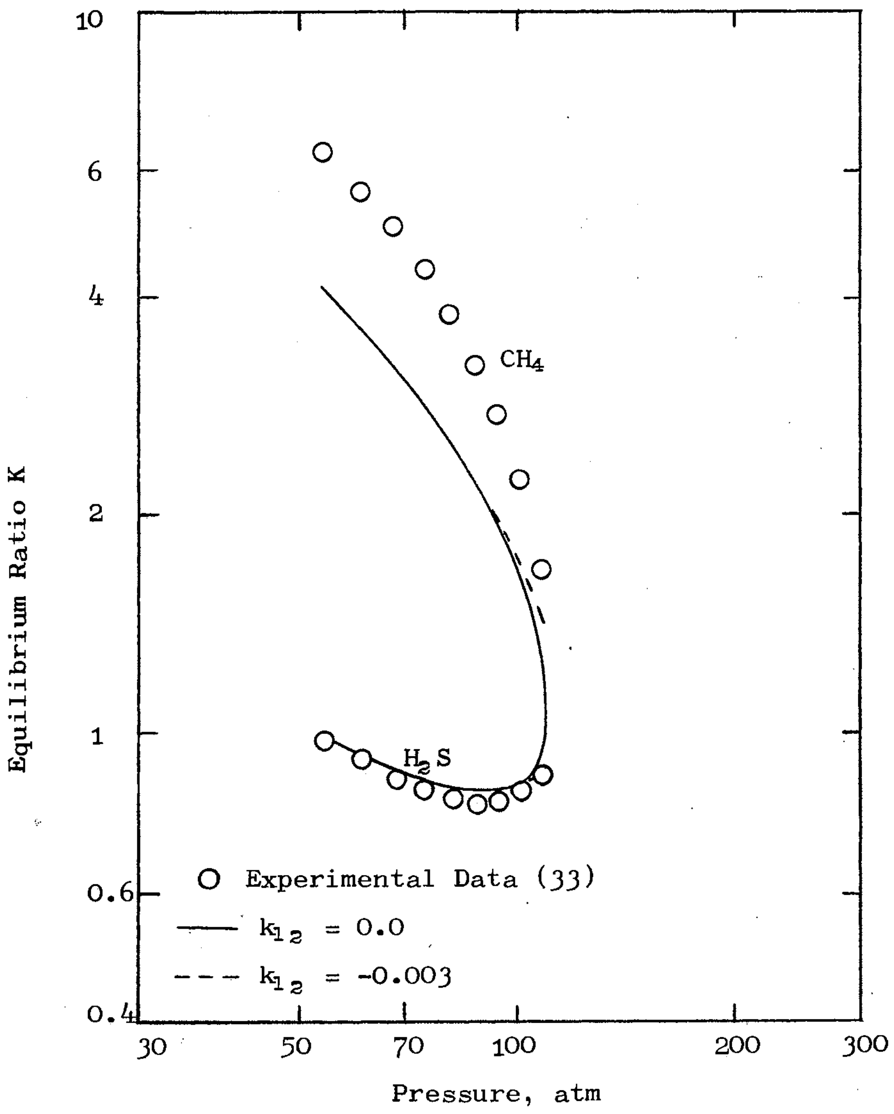


Figure 32. Equilibrium Ratios of Methane-Hydrogen Sulfide System at 344.27°K Calculated With Modified BWR Equation (C_0, α)

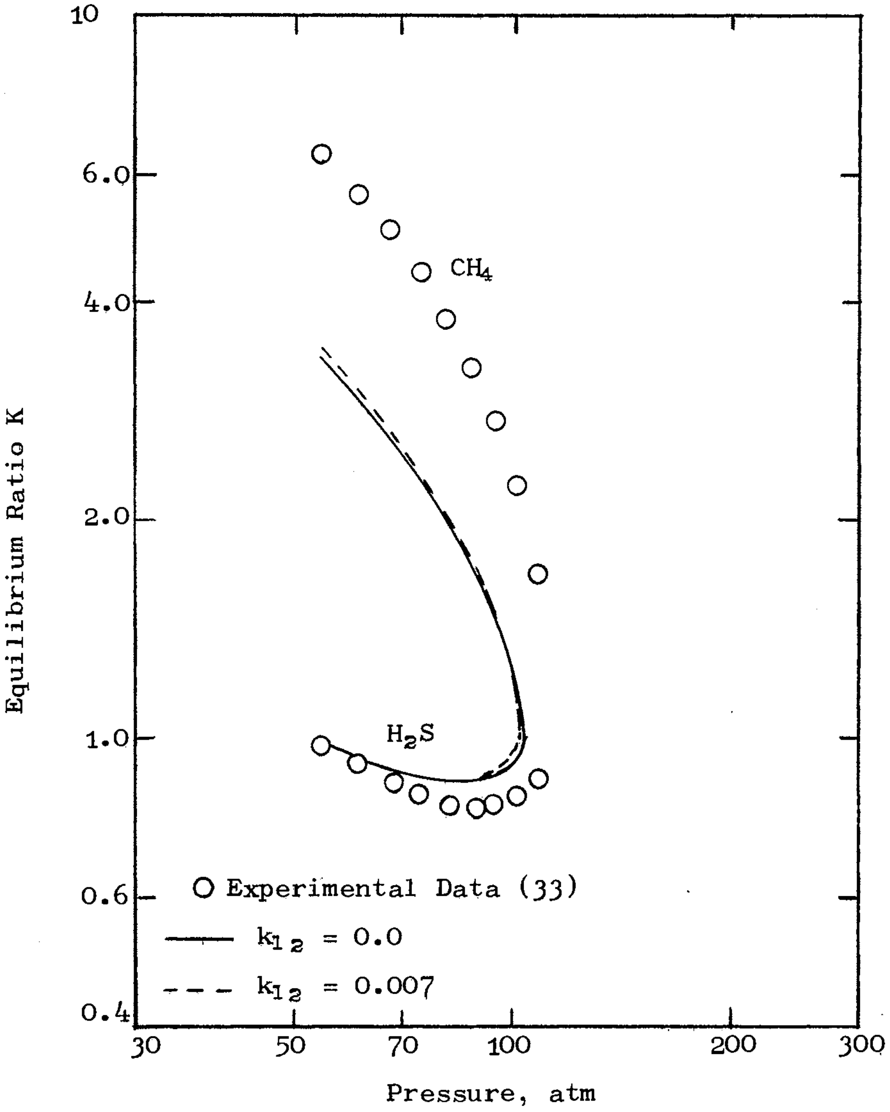


Figure 33. Equilibrium Ratios of Methane-Hydrogen Sulfide System at 344.27°K Calculated With Modified BWR Equation (C_o, α, c)

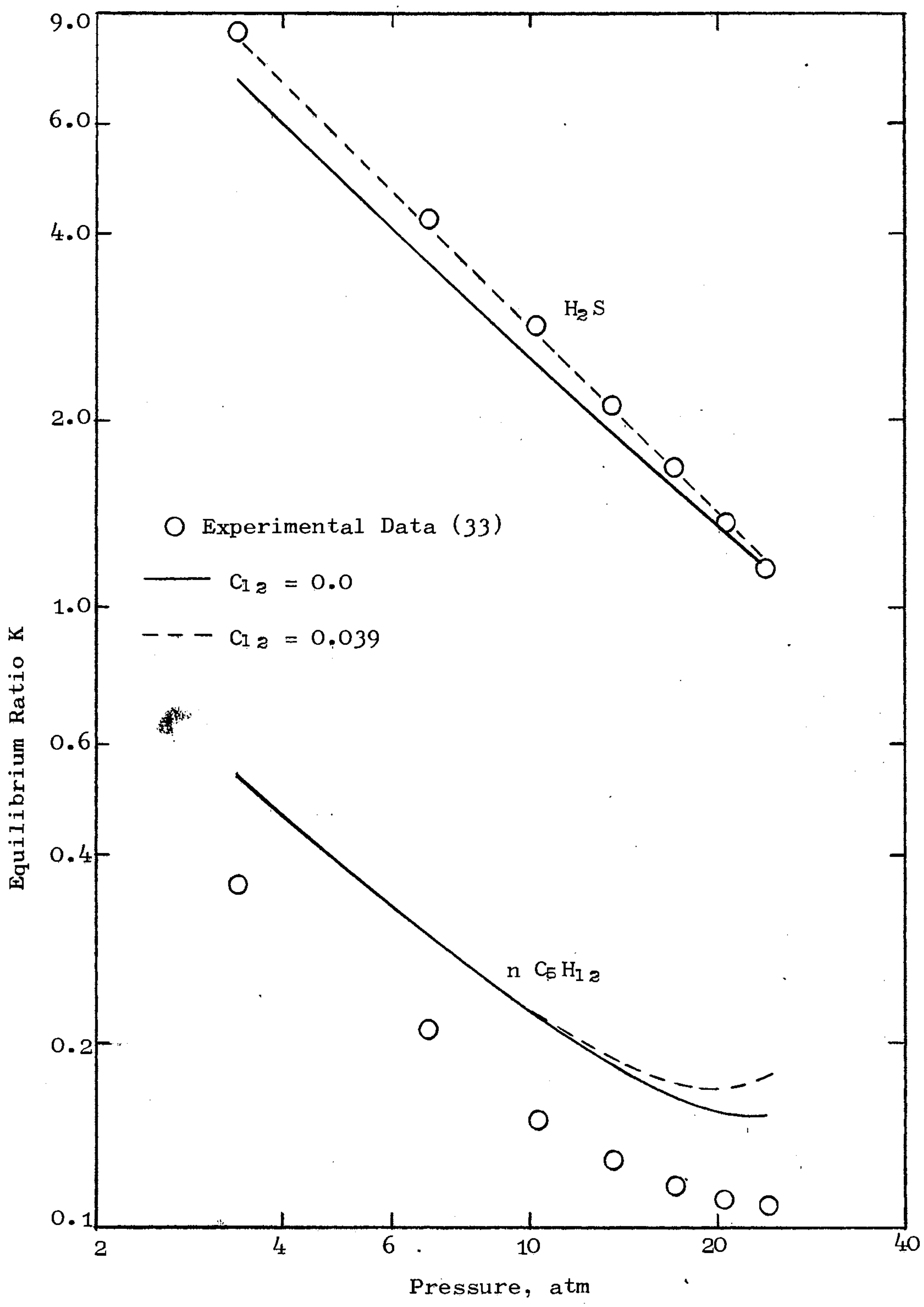


Figure 34. Equilibrium Ratios of n-Pentane-Hydrogen Sulfide System at 310.94°K Calculated With Unmodified RK Equation

