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FUGACITY AND ACTIVITY COEFFICIENTS FOR THE N-BUTANE-NITROGEN SYSTEM

BY

RICHARD E. WALTER

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ABSTRACT

Fugacity and activity coefficients were calculated for the nitrogen-n-butane system at 310°, 340°, 370°, and 400°F. in 100 atmosphere pressure intervals from 100 to 700 atmospheres for the pure components and mixtures of 10, 30, 50, 70, and 90 mol% n-butane. Calculations were based on a method proposed by Van Ness. This calculation procedure combines an analytical solution utilizing the Redlich and Kwong equation of state with a graphically obtained correction factor.

APPROVAL OF THESIS

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FOR

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TEXT

INTRODUCTION

The fugacity of a component is very important for the determination of chemical equilibrium and vapor-liquid equilibrium.

The most widely used technique for calculating approximate fungacities of components in gas mixtures employs the Lewis and Randall fugacity rule. This is based on the assumption that the gas mixture is an ideal solution. However, if the temperature and pressure of the system under study are far removed from conditions which approximate an ideal solution, the Lewis and Randall approximation fails. Fugacities calculated from experimental compressibility factor data do not agree with those calculated which assume that the gas mixture is an ideal solution.

There are three methods by which experimental compressibility data can be employed to calculate fugacities, fugacity coefficients, or activity coefficients. First, the required integrations and differentiations can be performed entirely by graphical techniques. However, this technique is inherently inaccurate and exceedingly large and unwieldy graphs are required to obtain any kind of accuracy.

A second method involves the use of an equation of state to represent the components over a wide range of temperature and pressure. The calculations can therefore be performed entirely by analytical means. However, no such equations of state are available which are sufficiently accurate.

It has been proposed that both of the above methods be combined, therefore combining the advantages of both. A relatively simple equation of state can be utilized to calculate, by analytical techniques, an approximate solution. Then by employing a residual compressibility for graphical

calculations, a small correction factor can be added to the approximate solution.

It is the purpose of this paper to calculate fugacity and activity coefficients for the n-butane-nitrogen system between 310 and 400°F and up to 700 atmospheres pressure. The method used is that proposed by Van Ness (10) which combines analytical and graphical techniques. The Redlich and Kwong equation of state was utilized for the analytical approximations and a graphical correction based on residuals was added to the analytical approximation.

Experimental compressibility data are available from the literature for pure n-butane and nitrogen (6) and for mixtures of these two components (4).

This method has been applied previously to the methane- CO_2 system (1,7) and the ethylene-nitrogen system (10) with satisfactory results.

CALCULATIONS

The general equation relating the compressibility of a gas to the fugacity is given by

$$\ln(f/p) = \int_{P*}^{P} (Z-1) \frac{dP}{P} \tag{1}$$

To utilize the calculation procedure outlined by Van Ness (1) we define a residual, Z, as

$$\Delta Z = Z - Z' \tag{2}$$

i.e., the difference between the experimental compressibility and compressibility as calculated by an equation of state.

Substituting equation 2 into equation 1 gives

$$\ln(f/p) = \int_{P*}^{P} (Z'-1) \frac{dP}{P} + \int_{P*}^{P} \Delta Z \frac{dP}{P} \tag{3}$$

Since Z' is defined by an equation of state, the Redlich and Kwong equation for this particular investigation, the first part of equation 3 can be solved analytically. The second part of equation is normally determined by performing the integration graphically. Utilizing an equation of state which successfully approximates actual behavior while being simple facilitates an easy analytical solution and reduces the graphically prepared part to a minor correction.

Redlich and Kwong (9) have developed an equation of state for gases which is a compromise between simplicity and high accuracy. This equation is given as:

$$Z' = \left(\frac{1}{1-h}\right) - \left(\frac{A^2}{B}\right) \left(\frac{h}{1+h}\right) \tag{4}$$

$$\text{where } h = \frac{Bp}{Z'} \tag{5}$$

The constants for this equation, A and B, are dependent on temperature only. When used for a gas mixture, the constants are calculated by:

$$A_{mix} = x_a A_a + x_b A_b + \cdots \tag{6}$$

$$B_{mix} = x_a B_a + x_b B_b + \cdots \tag{7}$$

The substitution of equation 4 into equation 3 and the subsequent integration of this expression has been performed by Redlich and Kwong. This reduces equation 3 to the following:

$$\ln\left(\frac{f}{P}\right) = (Z'-1) - \ln(Z'-Z'h) - \left(\frac{A^2}{B}\right)\ln(1+h) + \Delta\ln(f/p) \tag{8}$$

$$\text{where } \Delta\ln(f/p) = \int_{P*}^{P} \Delta Z \frac{dP}{P} \tag{9}$$

Therefore, using this expression, one can solve directly for the fugacity of a pure gas.

Obtaining values for the fugacity and activity coefficients for the components of a gas mixture is more difficult than the calculation of the fugacity. Fugacity coefficients are defined by the equation:

$$\phi_i = \frac{\bar{f}_i}{X_i P} \tag{10}$$

It has been shown that

$$\ln \frac{f}{P} = x_a \ln\phi_a + x_b \ln\phi_b + \cdots \tag{11}$$

The terms $\ln\phi_a$ and $\ln\phi_6$ are related to $\ln \frac{f}{P}$ exactly as partial molal properties are related to the total property (2). Therefore, using the equations for the partial molal properties and solving for $\ln\phi_i$, we obtain (4)

$$\ln\phi_i = \ln \frac{f}{P} - x_a \left[\frac{\partial \ln(f/p)}{\partial x_a}\right]_{x_b} + x_b \left[\frac{\partial \ln(f/p)}{\partial x_a}\right]_{x_b} \tag{12}$$

Substitution of the analytical solution of equation 8 into equation 12 and solving for the i^{th} component in the mixture yields (9).

$$\ln\phi_i = \text{approx. } \ln\phi_i + \Delta\ln\phi_i \tag{13}$$

$$\text{where approx. } \ln\phi_i = \left(\frac{B_i}{B}\right)(Z'-1) - \ln(Z'-Z'h) - \left(\frac{A^2}{B}\right)\left(\frac{2A_i}{A} - \frac{B_i}{B}\right)\ln(1+h) \tag{14}$$

$$\text{and } \Delta\ln\phi_i = \ln(f/P) - x_a\left[\frac{\partial(\Delta\ln f/P)}{\partial x_a}\right]_{x_b} - x_b\left[\frac{\partial(\Delta\ln f/P)}{\partial x_b}\right]_{x_a} \tag{15}$$

The value of $\Delta\ln f/P$ is obtained by graphical integration and the differentiations of equation 15 are performed graphically by the method of intercepts (5).

Activity coefficients are then obtained from the fugacity coefficients by employing the following relationship:

$$\gamma_i = \frac{\phi_i}{f_i/P} \tag{16}$$

To apply equations 8 and 13 values of the constants A and B must be determined for the pure components of the gas mixture under investigation. Redlich and Kwong proposed that (9)

$$B = 0.0867\,\frac{T_c}{P_c T} \tag{17}$$

$$A^2 = 0.4278\,\frac{T_c^{2.5}}{P_c T^{2.5}} \tag{18}$$

However, Van Ness proposes (10) that greater accuracy can be obtained if the values for the constants are selected by a trial procedure. His method involves the arbitrary selection of a value for B; a good initial approximation is the value calculated from equation 17. Then for a given temperature a series of values of pressure along with the corresponding experimental compressibilities for the pure components being considered are substituted into equation 4, rearranged below, to calculate values for A^2/B.

$$\frac{A^2}{B} = \left(\frac{1}{1-h} - Z\right) \frac{1+h}{h} \tag{19}$$

The optimum result would be the value of B which produces a very nearly constant A^2/B. Van Ness proposed that a better procedure would be to use a B which leads to a very nearly constant A^2/B at low pressures with increasing deviation at higher pressures. This procedure is suggested to minimize the correction applied to the analytical solution by graphically integrating $\Delta Z/P$. By having ΔZ small at low pressure and increasing with pressure $\Delta Z/P$ will always remain reasonably small.

The trial procedure for the calculation of the constants for the Redlich and Kwong equation was programmed for the IBM 7094 computer using Fortran IV language. The Fortran statements for this program are presented on page 100, a block flow plan of the program is given on page 101, and a sample printout is given on page 103. Initial values of B were calcualated by equation 17. Using this B values of A^2/B were calculated at each pressure for which experimental compressibility factor data were available. After calculating A^2/B for the pressure range under consideration, a small increment arbitrarily chosen, was added to the

initial B and the procedure repeated. The number of trials was controlled by the computer input. Therefore, with the computer to perform the trial calculations, it was possible to select values of B and A^2/B which closely approximated the optimum.

The value of the B constant for the pure components was chosen as the value which produced the minimum variation in the A^2/B term over the pressure range considered. The value of A^2/B was chosen arbitrarily from the range predicted by the trial procedure. At each temperature considered, the value of A^2/B for pure nitrogen was selected as the value calculated at 100 atm. and for n-butane the value of A^2/B was selected as the value calculated at 13 atm. The constants used for subsequent calculations are presented in Table 5.

Once having determined values of B and A^2/B for the pure components at the temperature levels to be considered, values of Z', the compressibility calculated by the equation of state, were then calculated. Again, this calculation procedure and the subsequent solution of the analytical portions of the equations for the determination of the fugacity coefficient were programmed for the IBM 7094 computer. The Fortran IV statements for this program are presented on pages 103 and 104, a block flow diagram of the calculation procedure is presented on pages 105 and 106 and a sample of the printout from this program is given on pages 107, 108, and 109.

The experimental compressibility is given by equations 4 and 5 which can be combined and simplified to yield the following expression:

$$Z'^3 - Z'^2 + \left[\frac{A^2}{B}(Bp) - Bp - (Bp)^2\right] Z' - \frac{A^2}{B}(Bp)^2 = 0 \qquad (20)$$

This expression can be solved directly for the compressibility at any given temperature and pressure by using the general solution for a cubic equation. The use of this technique is possible since there is only one unique solution applicable; i.e., a positive real number at each temperature, pressure, and composition.

The solution of the analytical portion of equation 13 is straight forward once the value of Z' is calculated. The analytical solution was incorporated into the program. A sample of the printout obtained from this program is given for a 50 mol% n-butane, 50 mol% nitrogen mixture at 400°F on pages 107, 108, and 109.

Values of $\Delta Z/P$ were plotted versus P, Figures 1-7 are representative of the plots obtained. These curves were graphically integrated using a compensating polar planimeter to obtain values of $\Delta \ln(f/p)$ at 100, 200, 300, 400, 500, 600, and 700 atm. Values of $\Delta \ln(f/P)$ were then plotted versus mol fraction of n-butane with parameters of pressure at each temperature, Figures 8-11. Using the method of intercepts (5) values of $\Delta \ln \phi_i$ were determined for the nitrogen and n-butane at each pressure, mol fraction, and temperature. These graphically obtained values were added to the analytical approximations to determine the fugacity coefficients. Activity coefficients were then calculated for the n-butane and nitrogen according to equation 16.

The calculated values of the fugacity and activity coefficients are presented in Tables 6 - 13 for nitrogen and n-butane in mixtures of 0, 10, 30, 50, 70, 90, and 100 mol% n-butane for temperatures of 310, 340, 370, and 400°F.

Redlich and Kister (8) have proposed a technique for evaluating the thermodynamic consistency of the activity coefficients. This involves a graphical method in which $\ln \frac{\gamma_{C_4}}{\gamma_{N_2}}$ is plotted versus composition. The criteria for thermodynamic consistency maintains that equal area segments be obtained above and below the ordinate; i.e., the area under the curve from 0 to 100 mol% should be zero. Figures 20 - 46 illustrate this method.

RESULTS

Fugacity and activity coefficients have been calculated for n-butane and nitrogen in mixtures at 310, 370, and 400°F for 100 atmosphere increments from 100 to 700 atmospheres. The calculated fugacity and activity coefficients are listed in Tables 6 through 13. The activity coefficients are also presented as plots of γ_{C_4} and γ_{N_2} versus pressure with parameters of composition for each temperature; Figures 12 through 19.

The calculated activity coefficients were checked for thermodynamic consistency using the method of Redlich and Kister. Plots of $\ln \frac{\gamma_{C_4}}{\gamma_{N_2}}$ versus mol% n-butane in the gas mixture are presented in Figures 20 through 46. The average deviation between the positive and negative area segments for all tests using this method was 1.6% with the greatest deviation being 3.2% for the gas mixtures at 400°F. The largest single deviation was of 10% for the gas mixture at 400°F and 400 ATM pressure.

CONCLUSIONS

Based on experimental compressibility factor data and a calculation method proposed by Van Ness, fugacity and activity coefficients were determined for the components in the n-butane-nitrogen system. The method combines an analytical approximation using the Redlich and Kwong equation of state with a graphically obtained correction factor.