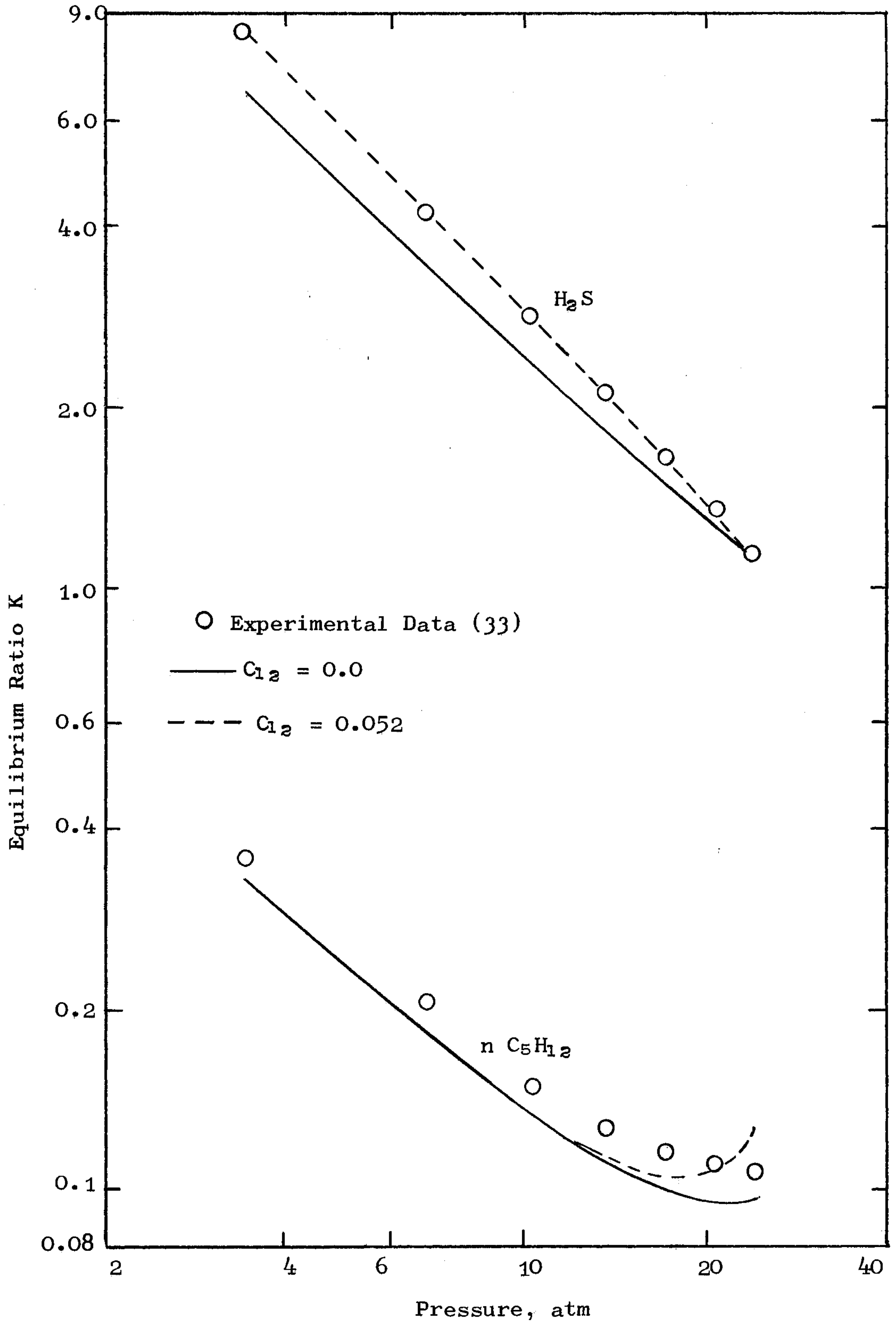


Figure 35. Equilibrium Ratios of n-Pentane-Hydrogen Sulfide System at 310.94°K Calculated With Modified RK Equation

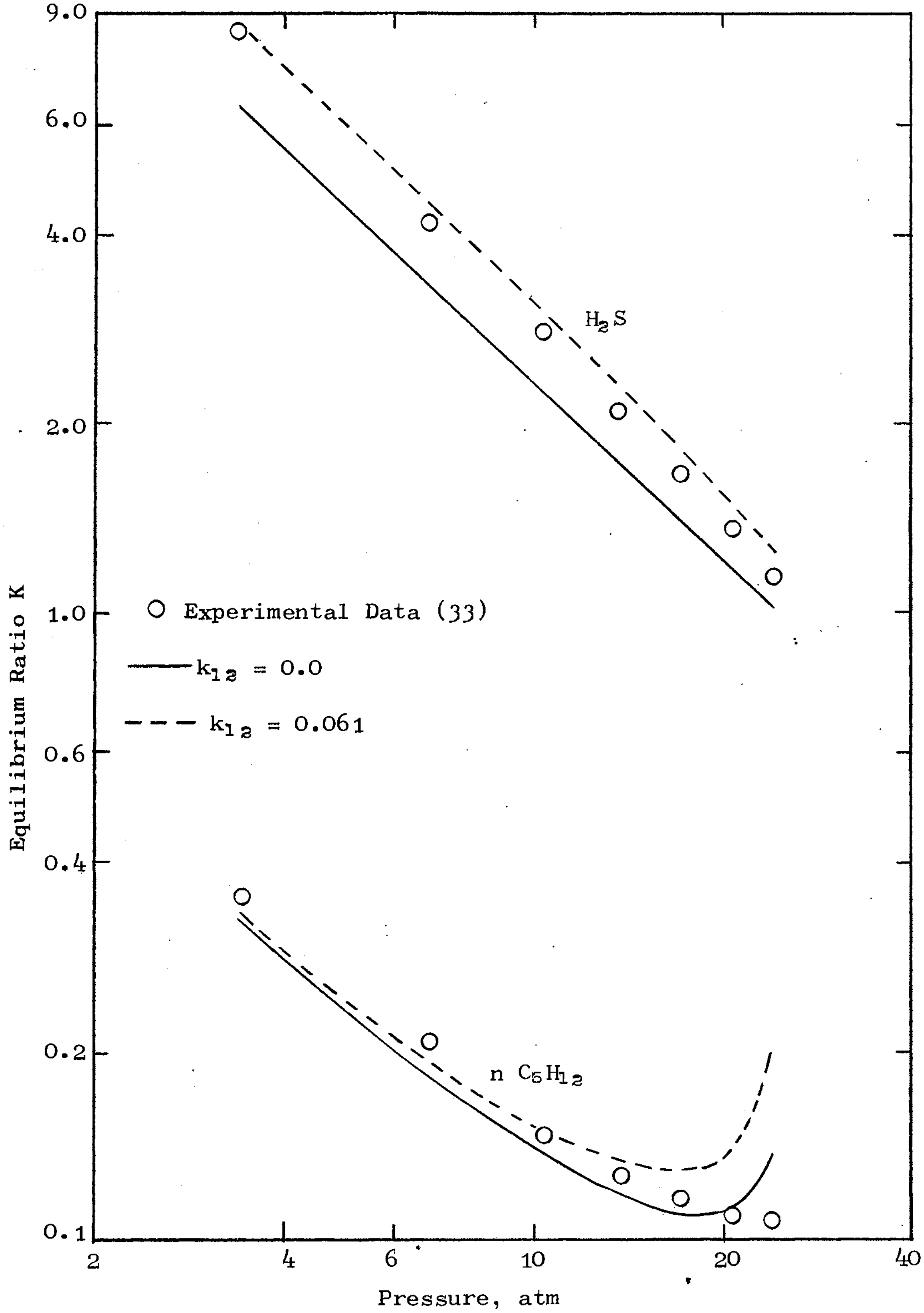


Figure 36. Equilibrium Ratios of n-Pentane-Hydrogen Sulfide System at 310.94°K Calculated With Unmodified BWR Equation

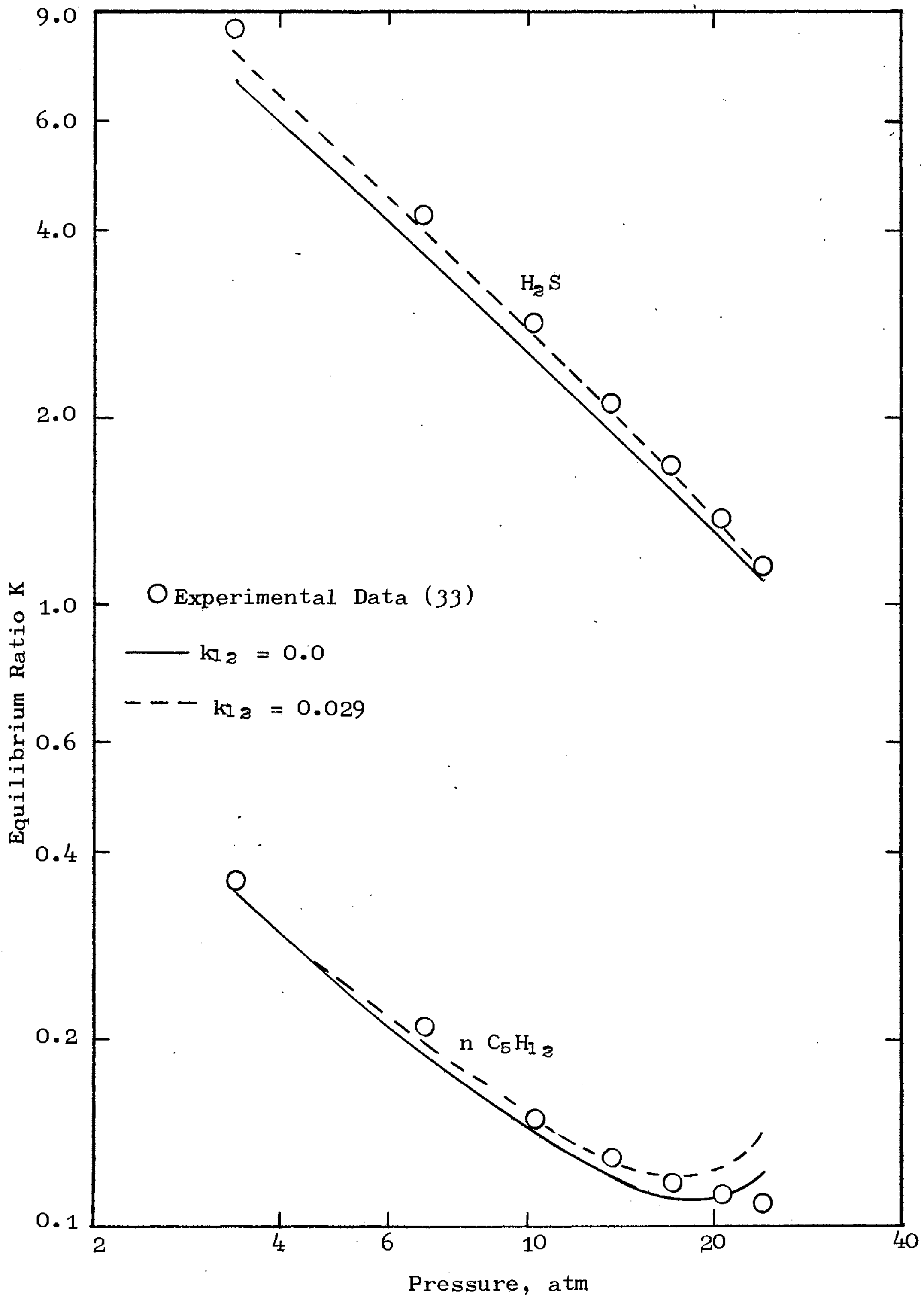


Figure 37. Equilibrium Ratios of n-Pentane-Hydrogen Sulfide System at 310.94°K Calculated With Modified BWR Equation (C_o, α)