For the most part, the graphical portion of the solution was normally between 1 and 10% of the analytical portion. However, when calculating the fugacity coefficient of either n-butane in 100% nitrogen or of nitrogen in 100% n-butane, the graphical part of the solution ranged for 20 to 600% of the analytical solution for the n-butane and from 20 to 120% for the nitrogen.

Greater accuracy could be obtained by selecting different values of the constants A and B, primarily those chosen for n-butane. The calculated residual compressibility for nitrogen was never greater than 0.0089 while the residual for n-butane was as high as 0.0619.

RECOMMENDATIONS

An initial step has been made to improve the accuracy of the calculation of fugacity and activity coefficients for the components of a gas mixture by utilizing the digital computer to perform the trial and analytical calculations required to implement the method proposed by Van Ness. Presently the trial calculations to obtain the constants for the Redlich and Kwong equation are performed with one program and then though a visual evaluation of the variations in A^2/B with pressure for various values of B, constants are selected for each component. Next, these constants and the experimental compressibility data are submitted to a second program to calculate the analytical approximations of the fugacity coefficient and values of $\Delta Z/P$. The values of $\Delta Z/P$ must be plotted and graphically integrated, and then the graphical integrations are plotted versus composition. These latter plots are graphically differentiated to obtain the correction which must be applied to the analytical solution to obtain the value of $\ln \phi_i$.

All of these operations could be incorporated into a single computer program by utilizing sufficient logic and curve fitting techniques. The results of this paper and those of Sievering (7), Capik (1) and Van Ness (10) are available to guide and test such a project. With such a tool, the graphical portion of the solution could be maintained at a minimum and thus improve the overall accuracy of the technique.

APPENDIX I

TABLES AND FIGURES

TABLE 1

COMPRESSIBILITY FACTORS

n-BUTANE - NITROGEN MIXTURES AT 310°F

Pressure, psia	Mol% n-Butane			
	0	10	30	50
0	1.000	1.000	1.000	1.000
200	1.00525	1.002	0.989	0.969
400	1.01075	1.004	0.978	0.938
600	1.01645	1.007	0.970	0.908
800	1.02225	1.010	0.962	0.882
1,000	1.0282	1.014	0.958	0.858
1,250	1.0358	1.019	0.952	0.833
1,500	1.0434	1.025	0.951	0.815
1,750	1.0522	1.032	0.952	0.810
2,000	1.0600	1.040	0.956	0.811
2,250	1.0693	1.048	0.963	0.819
2,500	1.0792	1.058	0.972	0.834
2,750	1.0897	1.068	0.983	0.853
3,000	1.1003	1.079	0.994	0.875
3,500	1.1238	1.102	1.025	0.925
4,000	1.1471	1.127	1.059	0.982
4,500	1.1710	1.153	1.097	1.040
5,000	1.1952	1.181	1.139	1.096
5,500	-	1.211	1.183	1.159
6,000	1.2443	1.244	1.229	1.222
6,500	-	1.276	1.277	1.285

TABLE 1 (Cont'd)

COMPRESSIBILITY FACTORS

n-BUTANE - NITROGEN MIXTURES AT 310°F

Pressure, psia	Mol% n-Butane			
	0	10	30	50
7,000	1.2976	1.309	1.325	1.348
7,500	-	1.342	1.372	1.411
8,000	1.3510	1.376	1.421	1.473
8,500	-	1.409	1.469	1.534
9,000	1.4070	1.442	1.516	1.595
9,500	-	1.474	1.564	1.657
10,000	1.4642	1.508	1.610	1.718

Pressure, psia	Mol% n-Butane		
	70	90	100
0	1.000	1.000	1.0000
200	0.937	0.895	0.8636
400	0.868	0.766	0.6887
600	0.796	0.600	0.2194
800	0.736	0.404	0.2424
1,000	0.674	0.356	0.2860
1,250	0.626	0.376	0.3414
1,500	0.609	0.424	0.3970
1,750	0.614	0.474	0.4507
2,000	0.635	0.522	0.5042
2,250	0.661	0.570	0.5578
2,500	0.692	0.618	0.6097
2,750	0.726	0.665	0.6614

TABLE 1 (Cont'd)

COMPRESSIBILITY FACTORS

n-BUTANE - NITROGEN MIXTURES AT 310°F

Pressure, psia	Mol% n-Butane		
	70	90	100
3,000	0.765	0.711	0.7131
3,500	0.843	0.806	0.8134
4,000	0.920	0.899	0.9130
4,500	0.996	0.993	1.0113
5,000	1.074	1.083	1.1075
5,500	1.153	1.173	-
6,000	1.231	1.262	1.2969
6,500	1.308	1.350	-
7,000	1.383	1.437	1.4816
7,500	1.460	1.522	-
8,000	1.535	1.609	1.6639
8,500	1.610	1.696	-
9,000	1.684	1.781	1.8428
9,500	1.757	1.865	-
10,000	1.827	1.948	2.0166

TABLE 2

COMPRESSIBILITY FACTORS

n-BUTANE - NITROGEN MIXTURES AT 340°F

Pressure, psia	Mol% n-Butane			
	0	10	30	50
0	1.0000	1.000	1.000	1.000
200	1.0054	1.003	0.991	0.974
400	1.0112	1.005	0.982	0.947
600	1.0172	1.008	0.975	0.922
800	1.0233	1.012	0.970	0.899
1,000	1.0297	1.016	0.966	0.880
1,250	1.0374	1.021	0.964	0.860
1,500	1.0452	1.028	0.963	0.848
1,750	1.0532	1.035	0.966	0.842
2,000	1.0616	1.043	0.970	0.844
2,250	1.0705	1.051	0.976	0.850
2,500	1.0803	1.061	0.985	0.861
2,750	1.0907	1.071	0.996	0.875
3,000	1.1013	1.982	1.007	0.894
3,500	1.1238	1.104	1.035	0.939
4,000	1.1474	1.128	1.068	0.991
4,500	1.1705	1.154	1.103	1.045
5,000	1.1936	1.180	1.143	1.098
5,500	-	1.209	1.184	1.158
6,000	1.2410	1.240	1.228	1.217
6,500	-	1.271	1.273	1.277
7,000	1.2920	1.302	1.319	1.337

TABLE 2 (Cont'd)

COMPRESSIBILITY FACTORS

n-BUTANE - NITROGEN MIXTURES AT 340°F

Pressure, psia	Mol% n-Butane			
	0	10	30	50
7,500	-	1.334	1.365	1.396
8,000	1.3439	1.366	1.410	1.456
8,500	-	1.399	1.456	1.516
9,000	1.3969	1.430	1.502	1.574
9,500	-	1.462	1.546	1.632
10,000	1.4517	1.494	1.591	1.689

Pressure, psia	Mol% n-Butane		
	70	90	100
0	1.0000	1.0000	1.0000
200	0.945	0.908	0.8828
400	0.888	0.804	0.7422
600	0.829	0.678	0.5445
800	0.775	0.541	0.3007
1,000	0.728	0.437	0.3142
1,250	0.686	0.428	0.3596
1,500	0.663	0.457	0.4098
1,750	0.660	0.496	0.4613
2,000	0.672	0.539	0.5125
2,250	0.693	0.583	0.5636
2,500	0.719	0.629	0.6142
2,750	0.749	0.674	0.6645

TABLE 2 (Cont'd)

COMPRESSIBILITY FACTORS

n-BUTANE - NITROGEN MIXTURES AT 340°F

Pressure, psia	Mol% n-Butane		
	70	90	100
3,000	0.782	0.720	0.7139
3,500	0.853	0.810	0.8118
4,000	0.926	0.900	0.9075
4,500	0.998	0.989	1.0026
5,000	1.148	1.076	1.0958
5,500	1.148	1.161	-
6,000	1.222	1.247	1.2792
6,500	1.296	1.332	-
7,000	1.396	1.416	1.4582
7,500	1.441	1.500	-
8,000	1.513	1.583	1.6356
8,500	1.584	1.666	-
9,000	1.657	1.749	1.8084
9,500	1.727	1.830	-
10,000	1.794	1.909	1.9768

TABLE 3

COMPRESSIBILITY FACTORS

n-BUTANE - NITROGEN MIXTURES AT 370°F

Pressure, psia	Mol% n-Butane			
	0	10	30	50
0	1.0000	1.0000	1.000	1.000
200	1.0058	1.003	0.993	0.978
400	1.0117	1.006	0.986	0.955
600	1.0177	1.009	0.981	0.934
800	1.0238	1.013	0.978	0.914
1,000	1.0303	1.018	0.975	0.899
1,250	1.0378	1.024	0.974	0.884
1,500	1.0460	1.030	0.974	0.874
1,750	1.0540	1.037	0.977	0.868
2,000	1.0626	1.045	0.982	0.871
2,250	1.0717	1.054	0.989	0.876
2,500	1.0812	1.064	0.997	0.886
2,750	1.0913	1.074	1.007	0.898
3,000	1.1018	1.085	1.018	0.914
3,500	1.1245	1.106	1.046	0.954
4,000	1.1469	1.129	1.076	1.000
4,500	1.1690	1.154	1.109	1.051
5,000	1.1917	1.180	1.146	1.101
5,500	-	1.207	1.186	1.158
6,000	1.2377	1.236	1.228	1.215
6,500	-	1.265	1.270	1.272
7,000	1.2869	1.295	1.314	1.328
7,500	-	1.326	1.357	1.385

TABLE 3 (Cont'd)

COMPRESSIBILITY FACTORS

n-BUTANE - NITROGEN MIXTURES AT 370°F

Pressure, psia	Mol% n-Butane			
	0	10	30	50
8,000	1.3369	1.357	1.400	1.441
8,500	-	1.388	1.443	1.408
9,000	1.3885	1.419	1.487	1.555
9,500	-	1.450	1.529	1.610
10,000	1.4408	1.481	1.572	1.665

Pressure, psia	Mol% n-Butane		
	70	90	100
0	1.000	1.000	1.0000
200	0.953	0.919	0.8984
400	0.904	0.828	0.7817
600	0.855	0.730	0.6838
800	0.808	0.628	0.4544
1,000	0.770	0.541	0.3698
1,250	0.732	0.482	0.3902
1,500	0.710	0.496	0.4312
1,750	0.704	0.524	0.4776
2,000	0.710	0.561	0.5258
2,250	0.725	0.600	0.5744
2,500	0.747	0.643	0.6227
2,750	0.773	0.686	0.6708
3,000	0.802	0.729	0.7183
3,500	0.865	0.815	0.8129

TABLE 3 (Cont'd)

COMPRESSIBILITY FACTORS

n-BUTANE - NITROGEN MIXTURES AT 370°F

Pressure, psia	Mol% n-Butane		
	70	90	100
4,000	0.934	0.902	0.9055
4,500	1.002	0.986	0.9975
5,000	1.072	1.069	1.0878
5,500	1.144	1.152	-
6,000	1.215	1.236	1.2650
6,500	1.286	1.319	-
7,000	1.356	1.400	1.4384
7,500	1.425	1.481	-
8,000	1.494	1.561	1.6110
8,500	1.563	1.640	-
9,000	1.632	1.721	1.7783
9,500	1.700	1.800	-
10,000	1.766	1.877	1.9412

TABLE 4

COMPRESSIBILITY FACTORS

n-BUTANE - NITROGEN MIXTURES AT 400°F

Pressure, psia	Mol% n-Butane			
	0	10	30	50
0	1.0000	1.000	1.000	1.000
200	1.0060	1.004	0.995	0.982
400	1.0121	1.007	0.990	0.962
600	1.0182	1.0011	0.986	0.945
800	1.0244	1.015	0.985	0.929
1,000	1.0307	1.020	0.984	0.916
1,250	1.0382	1.026	0.983	0.904
1,500	1.0469	1.032	0.985	0.896
1,750	1.0550	1.040	0.988	0.892
2,000	1.0634	1.048	0.993	0.893
2,250	1.0726	1.058	1.000	0.898
2,500	1.0820	1.067	1.009	0.908
2,750	1.0919	1.077	1.018	0.919
3,000	1.1022	1.087	1.029	0.933
3,500	1.1240	1.108	1.055	0.968
4,000	1.1464	1.130	1.084	1.009
4,500	1.1682	1.154	1.116	1.056
5,000	1.1900	1.179	1.149	1.103
5,500	-	1.205	1.187	1.158
6,000	1.2343	1.232	1.227	1.213
6,500	-	1.260	1.267	1.268
7,000	1.2823	1.280	1.308	1.322

TABLE 4 (Cont'd)

COMPRESSIBILITY FACTORS

n-BUTANE - NITROGEN MIXTURES AT 400°F

Pressure, psia	Mol% n-Butane			
	0	10	30	50
7,500	-	1.318	1.348	1.375
8,000	1.3299	1.348	1.389	1.429
8,500	-	1.378	1.430	1.483
9,000	1.3800	1.408	1.471	1.537
9,500	-	1.437	1.511	1.591
10,000	1.4301	1.467	1.552	1.643

Pressure, psia	Mol% n-Butane		
	70	90	100
0	1.000	1.000	1.0000
200	0.960	0.929	0.9116
400	0.919	0.858	0.8132
600	0.878	0.773	0.7012
800	0.839	0.700	0.5770
1,000	0.806	0.630	0.4725
1,250	0.772	0.569	0.4394
1,500	0.752	0.538	0.4630
1,750	0.744	0.555	0.5009
2,000	0.747	0.583	0.5442
2,250	0.757	0.617	0.5886
2,500	0.774	0.655	0.6345
2,750	0.796	0.696	0.6795
3,000	0.821	0.740	0.7255

TABLE 4 (Cont'd)

COMPRESSIBILITY FACTORS

n-BUTANE - NITROGEN MIXTURES AT 400°F

Pressure, psia	Mol% n-Butane		
	70	90	100
3,500	0.879	0.822	0.8167
4,000	0.943	0.905	0.9061
4,500	1.007	0.983	0.9947
5,000	1.071	1.064	1.0820
5,500	1.142	1.144	-
6,000	1.210	1.226	1.2541
6,500	1.278	1.307	-
7,000	1.345	1.387	1.4221
7,500	1.412	1.465	-
8,000	1.480	1.541	1.5895
8,500	1.545	1.619	-
9,000	1.610	1.695	1.7525
9,500	1.676	1.774	-
10,000	1.742	1.848	1.9107

TABLE 5

SUMMARY OF CONSTANTS FOR REDLICH AND KWONG EQUATION

n-BUTANE - NITROGEN MIXTURES

Temperature = 310°F

Mol% $n-C_4$	A	B	A^2/B
0	0.021995	0.000820	0.590000
10	0.030475	0.000965	0.962395
30	0.047433	0.001255	1.792770
50	0.064392	0.001545	2.683710
70	0.081351	0.001835	3.606499
90	0.098309	0.002125	4.548099
100	0.106789	0.002270	5.023700

Temperature = 340°F

Mol% $n-C_4$	A	B	A^2/B
0	0.020894	0.000800	0.54570
10	0.028893	0.000937	0.89092
30	0.044890	0.001211	1.664027
50	0.060888	0.001485	2.496512
70	0.076885	0.001759	3.360628
90	0.092883	0.002033	4.243586
100	0.100882	0.002170	4.689900

TABLE 5 (Cont'd)

SUMMARY OF CONSTANTS FOR REDLICH AND KWONG EQUATION

n-BUTANE - NITROGEN MIXTURES

Temperature = 370°F

Mol% $n\text{-}C_4$	A	B	A^2/B
0	0.02031	0.000780	0.514400
10	0.027604	0.000913	0.834601
30	0.042751	0.001179	1.550167
50	0.057898	0.001445	2.319831
70	0.073045	0.001711	3.118361
90	0.088191	0.001977	3.934106
100	0.095765	0.002110	4.346400

Temperature = 400°F

Mol% $n\text{-}C_4$	A	B	A^2/B
0	0.018765	0.000750	0.469500
10	0.025966	0.000881	0.765301
30	0.040368	0.001143	1.425688
50	0.054770	0.001405	2.135034
70	0.069172	0.001667	2.870253
90	0.083573	0.001929	3.620803
100	0.090774	0.002060	4.000000

TABLE 6

CALCULATED FUGACITY AND ACTIVITY COEFFICIENTS FOR n-BUTANE

n-BUTANE - NITROGEN MIXTURES AT 310°F

Mol% $n\text{-}C_4$	ln f/p	Approx. $\ln\phi_{C4}$	$\Delta\ln\phi_{C4}$	ϕ_{C4}	γ_{C4}
100 ATM					
0	0.0021	-0.15460	0.0355	0.8868	2.770
10	0.0054	-0.28075	0.0295	0.7780	2.430
30	0.0098	-0.51374	0.0360	0.6200	1.938
50	0.0205	-0.73955	0.250	0.4900	1.531
70	0.0188	-0.97335	0.0140	0.3840	1.200
90	0.0094	-1.1068	-0.0035	0.3300	1.031
100	-0.0228	-1.1175	-0.0228	0.3200	1.000
200 ATM					
0	0.0013	-0.23067	0.0615	0.8450	3.640
10	0.0076	-0.44680	0.0585	0.6780	2.920
30	0.0171	-0.83153	0.0630	0.4640	1.998
50	0.0294	-1.1479	0.0294	0.3270	1.410
70	0.0201	-1.3426	-0.0005	0.2610	1.124
90	-0.0086	-1.4116	-0.0335	0.2360	1.018
100	-0.0428	-1.4176	-0.0428	0.2320	1.000
300 ATM					
0	0.0016	-0.24281	0.0775	0.8478	3.870
10	0.0092	-0.51597	0.0785	0.6460	2.950
30	0.0229	-0.96060	0.0670	0.4100	1.871
50	0.0369	-1.2596	0.0320	0.2940	1.341

TABLE 6 (Cont'd)

CALCULATED FUGACITY AND ACTIVITY COEFFICIENTS FOR n-BUTANE

n-BUTANE - NITROGEN MIXTURES AT 310°F

Mol% $n\text{-}C_4$	ln f/p	Approx. $\ln\phi_{C4}$	$\Delta\ln\phi_{C4}$	ϕ_{C4}	γ_{C4}
300 ATM					
70	0.0204	-1.4109	-0.0220	0.2380	1.088
90	-0.0183	-1.4623	-0.0435	0.2220	1.012
100	-0.0535	-1.4670	-0.0535	0.2190	1.000
400 ATM					
0	0.0020	-0.20689	0.095	0.8940	3.910
10	0.0105	-0.51362	0.088	0.6540	2.860
30	0.0283	-0.97317	0.102	0.4190	1.830
50	0.0436	-1.2448	0.046	0.3020	1.320
70	0.0219	-1.3720	-0.037	0.2450	1.071
90	-0.0240	-1.4147	-0.053	0.2310	1.010
100	-0.0592	-1.4186	-0.0592	0.2285	1.000
500 ATM					
0	0.0024	-0.14324	0.1015	0.9592	3.865
10	0.0128	-0.46779	0.1045	0.6955	2.805
30	0.0348	-0.92545	0.1290	0.4510	1.820
50	0.0510	-1.1762	0.0390	0.3220	1.299
70	0.0253	-1.2895	-0.0360	0.2660	1.072
90	-0.0269	-1.3274	-0.0605	0.2500	1.008
100	-0.0628	-1.3309	-0.0628	0.2480	1.000

TABLE 6 (Cont'd)

CALCULATED FUGACITY AND ACTIVITY COEFFICIENTS FOR n-BUTANE

n-BUTANE - NITROGEN MIXTURES AT 310°F

Mol% $n\text{-}C_4$	ln f/p	Approx. $\ln\phi_{C4}$	$\Delta\ln\phi_{C4}$	$\bar{\phi}_{C4}$	$\bar{\gamma}_{C4}$
600 ATM					
0	0.0031	-0.04795	0.1185	1.0720	3.840
10	0.0156	-0.38385	0.1250	0.7720	2.760
30	0.0417	-0.83325	0.1510	0.5060	1.810
50	0.0587	-1.0659	0.0850	0.3760	1.342
70	0.0298	-1.1684	-0.0315	0.3015	1.078
90	-0.0277	-1.2026	-0.0660	0.2815	1.007
100	-0.0664	-1.2057	-0.0664	0.2800	1.000
700 ATM					
0	0.0040	0.06832	0.1420	1.2340	3.810
10	0.0180	-0.27377	0.1420	0.8768	2.705
30	0.0484	-0.71282	0.1735	0.5840	1.800
50	0.0661	-0.93097	0.0395	0.4105	1.268
70	0.0346	-1.0255	-0.0360	0.3460	1.068
90	-0.0277	-1.0570	-0.0680	0.3250	1.002
100	-0.692	-1.0599	-0.06921	0.3240	1.000

TABLE 7

CALCULATED FUGACITY AND ACTIVITY COEFFICIENTS FOR NITROGEN

n-BUTANE - NITROGEN MIXTURES AT 310°F

Mol% n-C_4	Approx. $\ln\phi N_2$	$\Delta\ln\phi N_2$	ϕN_2	γN_2	$\ln \frac{\gamma C_4}{\gamma N_2}$
100 ATM					
0	0.03901	0.0021	1.042	1.000	1.020
10	0.04567	0.0020	1.049	1.005	0.874
30	0.10494	-0.0015	1.109	1.061	0.601
50	0.25922	0.0155	1.275	1.222	0.234
70	0.62184	0.0305	1.920	1.841	-0.430
90	1.1321	0.1225	3.51	3.36	-1.180
100	1.3238	0.627	7.03	6.75	-1.910
200 ATM					
0	0.08620	0.00130	1.092	1.000	1.290
10	0.09761	0.0015	1.104	1.011	1.060
30	0.19477	-0.0020	1.212	1.110	0.588
50	0.40638	0.0294	1.547	1.423	-0.0105
70	0.69326	0.0690	2.143	1.965	-0.560
90	0.95669	0.2135	3.220	2.950	-1.065
100	1.0670	0.383	4.260	3.900	-1.363
300 ATM					
0	0.13986	0.0016	1.152	1.000	1.352
10	0.15415	0.0015	1.168	1.012	1.096
30	0.26466	-0.0040	1.298	1.126	0.509
50	0.46131	0.0420	1.655	1.436	-0.0673

TABLE 7 (Cont'd)

CALCULATED FUGACITY AND ACTIVITY COEFFICIENTS FOR NITROGEN

n-BUTANE - NITROGEN MIXTURES AT 310°F

Mol% n-C_4	Approx. $\ln\phi_{N2}$	$\Delta\ln\phi_{N2}$	ϕ_{N2}	γ_{N2}	$\ln \frac{\gamma_{C_4}}{\gamma_{N_2}}$
400 ATM					
0	0.19856	0.0020	1.222	1.000	1.362
10	0.21448	0.0020	1.242	1.017	1.034
30	0.32716	-0.0030	1.383	1.131	0.481
50	0.50435	0.0415	1.727	1.140	-0.066
70	0.68994	0.1605	2.340	1.911	-0.580
90	0.85405	0.2360	2.980	2.440	-0.884
100	0.92587	0.375	3.670	3.000	-1.100
500 ATM					
0	0.25470	0.0024	1.293	1.000	1.352
10	0.27143	0.0020	1.314	1.017	1.015
30	0.38262	-0.0055	1.458	1.126	0.481
50	0.54558	0.0635	1.839	0.915	-0.0889
70	0.71068	0.1680	2.410	1.862	-0.554
90	0.85634	0.2715	3.085	2.385	-0.864
100	0.92046	0.299	3.650	2.820	-1.037
600 ATM					
0	0.31879	0.0031	1.380	1.000	1.346
10	0.33600	0.0030	1.404	1.019	0.996
30	0.44437	-0.0050	1.552	1.127	0.475
50	0.59513	0.0320	1.872	1.358	-0.0101

TABLE 7 (Cont'd)

CALCULATED FUGACITY AND ACTIVITY COEFFICIENTS FOR NITROGEN

n-BUTANE - NITROGEN MIXTURES AT 310°F

Mol% n-C_4	Approx. $\ln\phi_{N2}$	$\Delta\ln\phi_{N2}$	ϕ_{N2}	γ_{N2}	$\ln \frac{\gamma_{C_4}}{\gamma_{N_2}}$
600 ATM					
70	0.74451	0.1735	2.500	1.812	-0.524
90	0.87605	0.312	3.280	2.380	-0.861
100	0.93418	0.326	3.525	2.560	-0.940
700 ATM					
0	0.38532	0.0040	1.476	1.000	1.338
10	0.40274	0.0040	1.502	1.020	0.975
30	0.50803	-0.0050	1.655	1.121	0.396
50	0.64917	0.0925	2.100	1.422	-0.1145
70	0.78694	0.1990	2.680	1.818	-0.531
90	0.90807	0.326	3.440	2.330	-0.845
100	0.96172	0.341	3.680	2.495	-0.915

TABLE 8

CALCULATED FUGACITY AND ACTIVITY COEFFICIENTS FOR n-BUTANE

n-BUTANE - NITROGEN MIXTURES AT 340°F

Mol% $n\text{-}C_4$	ln f/p	Approx. $\ln\phi_{C4}$	$\Delta\ln\phi_{C4}$	ϕ_{C4}	γ_{C4}
100 ATM					
0	0.0016	-0.1252	0.0555	0.9326	2.460
10	0.0036	-0.2368	0.0085	0.788	2.080
30	0.0063	-0.4399	0.0305	0.664	1.750
50	0.0164	-0.6289	0.0180	9.543	1.432
70	0.0112	-0.8145	0.0005	0.444	1.170
90	0.0024	-0.9393	-0.0065	0.3985	1.050
100	-0.0186	-0.9513	-0.0186	0.3795	1.000
200 ATM					
0	0.0004	-0.1806	0.0610	0.8872	3.220
10	0.0041	-0.3728	0.0330	0.7120	2.580
30	0.0111	-0.7111	0.0675	0.5260	1.910
50	0.0235	-0.9895	0.0190	0.3890	1.410
70	0.0117	-1.1708	-0.0165	0.3050	1.105
90	-0.0150	-1.2400	-0.0345	0.280	1.013
100	-0.0395	-1.2463	-0.0395	0.276	1.000
300 ATM					
0	0.0001	-0.1805	0.0580	0.8848	3.400
10	0.0042	-0.4247	0.0405	0.6810	2.620
30	0.0150	-0.8227	0.0775	0.4750	1.828
50	0.0288	-1.0968	0.0135	0.3380	1.300