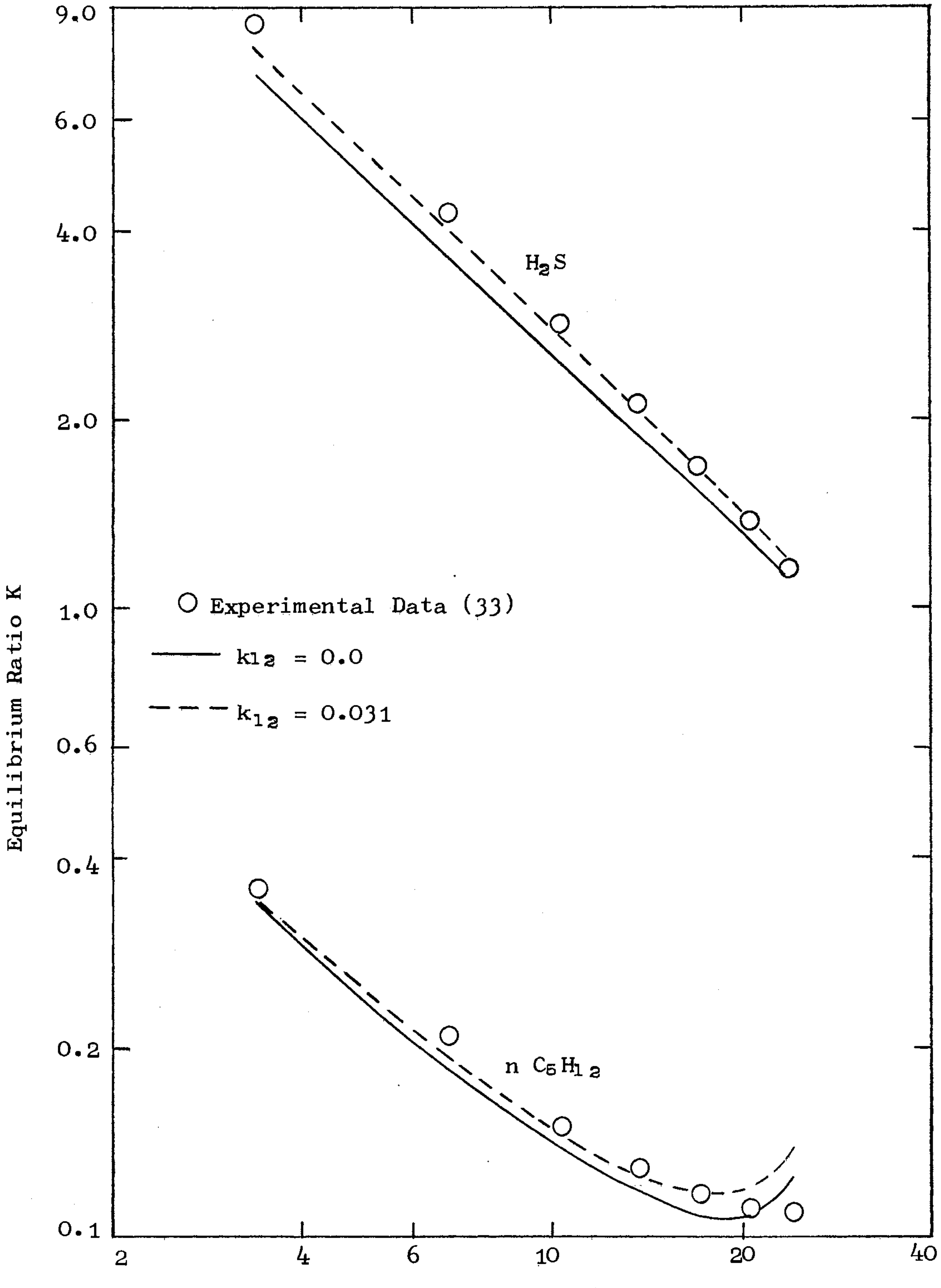


Figure 38. Equilibrium Ratios of n-Pentane-Hydrogen Sulfide System at 310.94°K Calculated with Modified BWR Equation (C_o, α, c)

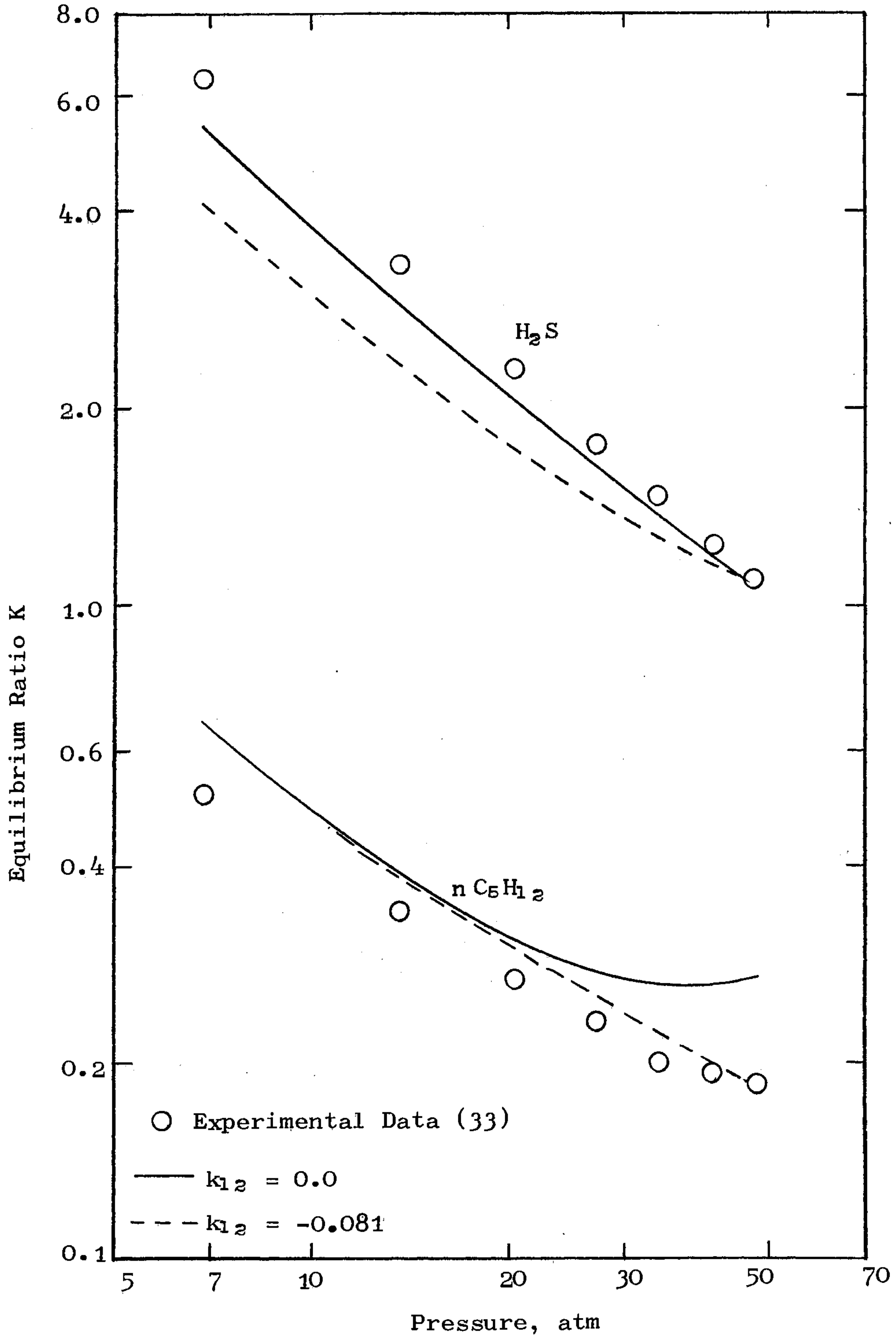


Figure 39. Equilibrium Ratios of n-Pentane-Hydrogen Sulfide System at 344.27°K Calculated With Unmodified RK Equation