TABLE 8 (Cont'd)

CALCULATED FUGACITY AND ACTIVITY COEFFICIENTS FOR n-BUTANE

n-BUTANE - NITROGEN MIXTURES AT 340°F

Mol% $n\text{-}C_4$	ln f/p	Approx. $\ln\phi_{C4-}$	$\Delta\ln\phi_{C4-}$	ϕ_{C4-}	γ_{C4-}
300 ATM					
70	0.0111	-1.2423	-0.0320	0.2800	1.078
90	-0.0233	-1.2938	-0.0460	0.262	1.008
100	-0.0487	-1.2985	-0.0487	0.260	1.000
400 ATM					
0	-0.0008	0.02429	0.0600	1.0880	3.605
10	0.0081	-0.2816	0.0820	0.8190	2.485
30	0.0357	-0.6974	0.1720	0.5920	1.796
50	0.0556	-0.9189	0.0270	0.4100	1.243
70	0.0256	-1.0192	-0.0475	0.3440	1.042
90	-0.0270	-1.0534	-0.0535	0.3310	1.002
100	-0.0530	1.0565	-0.0538	0.3295	1.000
500 ATM					
0	-0.0005	-0.07128	-0.057	0.9856	3.365
10	0.0053	-0.3652	0.066	0.7420	2.530
30	0.0242	-0.7852	0.113	0.5110	1.745
50	0.0411	-1.0223	0.020	0.3660	1.250
70	0.0163	-1.1328	-0.037	0.3100	1.059
90	-0.0287	-1.1707	-0.053	0.2940	1.002
100	-0.0538	-1.1742	-0.0538	0.2930	1.000

TABLE 8 (Cont'd)

CALCULATED FUGACITY AND ACTIVITY COEFFICIENTS FOR n-BUTANE

n-BUTANE - NITROGEN MIXTURES AT 340°F

Mol% $N\text{-}C_4$	ln f/p	Approx. $\ln\phi_{C4-}$	$\Delta\ln\phi_{C4-}$	ϕ_{C4-}	γ_{C4-}
600 ATM					
0	-0.0008	0.02429	0.0600	1.0880	3.605
10	0.0081	-0.2816	0.0820	0.8190	2.485
30	0.0357	-0.6974	0.1720	0.5920	1.796
50	0.0556	-0.9189	0.0270	0.4100	1.243
70	0.0256	-1.0192	-0.0475	0.3440	1.042
90	-0.0270	-1.0534	-0.0535	0.3310	1.002
100	-0.0530	1.0565	-0.0538	0.3295	1.000

TABLE 9

CALCULATED FUGACITY AND ACTIVITY COEFFICIENTS FOR NITROGEN

n-BUTANE - NITROGEN MIXTURES AT 340°F

Mol% $n\text{-}C_4$	Approx. $\ln\phi_{N_2}$	$\Delta\ln\phi_{N_2}$	ϕ_{N_2}	γ_{N_2}	$\ln \gamma_{C_4}$ / γ_{N_2}
100 ATM					
0	0.04129	0.0016	1.0438	1.000	0.900
10	0.04718	0.0030	1.0515	1.009	0.722
30	0.0970	-0.0045	1.0989	1.050	0.511
50	0.2273	0.0145	1.2740	1.220	0.161
70	0.5150	0.0360	1.6800	1.610	-1.006
90	1.0084	0.0820	2.9800	2.855	-1.006
100	1.2232	0.287	4.5200	4.320	-1.462
200 ATM					
0	0.08686	0.0004	1.0911	1.000	1.170
10	0.09998	0.0020	1.1073	1.014	0.932
30	0.1853	-0.0130	1.1880	1.088	0.564
50	0.3718	0.0280	1.4920	1.368	0.305
70	0.6406	0.0780	2.0520	1.880	-0.530
90	0.9064	0.167	2.9250	2.680	-0.972
100	1.0209	0.290	3.7000	3.390	-1.220
300 ATM					
0	0.1442	0.0001	1.155	1.000	1.223
10	0.1570	0.0005	1.171	1.013	0.948
30	0.2560	-0.0120	1.276	1.104	0.504
50	0.4368	0.0440	1.618	1.400	-0.074
70	0.6504	0.0117	2.155	1.866	-0.549

TABLE 9 (Cont'd)

CALCULATED FUGACITY AND ACTIVITY COEFFICIENTS FOR NITROGEN

n-BUTANE - NITROGEN MIXTURES AT 340°F

Mol% n-C_4	Approx. $\ln\phi_{N2}$	$\Delta\ln\phi_{N2}$	ϕ_{N2}	γ_{N2}	$\ln \frac{\gamma_{C_4}}{\gamma_{N_2}}$
300 ATM					
90	0.8481	0.178	2.790	2.420	-0.879
100	0.9349	0.241	3.240	2.800	-1.030
400 ATM					
0	0.2030	-0.0001	1.225	1.000	1.223
10	0.2173	-0.0001	1.242	1.014	0.932
30	0.3199	-0.0150	1.356	1.107	0.476
50	0.4862	0.0580	1.720	1.402	-0.101
70	0.6670	0.117	2.190	1.708	-0.467
90	0.8313	0.177	2.740	2.240	-0.799
100	0.9041	0.208	3.050	2.490	-0.912
500 ATM					
0	0.2589	-0.0005	1.295	1.000	1.214
10	0.2741	-0.0015	1.316	1.016	0.912
30	0.3764	-0.0145	1.457	1.124	0.412
50	0.5308	0.0620	1.810	1.398	-0.111
70	0.6923	0.105	2.220	1.639	-0.437
90	0.8379	0.199	2.820	2.180	-0.777
100	0.9027	0.199	3.010	2.325	-0.845

TABLE 9 (Cont'd)

CALCULATED FUGACITY AND ACTIVITY COEFFICIENTS FOR NITROGEN

n-BUTANE - NITROGEN MIXTURES AT 340°F

Mol% $n\text{-}C_4$	Approx. $\ln\phi_{N2}$	$\Delta\ln\phi_{N2}$	ϕ_{N2}	γ_{N2}	$\ln \frac{\gamma_{C_4}}{\gamma_{N_2}}$
600 ATM					
0	0.3224	-0.0008	1.379	1.000	1.282
10	0.3381	-0.0020	1.400	1.046	0.866
30	0.4387	-0.0300	1.505	1.091	0.496
50	0.5826	0.0700	1.920	1.392	-0.112
70	0.7290	0.180	2.480	1.799	-0.545
90	0.8603	0.194	2.870	2.080	-0.701
100	0.9190	0.198	3.060	2.220	-0.799

TABLE 10

CALCULATED FUGACITY AND ACTIVITY COEFFICIENTS FOR n-BUTANE

n-BUTANE - NITROGEN MIXTURES AT 370°F

Mol% $n\text{-}C_4$	ln f/p	Approx. $\ln\phi C_4$	$\Delta\ln\phi C_4$	ϕC_4	γC_4
100 ATM					
0	0.0019	-0.09996	0.0030	0.9076	2.075
10	0.0021	-0.19944	0.0040	0.8228	1.880
30	0.0043	-0.37787	0.0275	0.7040	1.610
50	0.0152	-0.53783	0.0230	0.5980	1.368
70	0.0084	-0.68489	-0.0105	0.4990	1.140
90	-0.0137	-0.79833	-0.0275	0.4420	1.010
100	-0.0252	-0.80167	-0.0252	0.4380	1.000
200 ATM					
0	0.0008	-0.13746	0.0050	0.8760	2.725
10	0.0016	-0.30867	0.0130	0.7445	2.310
30	0.0071	-0.60621	0.0450	0.5710	1.787
50	0.0224	-0.84757	0.0315	0.4425	1.377
70	0.0047	-1.0089	-0.0550	0.3450	1.074
90	-0.0390	-1.0746	-0.0560	0.3230	1.005
100	-0.0538	-1.0808	-0.0538	0.3220	1.000
300 ATM					
0	0.0005	-0.12510	0.0035	0.8860	2.935
10	0.0011	-0.34329	0.0180	0.7230	2.395
30	0.0092	-0.69681	0.0575	0.5280	1.750
50	0.0277	-0.94154	0.0280	0.4020	1.330

TABLE 10 (Con't)

CALCULATED FUGACITY AND ACTIVITY COEFFICIENTS FOR n-BUTANE

n-BUTANE - NITROGEN MIXTURES AT 370°F

Mol% $n\text{-}C_4$	ln f/p	Approx $\ln\phi_{C_4}$	$\Delta\ln\phi_{C_4}$	ϕ_{C_4}	γ_{C_4}
300 ATM					
70	0.0009	-1.0755	-0.0960	0.3100	1.028
90	-0.0516	-1.1244	-0.0700	0.3030	1.002
100	-0.0672	-1.290	-0.0672	0.3020	1.000
400 ATM					
0	0.0001	-0.07438	0.0030	0.9312	2.975
10	0.0003	-0.32206	0.0155	0.7360	2.350
30	0.0112	-0.69628	0.1230	0.5640	1.800
50	0.0334	-0.92627	0.0225	0.4055	1.298
70	0.0005	-1.0415	-0.0121	0.3130	1.000
90	-0.0598	-1.0821	-0.0790	0.3130	1.000
100	-0.0749	-1.0859	-0.0749	0.3130	1.000
500 ATM					
0	-0.0005	-0.00361	0.0007	1.0034	2.970
10	0.0001	-0.26804	0.0220	0.7820	2.310
30	0.0146	-0.64672	0.1180	0.5900	1.746
50	0.0399	-0.86334	0.0190	0.4310	1.275
70	0.0026	-0.96630	-0.1220	0.3380	1.000
90	-0.0635	-1.0022	-0.0840	0.3390	1.001
100	-0.0803	-1.0055	-0.803	0.3380	1.000

TABLE 10 (Con't)

CALCULATED FUGACITY AND ACTIVITY COEFFICIENTS FOR n-BUTANE

n-BUTANE - NITROGEN MIXTURES AT 370°F

Mol% $n\text{-}C_4$	ln f/p	Approx ln ϕ_{C_4}	$\Delta \ln \phi_{C_4}$	ϕ_{C_4}	γ_{C_4}
600 ATM					
0	-0.0010	0.09461	0.0050	1.1050	2.850
10	0.0003	-0.18138	0.0310	0.8605	2.220
30	0.0185	-0.55804	0.1580	0.6710	1.730
50	0.0469	-0.76137	0.0470	0.4900	1.263
70	0.0054	-0.85469	-0.1250	0.3860	0.995
90	-0.0652	-0.88722	-0.0860	0.3880	1.000
100	-0.0832	-0.89023	-0.0832	0.3880	1.000

TABLE 11

CALCULATED FUGACITY AND ACTIVITY COEFFICIENTS FOR NITROGEN

n-BUTANE - NITROGEN MIXTURES AT 370°F

Mol% $n\text{-}C_4$	Approx. $\ln\phi_{N2}$	$\Delta\ln\phi_{N2}$	ϕ_{N2}	γ_{N2}	$\ln \frac{\gamma_{C4}}{\gamma_{N2}}$
100 ATM					
0	0.04246	0.0019	1.0452	1.000	0.730
10	0.04770	0.0020	1.0510	1.007	0.625
30	0.09284	-0.0055	1.0914	1.045	0.4325
50	0.20130	0.0075	1.2320	1.180	0.1475
70	0.42820	0.05350	1.6190	1.549	-0.307
90	0.85287	0.1115	2.6200	2.510	-0.913
100	1.0774	0.0660	3.1400	3.000	-1.100
200 ATM					
0	0.09151	0.0008	1.0967	1.000	1.002
10	0.10051	0.000	1.1058	1.009	0.828
30	0.17539	-0.0085	1.1815	1.080	0.503
50	0.33707	0.0135	1.4200	1.297	0.058
70	0.57732	0.1330	2.0360	1.856	-0.547
90	0.83092	0.1160	2.5800	2.355	-0.852
100	0.94404	0.0770	2.7800	2.540	-0.932
300 ATM					
0	0.14577	0.0005	1.1576	1.000	1.076
10	0.15717	-0.0005	1.1646	1.008	0.865
30	0.24506	-0.0115	1.2630	1.092	0.470
50	0.40670	0.0270	1.5430	1.335	-0.004

TABLE 11 (Cont'd)