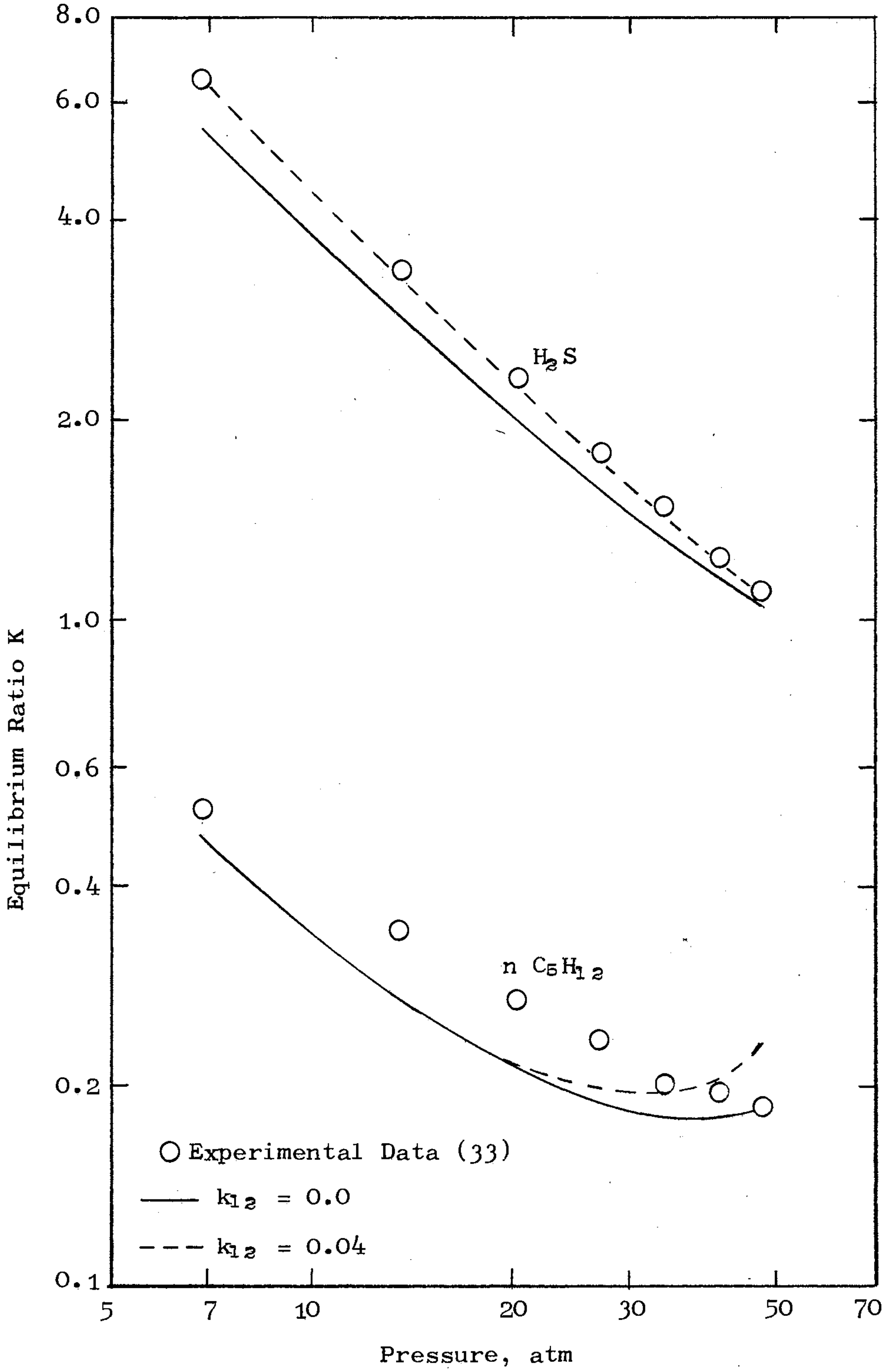


Figure 40. Equilibrium Ratios of n-Pentane-Hydrogen Sulfide System at 344.27°K Calculated With Modified RK Equation

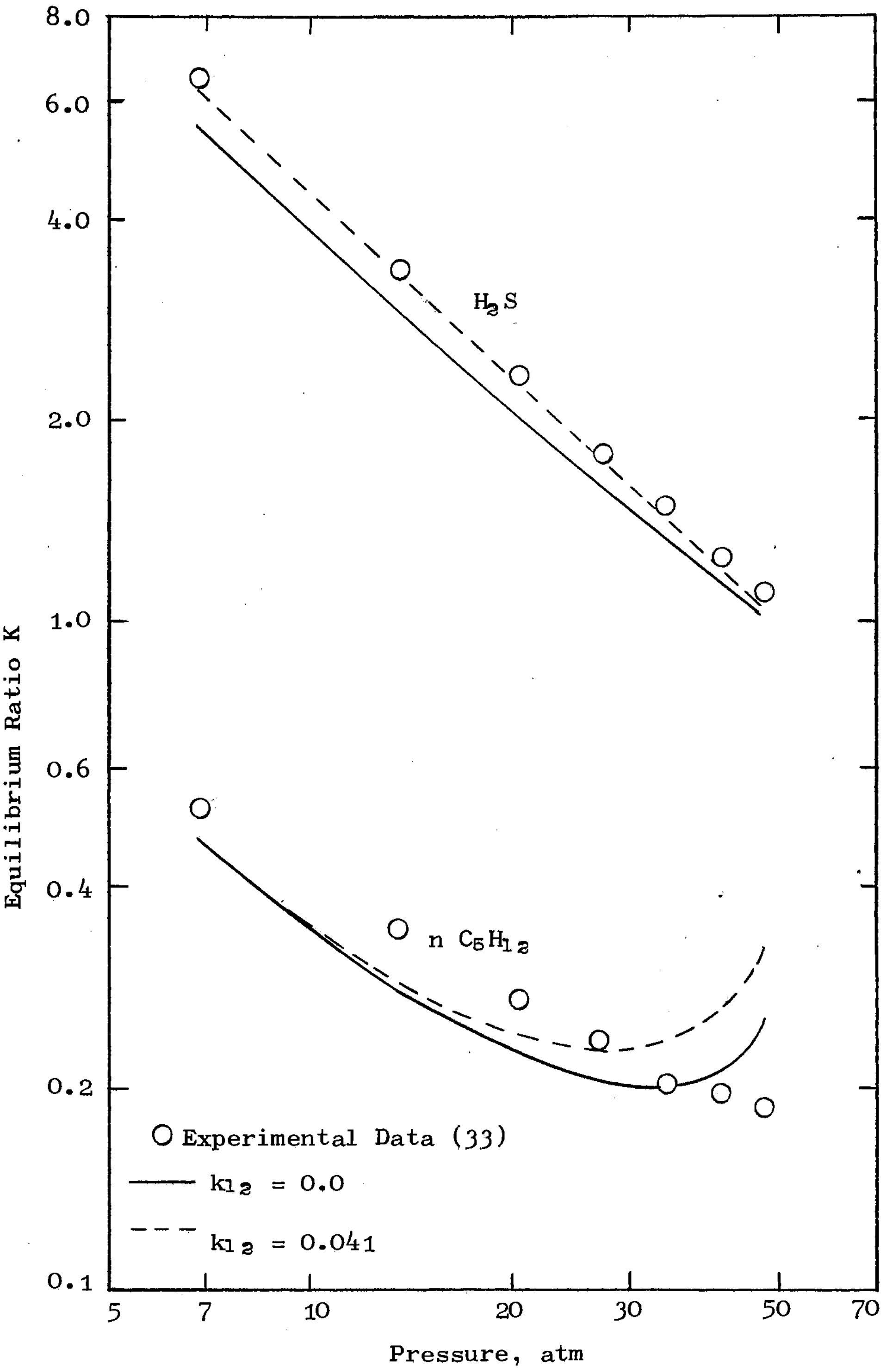


Figure 41. Equilibrium Ratios of n-Pentane-Hydrogen Sulfide System at 344.27°K Calculated With Unmodified BWR Equation

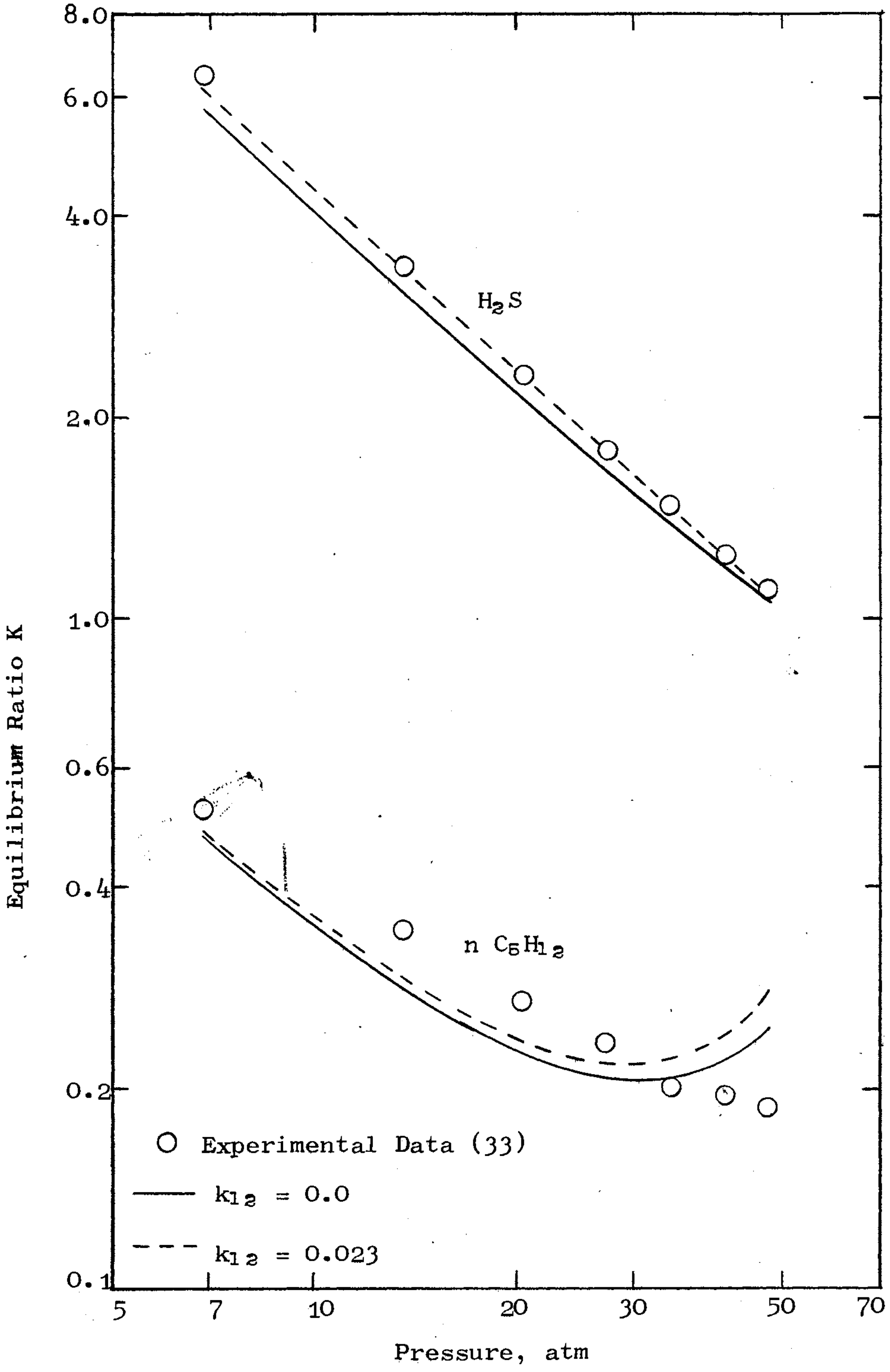


Figure 42. Equilibrium Ratios of n-Pentane-Hydrogen Sulfide System at 344.27°K Calculated With Modified BWR Equation (C_o, α)

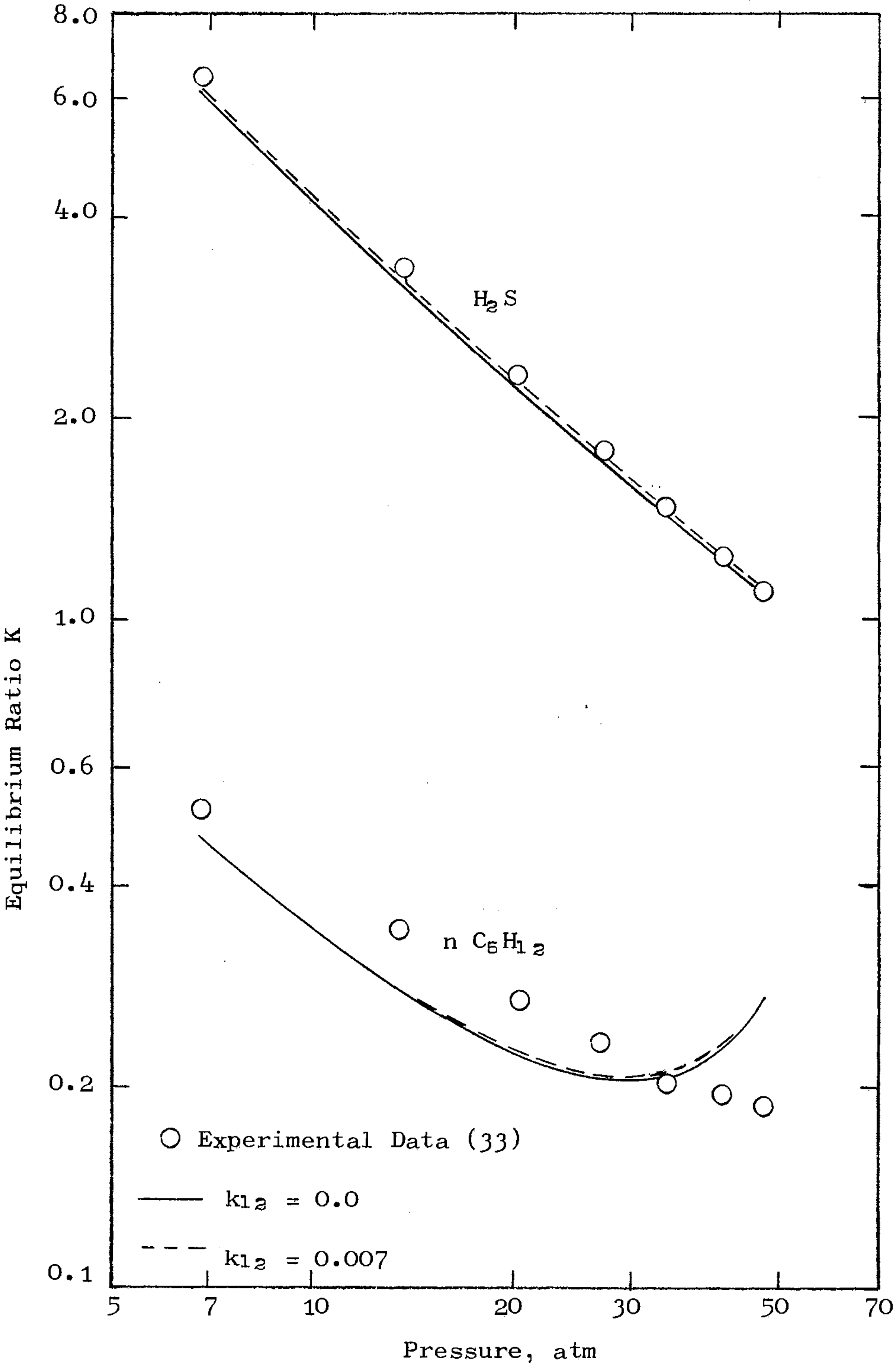


Figure 43. Equilibrium Ratios of n-Pentane-Hydrogen Sulfide System at 344.27°K Calculated With Modified BWR Equation (C_o, α, c)

TABLE XIV

SUMMARY OF RESULTS OF VAPOR-LIQUID EQUILIBRIUM CALCULATIONS FOR METHANE-HYDROGEN SULFIDE SYSTEM

Temp. $^{\circ}$K	Method	C_{12} or k_{12}	Per Cent Deviation in K, $\frac{(\text{cal-exp})}{\text{exp}}$ x 100				
			Methane		Hydrogen Sulfide		Sum of Avg.
			Max.	Avg.	Max.	Avg.	
310.94	Unmod. RK	0.0	-48.38	42.92	50.05	18.73	61.65
		0.140	17.63	7.81	-6.28	4.61	12.42
	Mod. RK	0.0	-44.42	31.02	43.09	7.89	38.91
		0.071	10.83	8.12	-8.35	2.15	10.27
	Unmod. BWR	0.0	-45.34	31.29	-8.23	6.12	37.41
		0.01	-43.19	28.47	-7.07	5.79	34.26
	Mod. BWR (C_0, α)	0.0	-47.82	35.87	4.55	2.03	37.90
		0.006	-46.60	34.40	5.45	2.44	36.84
	Mod. BWR (C_0, α, c)	0.0	-53.00	42.04	18.19	6.58	48.62
		0.001	-52.82	41.83	19.43	6.74	48.57
344.27	Unmod. RK	0.0	-42.20	41.09	13.76	7.94	49.03
		0.227	30.05	7.43	5.00	3.80	11.23
	Mod. RK	0.0	-39.75	25.57	13.76	3.00	28.57
		0.103	31.32	7.54	-7.88	1.80	9.34
	Unmod. BWR	0.0	-39.80	30.28	13.79	2.66	32.94
		-0.005	-34.96	27.45	-4.65	1.65	29.10
	Mod. BWR (C_0, α)	0.0	-39.80	32.46	13.79	3.44	35.90
		-0.003	-36.12	30.20	3.60	1.93	32.13
	Mod. BWR (C_0, α, c)	0.0	-53.92	47.28	20.22	8.79	56.07
		0.007	-55.05	46.84	21.13	9.03	55.87

TABLE XV

SUMMARY OF RESULTS OF VAPOR-LIQUID EQUILIBRIUM CALCULATIONS FOR n-PENTANE-HYDROGEN SULFIDE SYSTEM

Temp. °K	Method	C_{12} or k_{12}	Per Cent Deviation in K, $\frac{(\text{cal-exp})}{\text{exp}}$ x 100				
			n-Pentane		Hydrogen Sulfide		Sum of Avg.
			Max.	Avg.	Max.	Avg.	
310.94	Unmod. RK	0.0	52.50	44.40	-18.19	9.94	54.34
		0.039	60.06	49.05	6.17	2.47	51.52
	Mod. RK	0.0	-14.33	11.16	-21.73	13.99	25.15
		0.052	19.57	9.90	0.89	0.67	10.57
	Unmod. BWR	0.0	29.25	10.80	-24.39	18.00	28.80
		0.061	85.32	20.49	-5.64	2.16	22.65
	Mod. BWR (C_0, α)	0.0	15.34	6.17	-17.89	10.76	16.93
		0.029	32.54	8.70	-8.07	3.38	12.08
	Mod. BWR (C_0, α, c)	0.0	15.66	7.89	-17.47	9.95	17.84
		0.031	29.33	7.65	-6.89	3.24	10.89
344.27	Unmod. RK	0.0	46.48	26.90	-15.85	8.46	35.36
		-0.081	25.83	11.06	-36.07	18.13	29.19
	Mod. RK	0.0	-20.50	12.41	-14.22	8.73	21.14
		0.04	24.53	14.34	-2.72	1.45	15.79
	Unmod. BWR	0.0	37.51	15.71	-14.14	9.78	25.49
		0.041	74.30	23.44	-3.70	1.36	24.80
	Mod. BWR (C_0, α)	0.0	34.05	14.67	-10.29	5.82	20.49
		0.023	51.79	18.39	-3.43	0.93	19.32
	Mod. BWR (C_0, α, c)	0.0	46.94	17.42	-5.52	2.26	19.68
		0.007	51.31	18.28	-3.37	0.81	19.09

In predicting the vapor-liquid equilibrium ratios, the following observations may be made based from these calculations:

1. The unmodified BWR equation is better than the unmodified RK equation (using basic mixing rules).
2. For systems containing a supercritical component and when an interaction coefficient is introduced into the mixing rule, the unmodified RK equation is better than the unmodified BWR equation.
3. Whether the interaction coefficient is introduced into the mixing rule or not, the modified RK equation gives better results than the unmodified RK equation.
4. A surprising result shows that the modified BWR equation is less accurate than the unmodified BWR equation for the methane-hydrogen sulfide system.
5. When methane is a supercritical component in the methane-hydrogen sulfide system, large deviations between its predicted and experimental equilibrium ratios are introduced. This indicates that the temperature effects on the parameters for pure methane should be considered when the system temperature is above the critical temperature of methane. This fact has been demonstrated by Hsi and Lu (21).
6. The introduction of the interaction coefficient k_{12} into the mixing rule of A_o for the BWR equation does not significantly improve the vapor-liquid equilibrium calculations.
7. The most accurate results in the prediction of K values

were obtained by using the modified RK equation with the interaction coefficient.

8. The unsatisfactory results in the BWR equation indicate that more interaction coefficients may be needed in the mixing rules.

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The purpose of this investigation was to study the equations of state in the saturated phase region and to apply them to some binary mixtures. The major conclusions are presented along with each of the primary objectives.

The first objective was to determine which parameters of the Benedict-Webb-Rubin equation would be best suited for modification as functions of temperature. The results of the preliminary investigations indicated that C_o, α, and c may be most suitable for modification as functions of temperature to predict more accurate saturated phase properties.

The second objective was to simultaneously modify certain parameters for the pure components. The temperature dependence of the Redlich-Kwong parameters for various components appears to be of similar functional form. However, the temperature dependence of the Benedict-Webb-Rubin parameters is not of similar functional form. There is no generality in behavior of temperature dependence of the Benedict-Webb-Rubin parameters for different components. The saturated phase properties were predicted by using both the unmodified and modified equations. The predicted values were compared with experimental data. The comparison showed that (a) the Benedict-Webb-Rubin equation gave better results than the Redlich-Kwong equation when the equations were applied in their original form, (b) the unmodified Redlich-Kwong equation showed considerable errors in predicting the saturated liquid volumes, especially near critical region, (c) equations modified to represent vapor pressures and liquid volumes not only predicted very accurate vapor pressures and liquid volumes, but also predicted more accurate vapor volumes and fugacities than the unmodified equations, and (d) the Benedict-Webb-Rubin equation with three modified parameters predicted more accurate vapor volumes and fugacities than the Benedict-Webb-Rubin equation with two modified parameters.