CALCULATED FUGACITY AND ACTIVITY COEFFICIENTS FOR NITROGEN

n-BUTANE - NITROGEN MIXTURES AT 370°F

Mol% n-C_4	Approx. $\ln\phi_{N2}$	$\Delta\ln\phi_{N2}$	ϕ_{N2}	γ_{N2}	$\ln \gamma_{C4}$
300 ATM					
70	0.60369	0.2580	2.3700	2.050	-0.692
90	0.79227	0.1215	2.4950	2.155	-0.765
100	0.87657	0.0780	2.6000	2.250	-0.810
400 ATM					
0	0.20412	0.0001	1.2360	1.000	1.090
10	0.21697	-0.0015	1.2400	1.003	0.850
30	0.30894	-0.0320	1.3190	1.068	0.524
50	0.45990	0.0445	1.6550	1.340	-0.033
70	0.62807	0.299	2.5030	2.030	-0.710
90	0.78428	0.118	2.4650	1.998	-0.695
100	0.85434	0.0500	2.4700	2.000	-0.695
500 ATM					
0	0.25932	-0.0005	1.2960	1.000	1.090
10	0.27297	-0.0020	1.3115	1.015	0.824
30	0.36527	-0.0260	1.4040	1.085	0.475
50	0.50655	0.0600	1.6700	1.290	-0.010
70	0.65713	0.292	2.5800	1.990	-0.689
90	0.79520	0.124	2.5050	1.935	-0.659
100	0.85722	0.0485	2.4750	1.910	-0.647

TABLE 11 (Cont'd)

CALCULATED FUGACITY AND ACTIVITY COEFFICIENTS FOR NITROGEN

n-BUTANE - NITROGEN MIXTURES AT 370°F

Mol% n-C_4	Approx. $\ln\phi_{N2}$	$\Delta\ln\phi_{N2}$	ϕ_{N2}	γ_{N2}	$\ln \frac{\gamma_{C4}}{\gamma_{N2}}$
600 ATM					
0	0.32190	-0.0010	1.3780	1.000	1.048
10	0.33605	-0.0030	1.3950	1.013	0.784
30	0.42723	-0.0370	1.4770	1.071	0.480
50	0.55942	0.0470	1.8330	1.332	-0.052
70	0.69614	0.309	2.7400	1.990	-0.694
90	0.82041	0.128	2.5800	1.875	-0.628
100	0.87627	0.0605	2.5500	1.852	-0.617
700 ATM					
0	0.38650	-0.0015	1.470	1.000	1.060
10	0.40094	-0.0045	1.486	1.010	0.801
30	0.49037	-0.0510	1.551	1.050	0.540
50	0.61496	0.0645	1.971	1.341	-0.047
70	0.74136	0.353	2.990	2.035	-0.733
90	0.85549	0.1515	2.740	1.865	-0.626
100	0.90681	0.0770	2.675	1.820	-0.599

TABLE 12

CALCULATED FUGACITY AND ACTIVITY COEFFICIENTS FOR n-BUTANE

n-BUTANE - NITROGEN MIXTURES AT 400°F

Mol% n-C_4	ln f/p	Approx. $\ln\phi_{C4}$	$\Delta\ln\phi_{C4}$	ϕ_{C4}	γ_{C4}
100 ATM					
0	0.0017	-0.0705	-0.0175	0.9158	1.861
10	0.0006	-0.1598	-0.0060	0.8472	1.722
30	0.0032	-0.3176	0.0340	0.7504	1.525
50	0.0056	-0.4542	0.0000	0.6350	1.291
70	0.0002	-0.5722	-0.090	0.5590	1.136
90	-0.0080	-0.6547	-0.0230	0.5080	1.033
100	-0.0424	-0.6663	-0.0424	0.4920	1.000
200 ATM					
0	0.0008	-0.0866	-0.0265	0.8930	2.440
10	-0.0007	-0.2404	-0.0060	0.7820	2.137
30	0.0035	-0.5036	0.0295	0.6230	1.702
50	0.0034	-0.7131	-0.0225	0.4800	1.311
70	-0.0133	-0.8549	-0.0490	0.4060	1.109
90	-0.0435	-0.9158	-0.0670	0.3475	1.023
100	-0.0833	-0.9218	-0.0833	0.3660	1.000
300 ATM					
0	0.0007	-0.05936	-0.0385	0.9070	2.629
10	-0.0022	-0.2561	-0.0125	0.7690	2.229
30	0.0033	-0.5719	0.0545	0.5960	1.728
50	-0.0001	-0.7902	-0.0415	0.4360	1.264

TABLE 12 (Cont'd)

CALCULATED FUGACITY AND ACTIVITY COEFFICIENTS FOR n-BUTANE

n-BUTANE - NITROGEN MIXTURES AT 400°F

Mol% $n\text{-}C_4$	ln f/p	Approx. $\ln\phi_{C4}$	$\Delta\ln\phi_{C4}$	ϕ_{C4}	γ_{C4}
300 ATM					
70	-0.0246	-0.9124	-0.0685	0.3750	1.087
90	-0.0598	-0.9584	-0.0880	0.3520	1.020
100	-0.1033	-0.9628	-0.1033	0.3450	1.000
400 ATM					
0	0.0006	0.00139	-0.0620	0.9412	2.644
10	-0.0037	-0.2230	-0.0225	0.7825	2.198
30	0.0033	-0.5605	0.0470	0.6120	1.719
50	-0.0023	-0.7693	-0.0560	0.4882	1.371
70	-0.0307	-0.8753	-0.0775	0.4265	1.198
90	-0.0688	-0.9135	-0.0975	0.3640	1.022
100	-0.1153	-0.7171	-0.1153	0.3560	1.000
500 ATM					
0	0.0003	0.07817	-0.0820	0.9962	2.594
10	-0.0048	-0.1624	-0.0195	0.8340	2.172
30	0.0046	-0.5061	0.0765	0.6510	1.695
50	-0.0013	-0.7040	-0.0865	0.4540	1.182
70	-0.0332	-0.7995	-0.0800	0.4155	1.082
90	-0.0733	-0.8331	-0.1050	0.3920	1.021
100	-0.1225	-0.8363	-0.1225	0.3840	1.000

TABLE 12 (Cont'd)

CALCULATED FUGACITY AND ACTIVITY COEFFICIENTS FOR n-BUTANE

n-BUTANE - NITROGEN MIXTURES AT 400°F

Mol% $N\text{-}C_4$	ln f/p	Approx. $\ln\phi_{C4}$	$\Delta\ln\phi_{C4}$	ϕ_{C4}	γ_{C4}
600 ATM					
0	-0.001	0.1806	-0.0800	1.1059	2.566
10	-0.0052	-0.07146	-0.0220	0.9109	2.113
30	0.0065	-0.4151	0.1340	0.7553	1.752
50	0.0005	-0.6019	-0.0870	0.5020	1.165
70	-0.0344	-0.6887	-0.0865	0.4620	1.072
90	-0.0753	-0.7189	-0.1050	0.4390	1.019
100	-0.1276	-0.7217	-0.1276	0.4310	1.000
700 ATM					
0	-0.0003	0.2984	-0.0790	1.2455	2.553
10	-0.0055	0.0392	-0.0155	1.0240	2.100
30	0.0082	-0.0311	0.133	0.8452	1.732
50	0.0025	-0.4780	-0.0900	0.6150	1.260
70	-0.0344	-0.5584	-0.0865	0.5250	1.078
90	-0.0753	-0.5860	-0.1050	0.5020	1.030
100	-0.1310	-0.5886	-0.131	0.4880	1.000

TABLE 13

CALCULATED FUGACITY AND ACTIVITY COEFFICIENTS FOR NITROGEN

n-BUTANE - NITROGEN MIXTURES AT 400°F

Mol% n-C_4	Approx. $\ln\phi_{N2}$	$\Delta\ln\phi_{N2}$	ϕ_{N2}	γ_{N2}	$\ln \frac{\gamma_{C_4}}{\gamma_{N_2}}$
100 ATM					
0	0.04387	0.0017	1.0466	1.000	0.621
10	0.04857	0.0010	1.0507	1.004	0.540
30	0.8838	-0.0100	1.0815	1.035	0.385
50	0.1807	0.0110	1.2110	1.160	0.107
70	0.3618	0.0220	1.4680	1.403	-0.212
90	0.7024	0.1235	2.2850	2.185	-0.750
100	0.9180	0.5077	4.1600	3.980	-1.382
200 ATM					
0	0.09338	0.0008	1.0988	1.000	0.982
10	0.1015	0.0000	1.1070	1.007	0.752
30	0.1675	-0.0080	1.1730	1.068	0.465
50	0.3078	0.0315	1.4040	1.278	0.256
70	0.5195	0.0710	1.8050	1.643	-0.394
90	0.7564	0.1625	2.5030	2.278	-0.801
100	0.8664	0.5132	3.9700	3.613	-1.283
300 ATM					
0	0.1474	0.0007	1.1598	1.000	0.966
10	0.1576	-0.0010	1.1695	1.008	0.793
30	0.2361	-0.0185	1.2430	1.072	0.477
50	0.3804	0.0410	1.5240	1.314	-0.0389

TABLE 13 (Cont'd)

CALCULATED FUGACITY AND ACTIVITY COEFFICIENTS FOR NITROGEN

n-BUTANE - NITROGEN MIXTURES AT 400°F

Mol% n-C_4	Approx. $\ln\phi_{N_2}$	$\Delta\ln\phi_{N_2}$	ϕ_{N_2}	γ_{N_2}	$\ln \frac{\gamma_{C_4}}{\gamma_{N_2}}$
300 ATM					
70	0.5604	0.0785	1.8950	1.634	-0.408
90	0.7382	0.1910	2.5170	2.165	-0.755
100	0.8191	0.4882	3.6950	3.186	-1.160
400 ATM					
0	0.2049	0.0006	1.2280	1.000	0.974
10	0.2165	-0.0020	1.2398	1.010	0.776
30	0.2994	-0.0140	1.3162	1.072	0.471
50	0.4363	0.0510	1.6280	1.326	0.0334
70	0.5918	0.0800	1.9580	1.594	-0.286
90	0.7389	0.1850	2.5200	2.052	-0.697
100	0.8055	0.6100	3.9700	3.233	-1.170
500 ATM					
0	0.2590	0.0003	1.296	1.000	0.990
10	0.2714	-0.0030	1.308	1.010	0.765
30	0.3552	-0.0265	1.390	1.073	0.457
50	0.4843	0.0830	1.765	1.362	-0.142
70	0.6240	0.0755	2.020	1.560	-0.367
90	0.7537	0.2100	2.620	2.020	-0.684
100	0.8124	0.7850	4.160	3.220	-1.170

TABLE 13 (Cont'd)

CALCULATED FUGACITY AND ACTIVITY COEFFICIENTS FOR NITROGEN

n-BUTANE - NITROGEN AT 400°F

Mol% $n\text{-}C_4$	Approx. $\ln\phi_{N2}$	$\Delta\ln\phi_{N2}$	ϕ_{N2}	γ_{N2}	$\ln\frac{\gamma_{C_4}}{\gamma_{N_2}}$
600 ATM					
0	0.3200	-0.0001	1.377	1.000	0.967
10	0.3330	-0.0035	1.39	1.018	0.732
30	0.4162	-0.0490	1.44	1.048	0.515
50	0.5376	0.0845	1.862	1.352	-0.149
70	0.6646	0.0870	2.120	1.540	-0.361
90	0.7810	0.196	2.630	1.910	-0.630
100	0.8336	0.715	4.700	3.420	-1.230
700 ATM					
0	0.3829	-0.0003	1.466	1.000	0.959
10	0.3961	-0.0045	1.480	1.010	0.732
30	0.4780	-0.0455	1.525	1.040	0.510
50	0.5929	0.0950	1.990	1.360	-0.076
70	0.7102	0.0870	2.220	1.515	-0.342
90	0.8169	0.196	2.730	1.862	-0.591
100	0.8650	1.009	6.500	4.440	-1.490

FIGURE 1

CURVE FOR GRAPHICAL INTEGRATION

n-BUTANE - NITROGEN SYSTEM

100% NITROGEN at 310°F

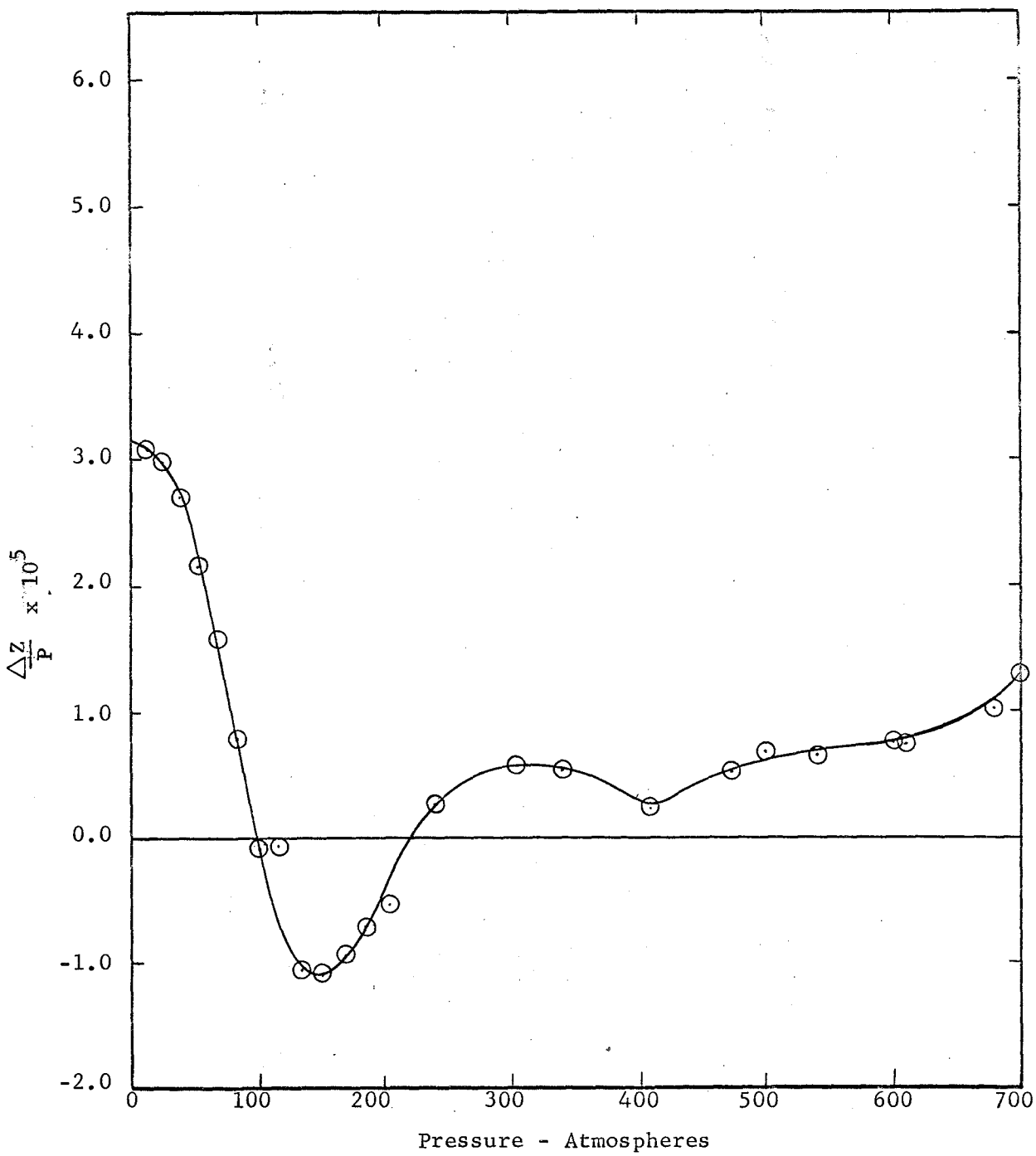


FIGURE 2

CURVE FOR GRAPHICAL INTEGRATION

n-BUTANE - NITROGEN SYSTEM

10% n-BUTANE at 310°F

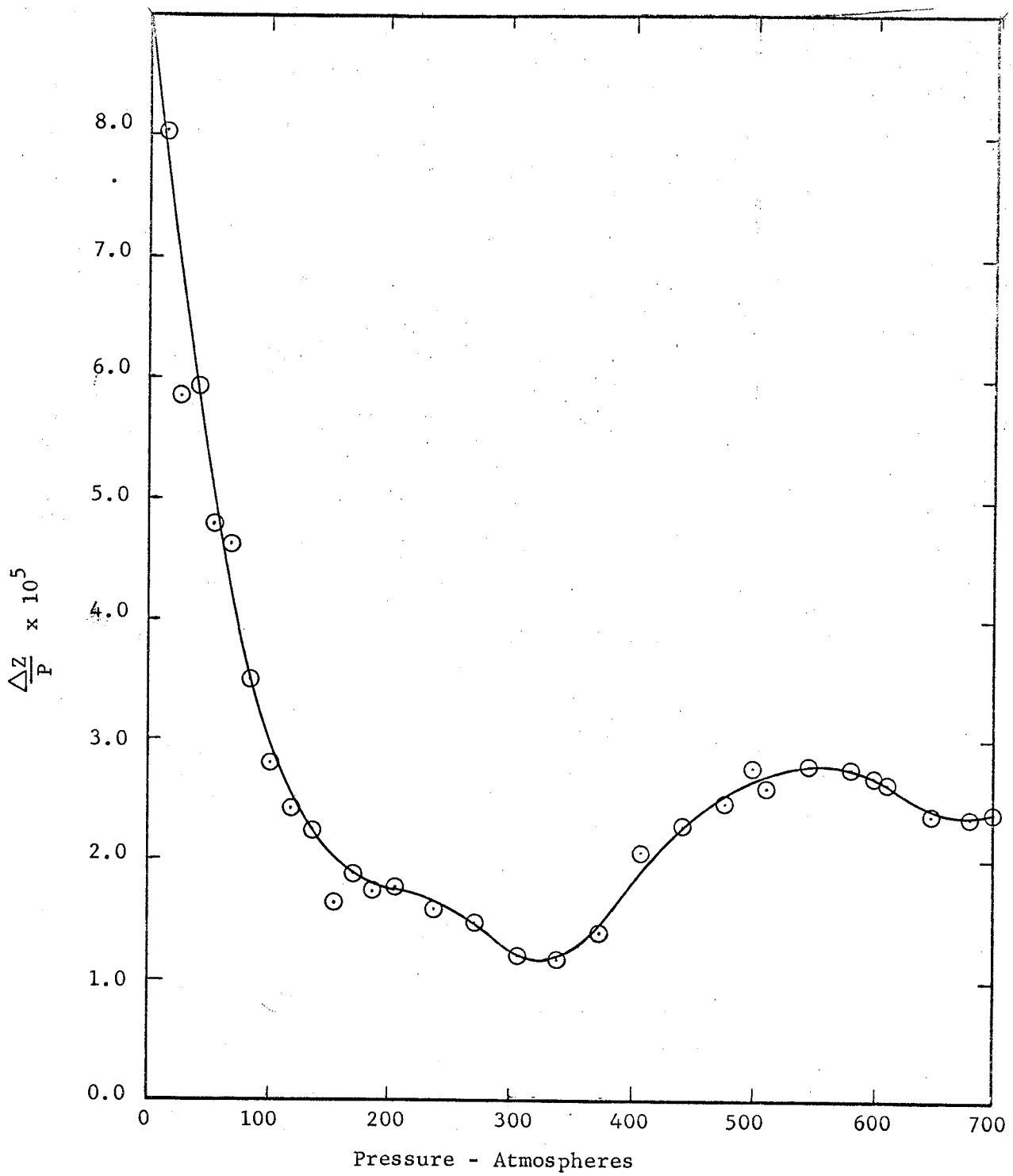


FIGURE 3

CURVE FOR GRAPHICAL INTEGRATION

n-BUTANE - NITROGEN SYSTEM

30% n-BUTANE at 310°F

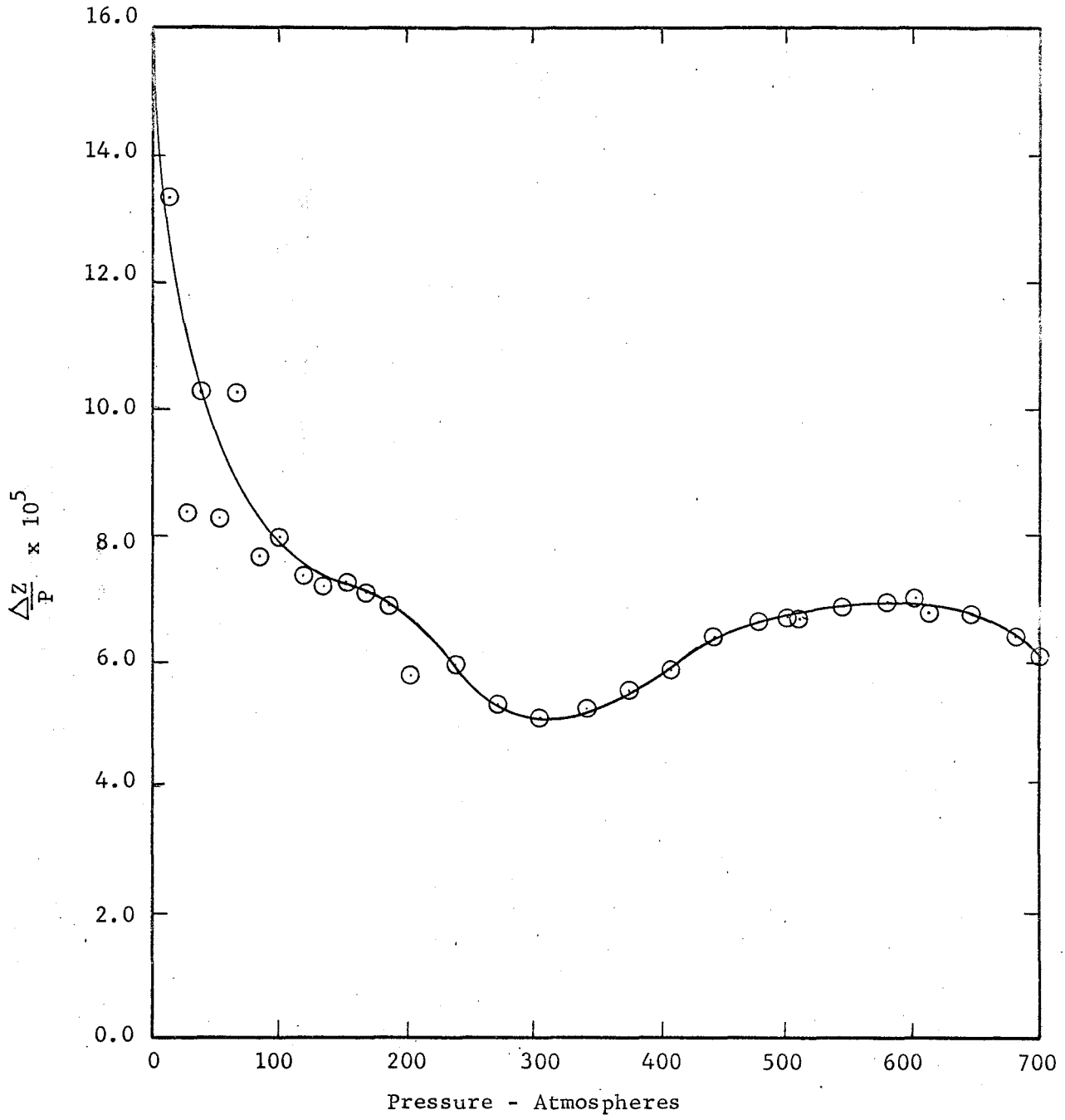


FIGURE 4

CURVE FOR GRAPHICAL INTEGRATION

n-BUTANE - NITROGEN SYSTEM