The third objective was to predict vapor-liquid equilibrium ratios for binary mixtures. The conclusions for this portion were (a) the unmodified Benedict-Webb-Rubin equation predicted better results than the unmodified Redlich-Kwong equation, using basic mixing rules, (b) the modified Redlich-Kwong equation gave more accurate K values than the unmodified Redlich-Kwong equation for both systems, (c) the modifications of the Benedict-Webb-Rubin equation did not yield more satisfactory results for methane-hydrogen sulfide system, (d) the temperature effects on the parameters for pure component i should be considered when the system temperature is above the critical temperature of pure component i, (e) the introduction of the interaction coefficient k_{12} into the mixing rule of A_o of the Benedict-Webb-Rubin equation did not significantly improve the vapor-liquid equilibrium calculations, and (f) the most accurate results in the prediction of K values were obtained using the modified Redlich-Kwong equation with the interaction coefficient C_{12} applied to the mixing rule of parameter "a".

Recommendations

Some recommendations for future studies of these equations of state have arisen from this investigation.

1. The Redlich-Kwong parameters, Ω_a and Ω_b, of hydrocarbons could be generalized as functions of reduced temperature and acentric factor.
2. The effects of pressure and temperature on the binary interaction coefficients could be found by establishing the interaction coefficients at each given data point.
3. A different interaction coefficient could be introduced into the Benedict-Webb-Rubin parameter to see if calculated equilibrium ratios were better predicted.
4. Two or more interaction coefficients might be simultaneously introduced into the mixing rules of the Benedict-Webb-Rubin equation to see if the equilibrium ratios could be predicted more accurately.

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APPENDIX A

METHOD FOR CALCULATING SENSITIVITIES OF SATURATED PHASE PROPERTIES TO EACH BWR PARAMETER

The calculation of sensitivities of saturated phase properties to each BWR parameter includes a flash calculation of the saturated phase properties. The phase rule shows that only one variable needs to be specified for pure component flash calculation. In this case, the temperature is specified. From the definition of the vapor-liquid equilibrium, the following conditions must exist:

$$P^L = P^V$$

$$T^L = T^V$$

$$f^L = f^V \text{ .}$$

Equation (3-1) was used to calculate vapor pressure:

$$P = \frac{RT}{V} + (B_oRT - A_o - \frac{C_o}{T^2})\frac{1}{V^2} + (bRT - a)\frac{1}{V^3} + \frac{a\alpha}{V^6} + \frac{c}{T^2V^3}(1 + \frac{\gamma}{V^2})\exp(-\frac{\gamma}{V^2}). \tag{3-1}$$

The equation for calculating fugacity is derived from:

$$RT\ln(\frac{f}{p}) = \int_{\infty}^{V}\left[\frac{RT}{V} - P\right]dV + PV - RT - RT\ln\frac{PV}{RT} \text{ .} \tag{A-1}$$

Using Equation (3-1), the resulting equation is:

$$RT\ln f = RT\ln\frac{RT}{V} + (B_oRT - A_o - \frac{C_o}{T^2})\frac{2}{V} + (bRT - a)\frac{3}{2V^2}$$

$$+ \frac{6a\alpha}{5V^5} + \frac{c}{T^2V^2}\left[\frac{V^2}{\gamma} - \left(\frac{V^2}{\gamma} - \frac{1}{2} - \frac{\gamma}{V^2}\right)\exp\left(-\frac{\gamma}{V^2}\right)\right] . \qquad \text{(A-2)}$$

Figure 44 is a flow diagram for calculating sensitivities of phase properties to change in parameters. The procedure used for calculating saturated phase properties is shown in Figure 45.

The equation for assuming vapor pressure is derived from a plot of 1/Tr versus P/P_c (17).

$$P_{ass} = P_c \exp\left(5.39 - \frac{5.39}{Tr}\right). \qquad \text{(A-3)}$$

The equation for estimating saturated liquid volume is (29):

$$V^L_{ass} = V_c Z_c^{(1-Tr)^{2/7}} . \qquad \text{(A-4)}$$

The saturated vapor volume was calculated from an assumed compressibility factor:

$$V^V_{ass} = \frac{Z_{ass}\ RT}{P_{ass}} . \qquad \text{(A-5)}$$

The Newton-Raphson technique was used to change the volumes if calculated pressure did not agree with the assumed pressure.

$$V_2 = V_1 - \frac{P_{calc} - P_{ass}}{\left(\frac{\partial P}{\partial V}\right)} . \qquad \text{(A-6)}$$

When correct liquid volume and vapor volume were found, Equation (A-2) was used to calculate liquid and vapor fugacities. If the calculated fugacities were not equal, a new assumed vapor pressure was calculated from the following equation (20):

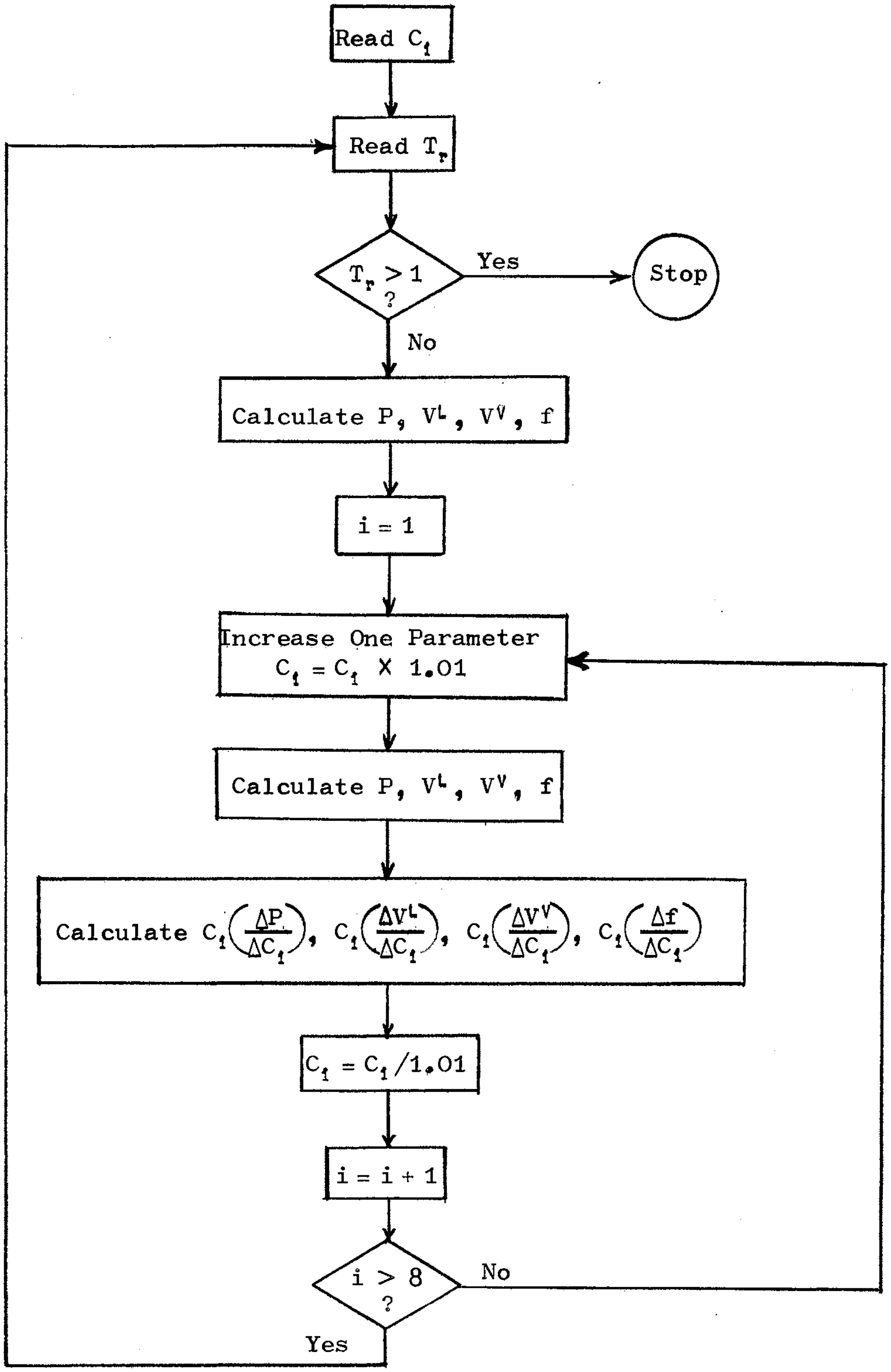

Figure 44. Flow Diagram for Calculating Sensitivities of Saturated Phase Properties to Changes in Parameters

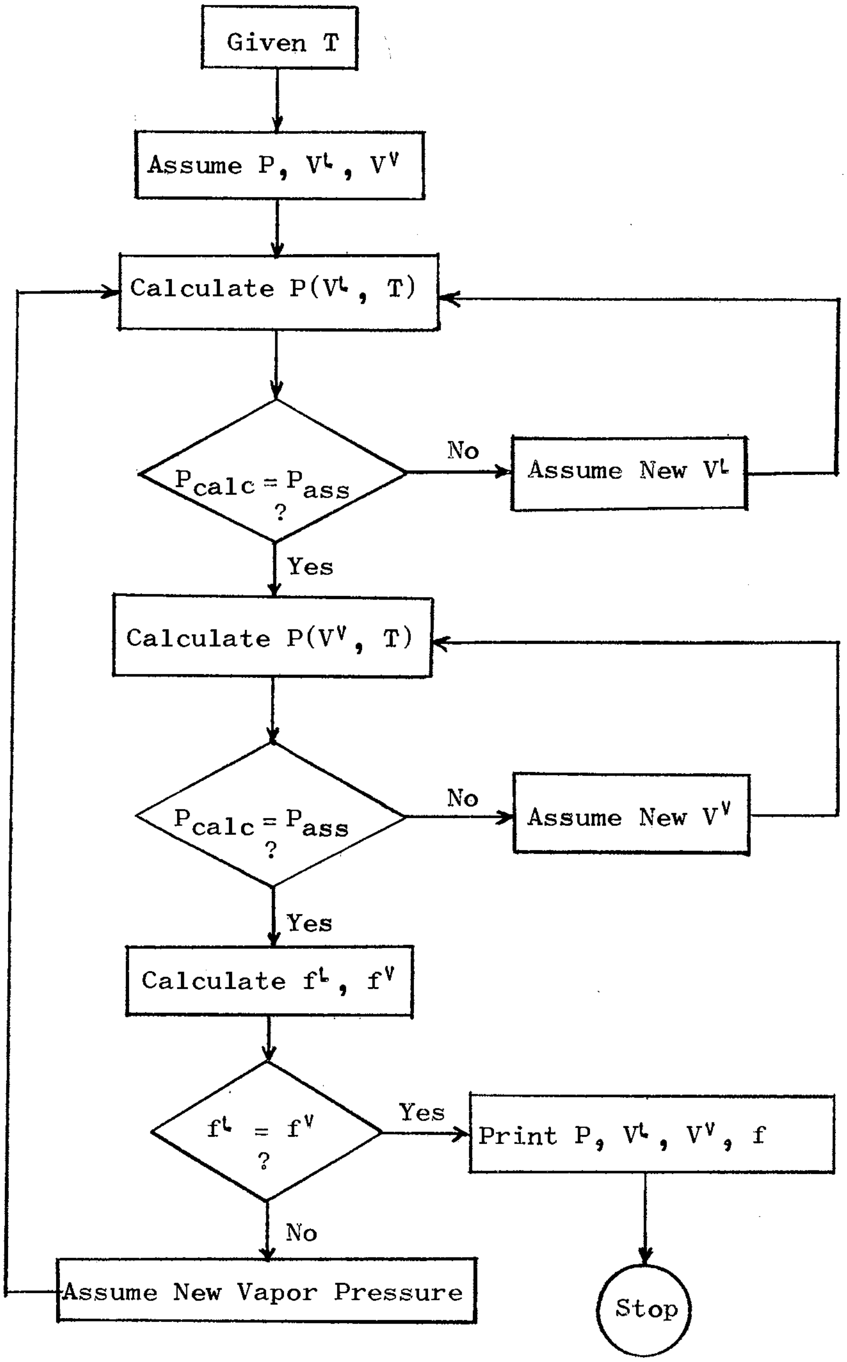

Figure 45. Flow Diagram for Calculating Saturated Phase Properties

$$P_2 = P_1 - \left(\frac{RT}{V^L - V^V}\right) \ln\left(\frac{f^L}{f^V}\right) . \qquad \text{(A-7)}$$

Then P_2 becomes the new assumed vapor pressure and the trial-and-error procedure is repeated until the calculated liquid and vapor fugacities are equal.

APPENDIX B

METHOD FOR SIMULTANEOUS MODIFICATION OF REDLICH-KWONG PARAMETERS

The RK parameters were modified to fit experimental vapor pressures and liquid volumes. Figure 46 is a flow diagram describing the procedure for calculating the constants Ω_a and Ω_b at a given temperature.

The saturated liquid and vapor volumes were first calculated with unmodified constants, at given temperature and experimental vapor pressure by using the cubic form of the RK equation. Then, the experimental and calculated liquid volumes were compared. If the liquid volumes did not agree, the constant b was adjusted by the following method:

$$b_2 = b_1 - \frac{V^L_{calc} - V^L_{exp}}{\left(\frac{\partial V}{\partial b}\right)_{T,P,a}}$$

where

$$\left(\frac{\partial V}{\partial b}\right)_{T,P,a} = \frac{\frac{RT}{(V-b)^2} + \frac{a}{T^{1/2}\,V(V+b)^2}}{\frac{RT}{(V-b)^2} - \frac{a(2V+b)}{T^{1/2}\,V^2(V+b)^2}} \, .$$

With the new value of b, the volumes were calculated and compared. Iterations were repeated until the liquid volumes agreed. After agreement of liquid volumes was obtained, the saturated liquid phase and vapor phase fugacities were calculated. Equation (B-1) was used to calculate fugacity for pure component.

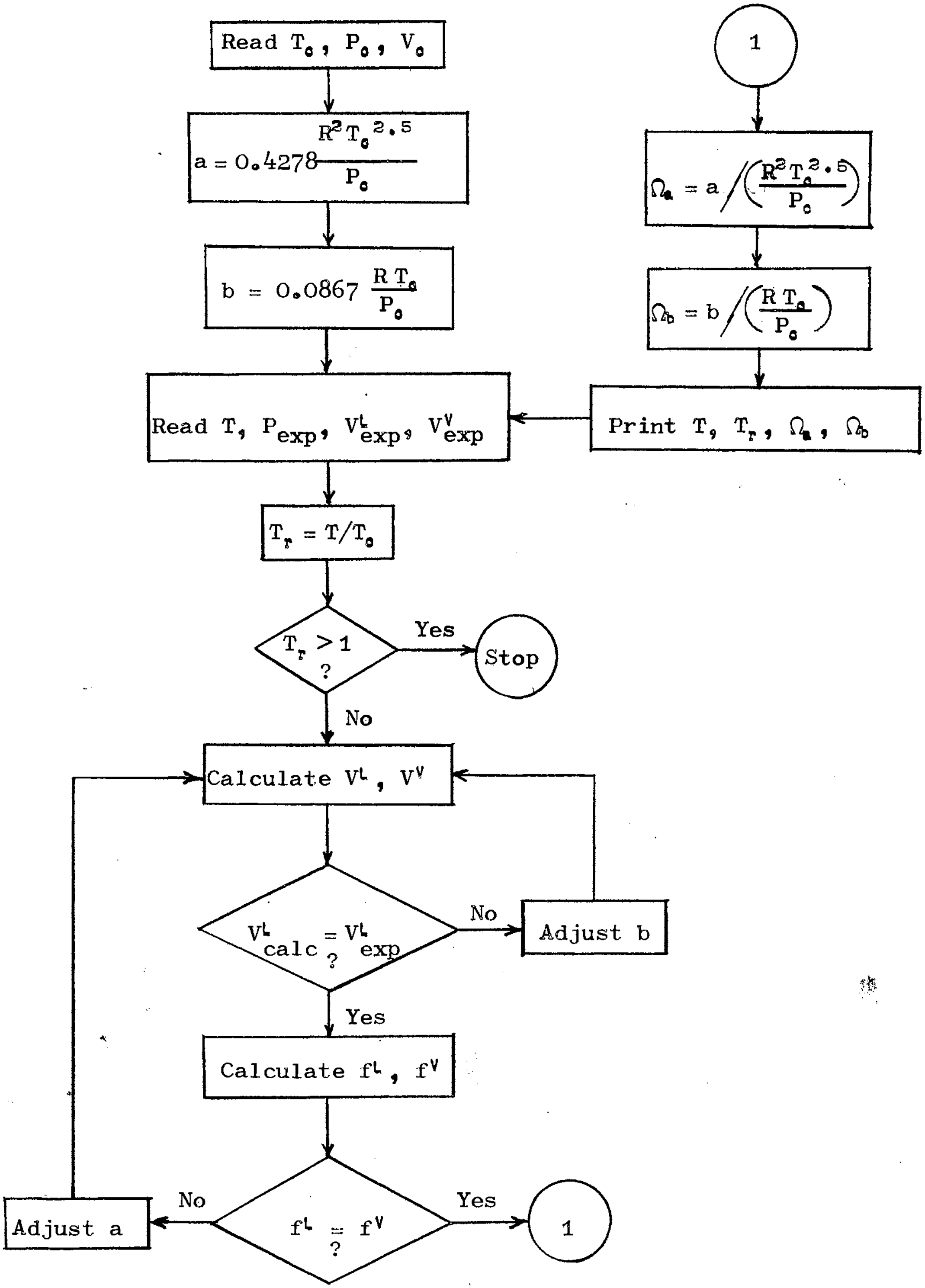

Figure 46. Flow Diagram for Calculating the Constants Ω_a and Ω_b

$$\ln\left(\frac{f}{P}\right) = \ln\frac{RT}{P(V-b)} + \frac{PV}{RT} - 1 - \frac{a}{RT^{3/2}\,b}\ln\left(\frac{V+b}{V}\right). \qquad \text{(B-1)}$$

If calculated liquid fugacity and vapor fugacity were not equal, the constant "a" was adjusted by the following method:

$$a_2 = a_1 - \frac{\ln\left(\frac{f^L}{P}\right) - \ln\left(\frac{f^V}{P}\right)}{\frac{\partial\ln\left(\frac{f^L}{P}\right)}{\partial a} - \frac{\partial\ln\left(\frac{f^V}{P}\right)}{\partial a}}$$

where

$$\frac{\partial\ln\left(\frac{f}{P}\right)}{\partial a} = -\frac{1}{RT^{3/2}b}\ln\frac{V+b}{V}.$$

Iterations were repeated again until the calculated liquid fugacity and vapor fugacity were equal. Then Ω_a and Ω_b were calculated by Equations (B-2) and (B-3).

$$\Omega_a = a\left(\frac{P_c}{R^2 T_c^{2.5}}\right) \qquad \text{(B-2)}$$

$$\Omega_b = b\left(\frac{P_c}{R\,T_c}\right) \qquad \text{(B-3)}$$

APPENDIX C

METHOD FOR SIMULTANEOUS MODIFICATION OF BENEDICT-WEBB-RUBIN PARAMETERS

Modification of Parameters C_o and α

The BWR parameters C_o and α were simultaneously modified as functions of temperature to fit experimental vapor pressures and liquid volumes. A flow diagram describing the procedure for modifying the parameters C_o and α at a given temperature is shown in Figure 47.

The parameter α was first calculated by the following equation with experimental saturated liquid volume and vapor pressure at a given temperature.

$$\alpha = \frac{V^6}{a}\left[P - \frac{RT}{V} - \left(B_oRT - A_o - \frac{C_o}{T^2}\right)\frac{1}{V^2} - (bRT - a)\frac{1}{V^3} - \frac{c}{T^2V^3}\left(1 + \frac{\gamma}{V^2}\right)\exp\left(-\frac{\gamma}{V^2}\right)\right]. \tag{C-1}$$

Saturated vapor volume was estimated from an assumed compressibility factor.

$$V^v_{ass} = \frac{Z_{ass}\ RT}{P}.$$

The pressure was calculated using the value of V^v_{ass}. If the calculated pressure and the experimental pressure did not agree, the vapor volume was adjusted by using the Newton-Raphson technique.

$$V^v_2 = V^v_1 - \frac{P_{calc} - P_{exp}}{\left(\frac{\partial P}{\partial V}\right)_{T,s_1}} \tag{C-2}$$