50% n BUTANE at 310°F

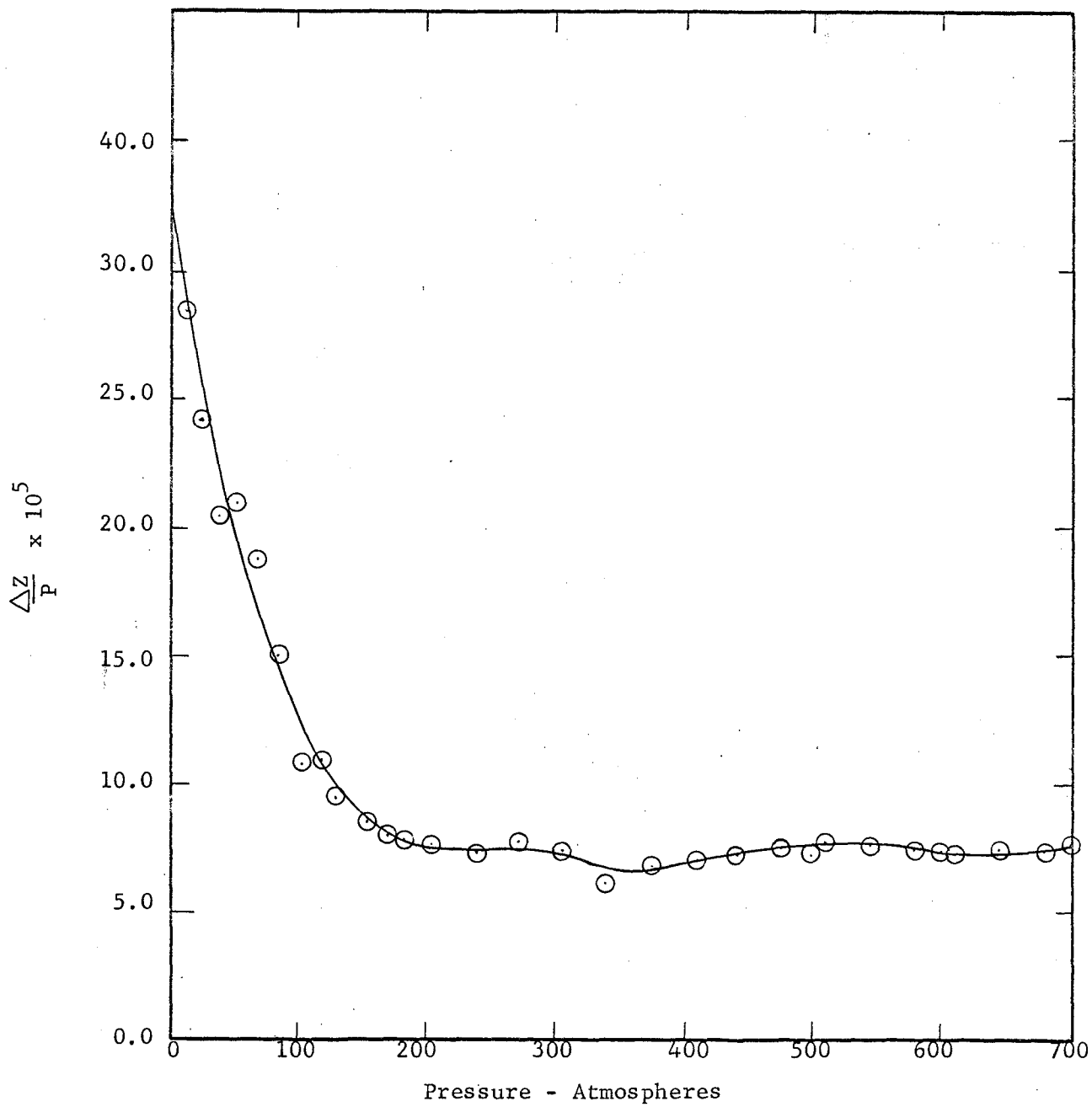


FIGURE 5

CURVE FOR GRAPHICAL INTEGRATION

n-BUTANE - NITROGEN SYSTEM

70% n-BUTANE at 310°F

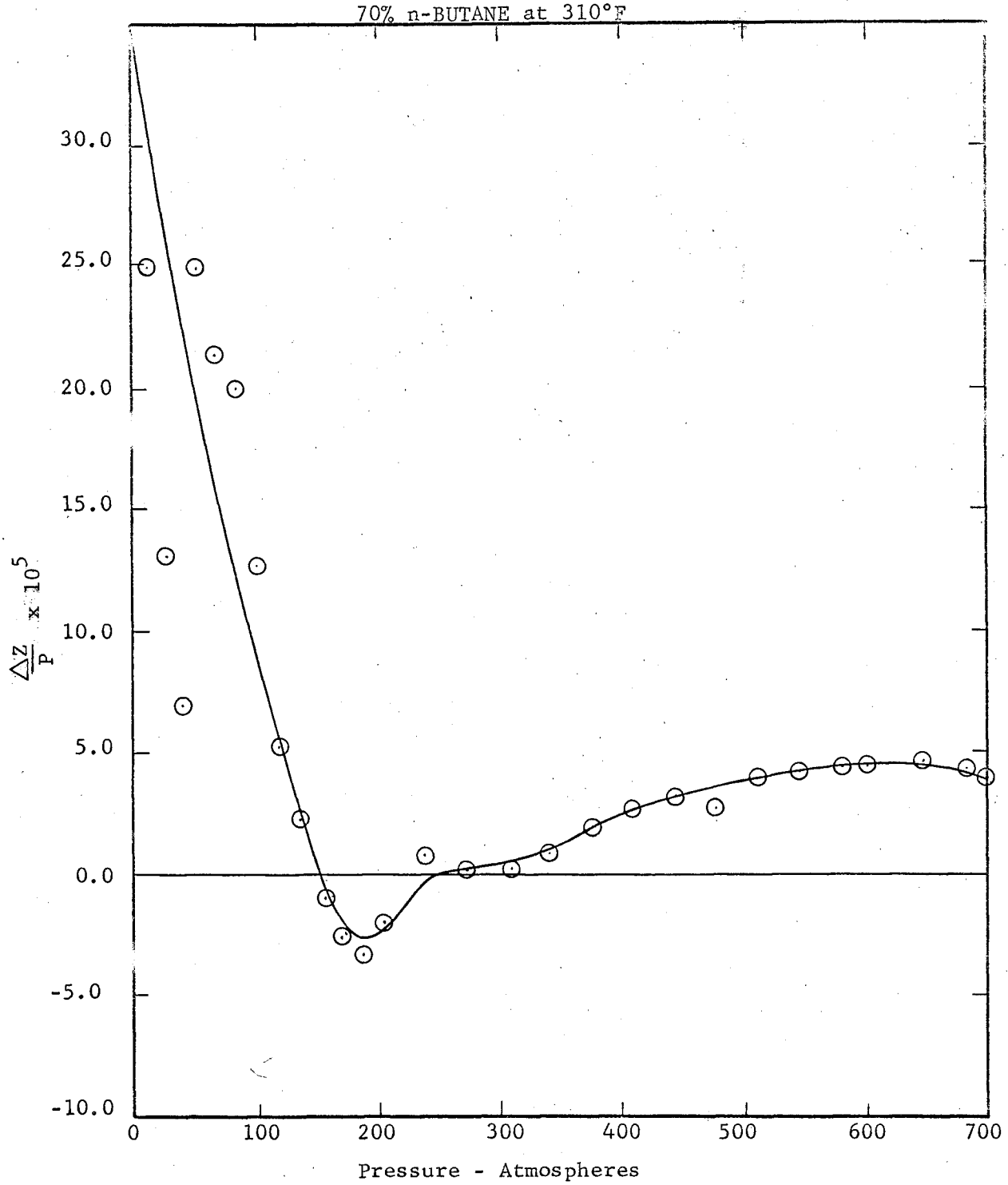


FIGURE 6

CURVE FOR GRAPHICAL INTEGRATION

n-BUTANE - NITROGEN SYSTEM

90% n-BUTANE at 310°F

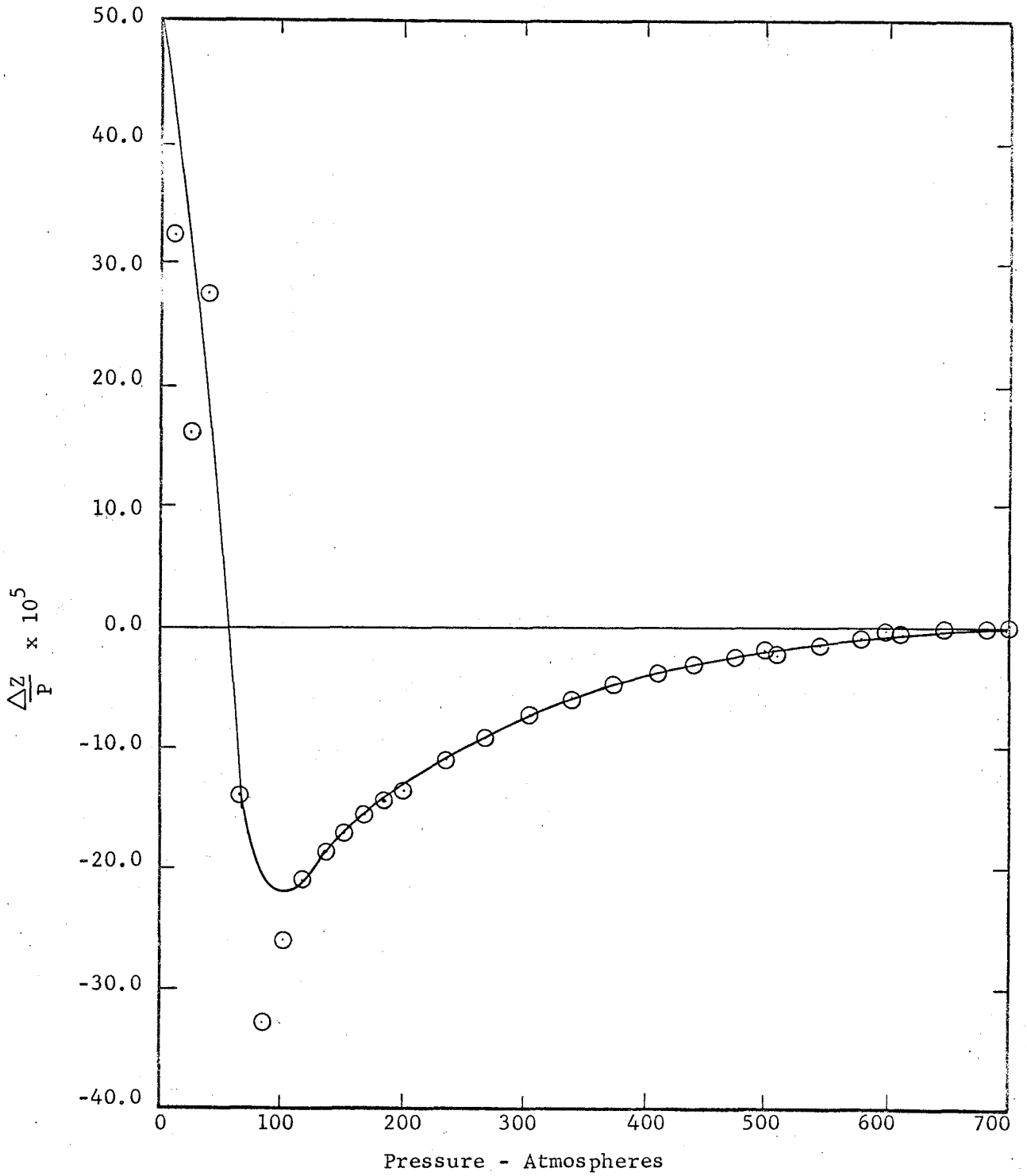


FIGURE 7

CURVE FOR GRAPHICAL INTEGRATION

n-BUTANE - NITROGEN SYSTEM

100% n-BUTANE at 310°F

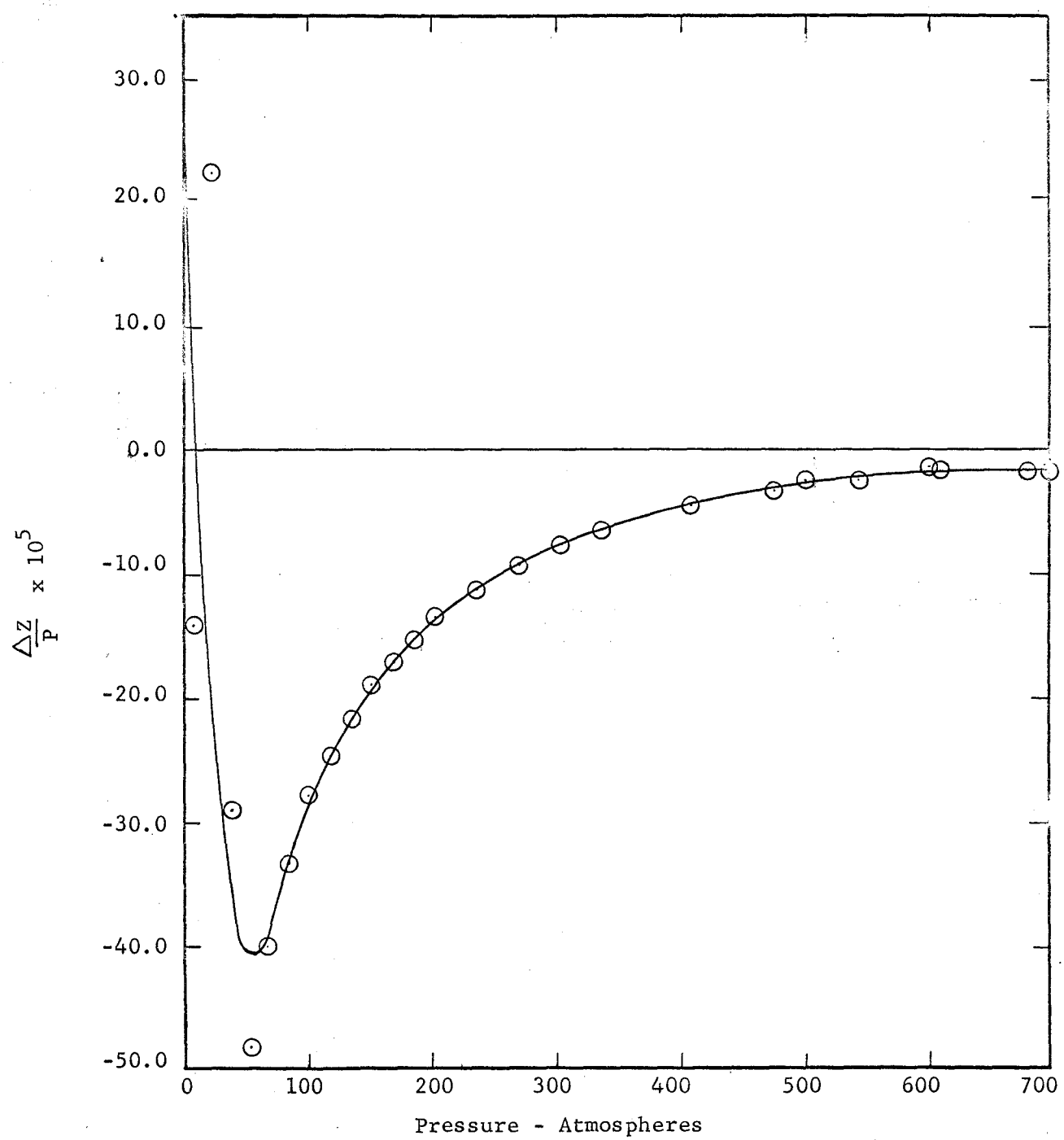