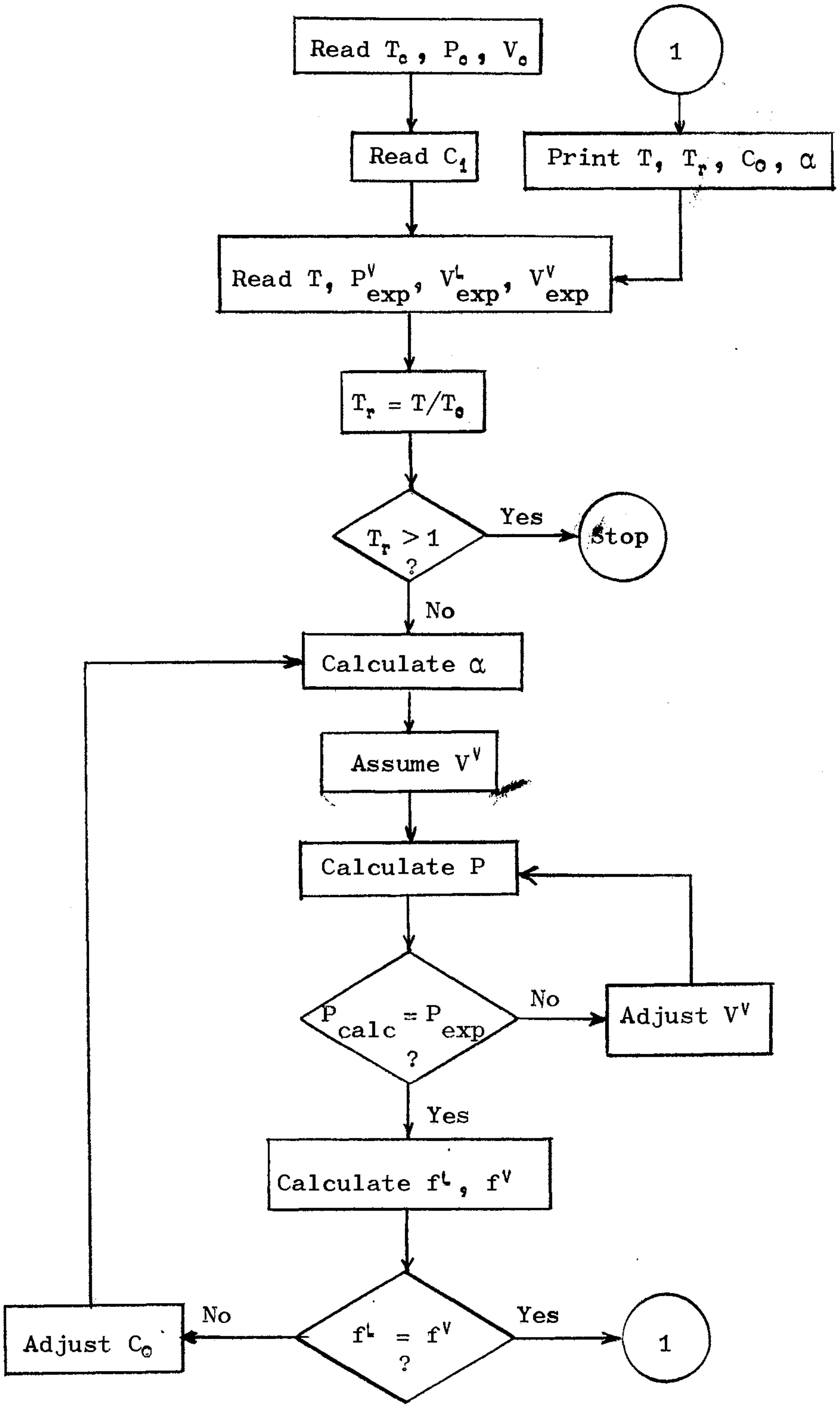

Figure 47. Flow Diagram for Modifying the Parameters C_0 and α

After agreement of vapor pressures was obtained, Equation (C-3) was applied to calculate vapor and liquid phase fugacities.

$$RT\ln f = RT\ln\frac{RT}{V} + \left(B_oRT - A_o - \frac{C_o}{T^2}\right)\frac{2}{V} + (bRT - a)\frac{3}{2V^2} + \frac{6a\alpha}{5V^5} + \frac{c}{T^2V^2}\left[\frac{V^2}{\gamma} - \left(\frac{V^2}{\gamma} - \frac{1}{2} - \frac{\gamma}{V^2}\right)\exp\left(-\frac{\gamma}{V^2}\right)\right] \tag{C-3}$$

If calculated liquid and vapor fugacities were not equal, the parameter C_o was adjusted by the following method:

$$C_{o,2} = C_{o,1} - \frac{RT\ln f^L - RT\ln f^V}{\frac{\partial(RT\ln f^L)}{\partial C_o} - \frac{\partial(RT\ln f^V)}{\partial C_o}} \tag{C-4}$$

where

$$\frac{\partial(RT\ln f)}{\partial C_o} = -\frac{2}{T^2V} .$$

With new value of C_o, the parameter α was calculated. Iterations were repeated until the calculated liquid and vapor fugacities agreed.

Modification of Parameters C_o, α, and c

The BWR parameters C_o, α, and c were simultaneously modified to fit experimental vapor pressures, liquid volumes, and vapor volumes. The procedure for modification used in this section is shown in Figure 48.

The method for calculating α and the techniques for adjusting vapor volume and C_o were shown in the previous section. If the calculated vapor volume did not equal the experimental value, the Newton-Raphson technique was used to adjust c.

$$c_2 = c_1 - \frac{V^v_{calc} - V^v_{exp}}{\left(\frac{\partial V}{\partial c}\right)_{T,P,c_j}} \qquad \text{(C-5)}$$

where

$$\left(\frac{\partial V}{\partial c}\right)_{T,P,c_j} = \frac{\left(\frac{\partial P}{\partial c}\right)_{T,V,c_j}}{\left(\frac{\partial P}{\partial V}\right)_{T,c_i}} .$$

Iterations were repeated until the calculated and experimental vapor volumes agreed.

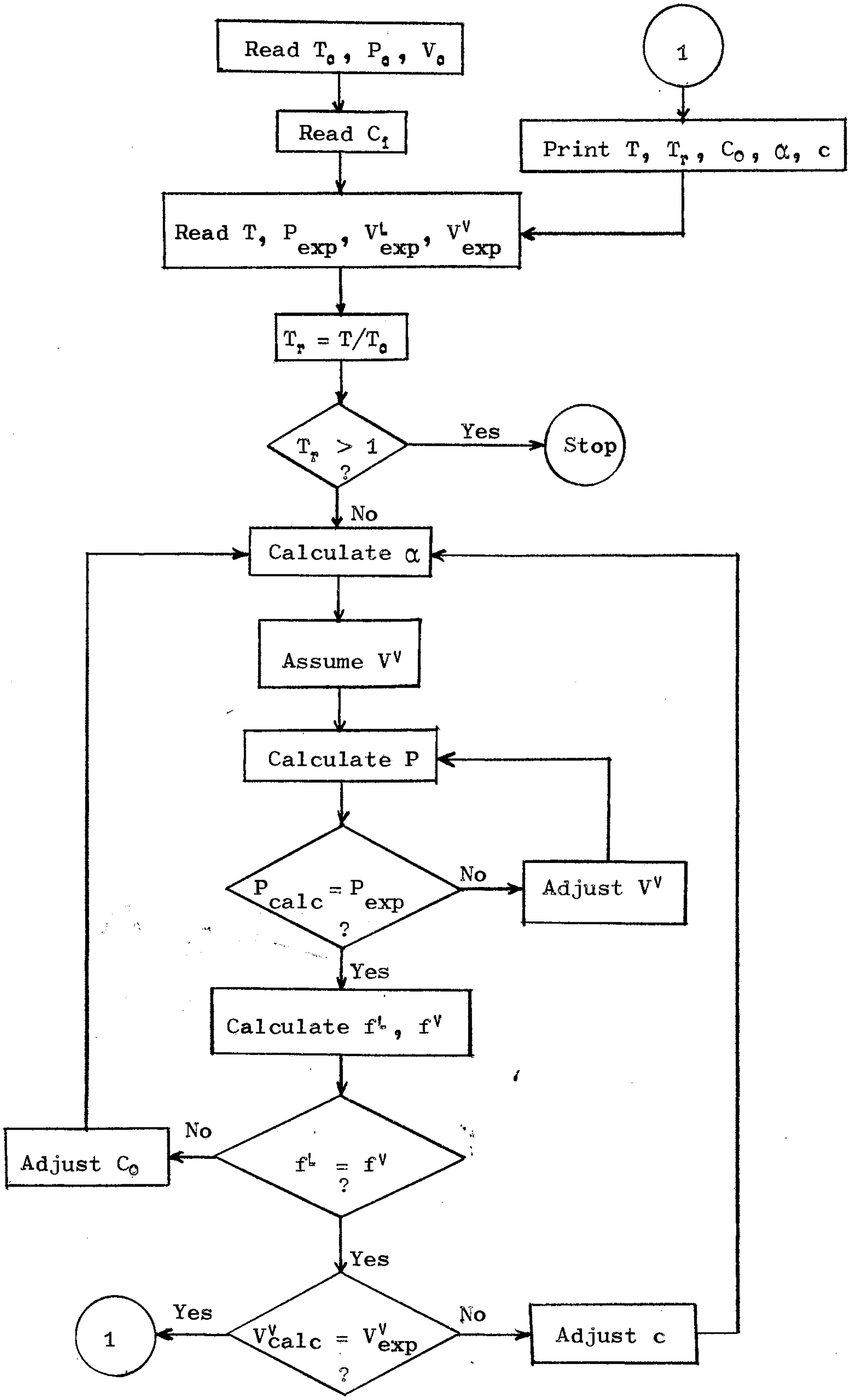

Figure 48. Flow Diagram for Modifying the Parameters C_0, α, and c

APPENDIX D

NOMENCLATURE

Major Symbols

English Letters

a = BWR parameter, Equation (3-1), (liters/gm-mole)^3 atm

RK parameter, Equation (4-1), (liters/gm-mole)^2 atm $^\circ K^{0.5}$

A_o = BWR parameter, (liters/gm-mole)^2 atm

b = BWR parameter, Equation (3-1), (liters/gm-mole)^2

RK parameter, Equation (4-1), liters/gm-mole

B_o = BWR parameter, liters/gm-mole

c = BWR parameter, (liters/gm-mole)^3 ($^\circ$K)^2 atm

C_i = General BWR parameter

C_o = BWR parameter, (liters/gm-mole)^2 ($^\circ$K)^2 atm

C_{12} = Interaction coefficient for RK equation of component 1 and 2

f = Fugacity, atm

k_{12} = Interaction coefficient for BWR equation of component 1 and 2

K = Vapor-liquid equilibrium ratio

P = Pressure, atm

R = Gas constant, (liters/gm-mole) atm/$^\circ$K

T = Temperature, degree Kelvin

V = Volume, liters/gm-mole

x = Liquid mole fraction

y = Vapor mole fraction

English Letters (Continued)

Z = Compressibility factor

Greek Letters

α = BWR parameter, $(\text{liters/gm-mole})^3$

γ = BWR parameter, $(\text{liters/gm-mole})^2$

ρ = Molar density, gm-moles/liter

φ = Fugacity coefficient

Ω = RK coefficient

Subscripts

c = Critical state

i = Component number

m = Mixture property

r = Reduced property

Superscripts

L = Liquid phase

V = Vapor phase

Abbreviations

ass = Assumed value

atm = Atmosphere

BWR = Benedict-Webb-Rubin

calc = Calculated value

exp = Experimental Value

mod = Modified

Abbreviations (Continued)

RK = Redlich-Kwong

unmod = Unmodified

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