FIGURE 8

CURVES FOR GRAPHICAL DIFFERENTIATIONS

n-BUTANE - NITROGEN MIXTURES AT 310°F

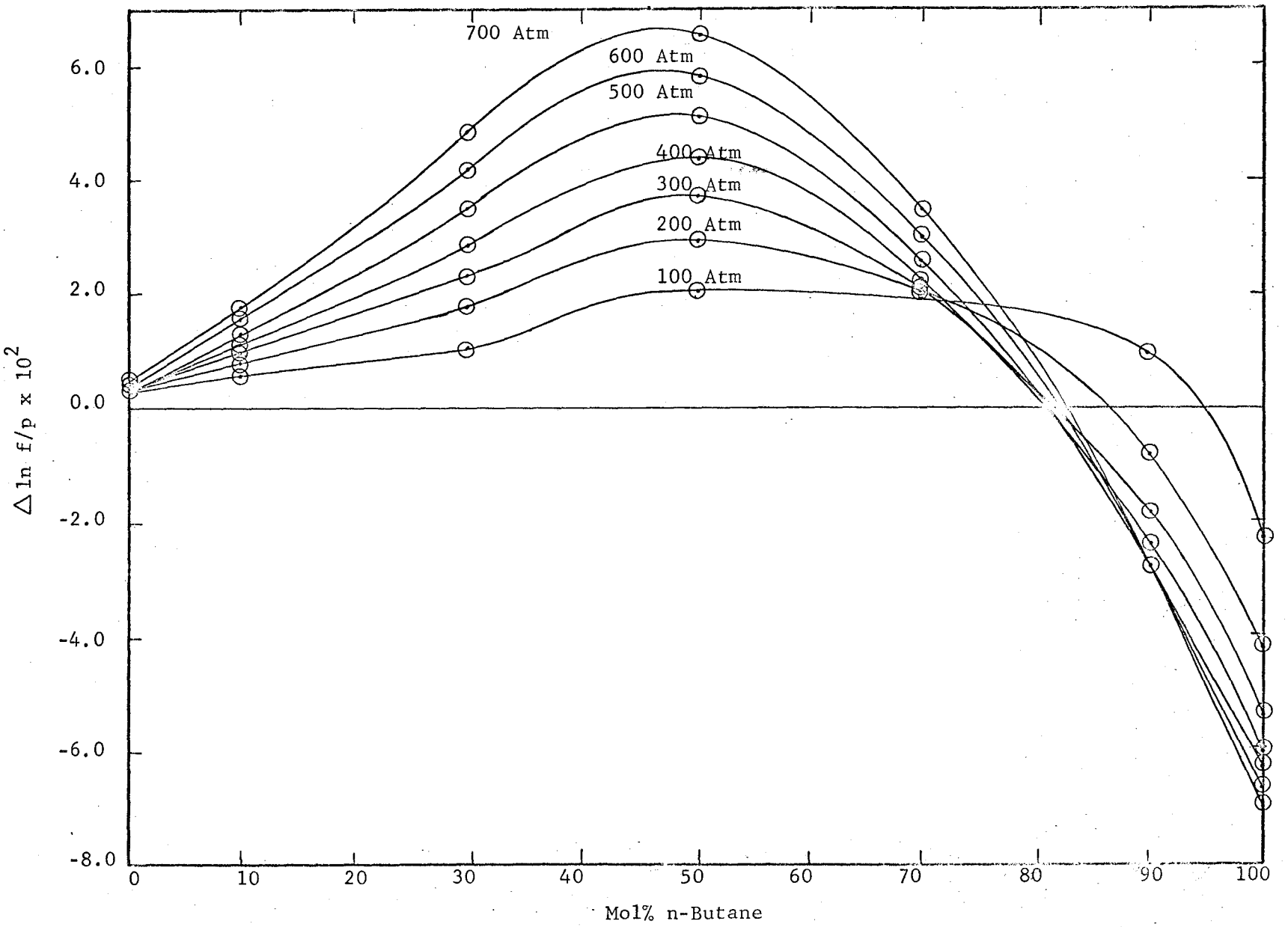


FIGURE 9

CURVES FOR GRAPHICAL DIFFERENTIATION

n-BUTANE - NITROGEN MIXTURES AT 340°F

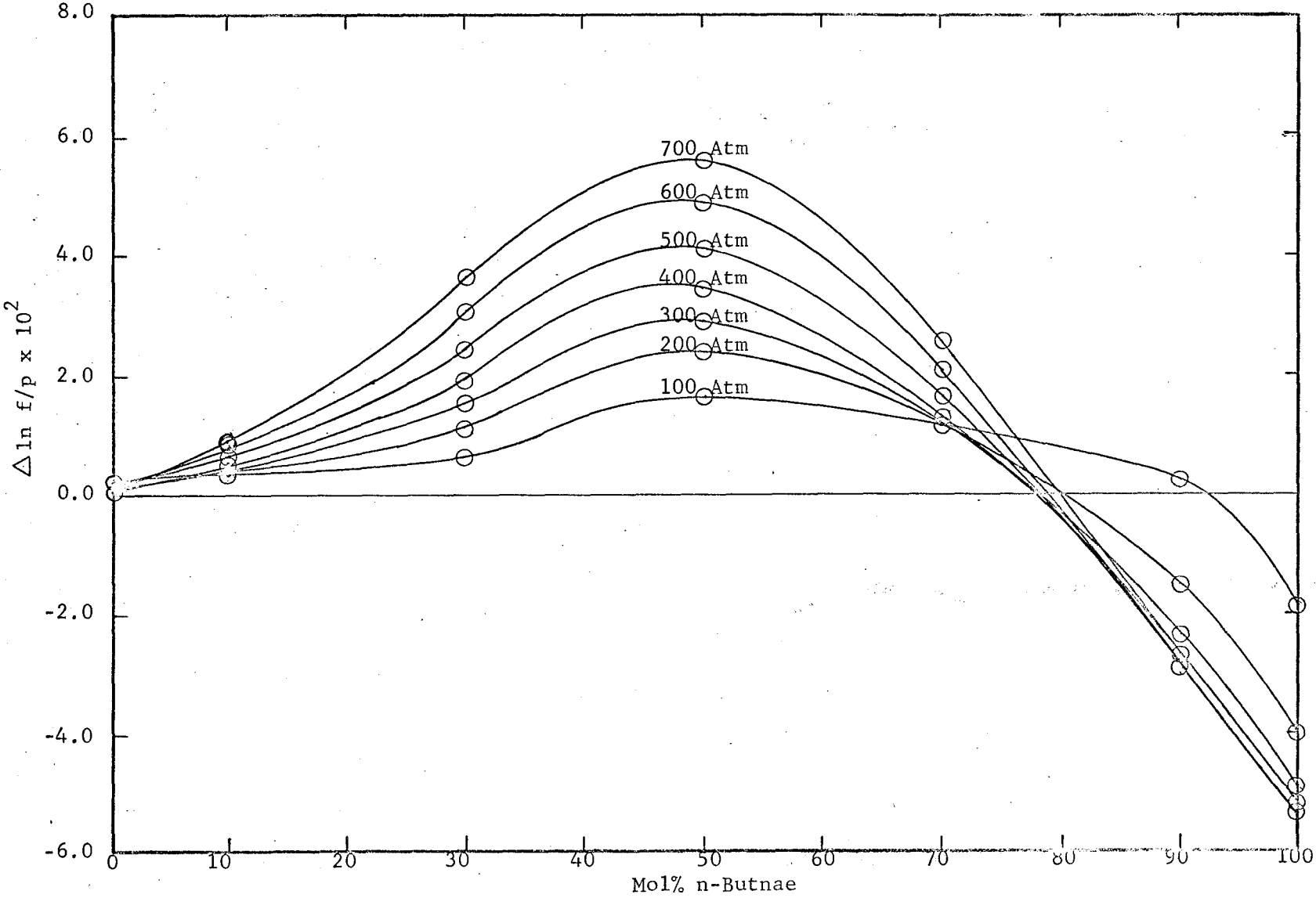


FIGURE 10

CURVES FOR GRAPHICAL DIFFERENTIATIONS

n-BUTANE - NITROGEN MIXTURES AT 370°F

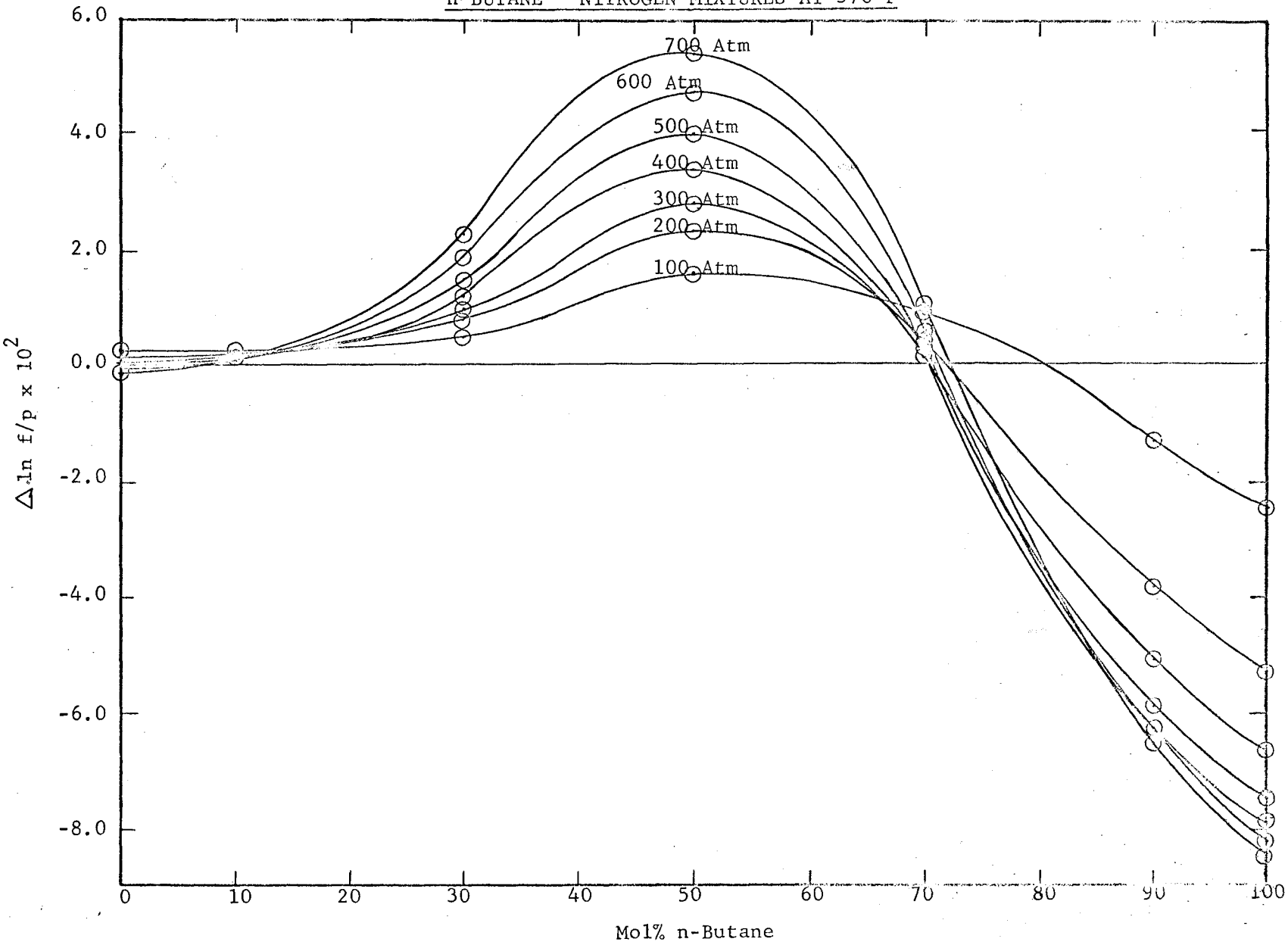


FIGURE 11

CURVES FOR GRAPHICAL DIFFERENTIATIONS

n-BUTANE - NITROGEN MIXTURES AT 400°F

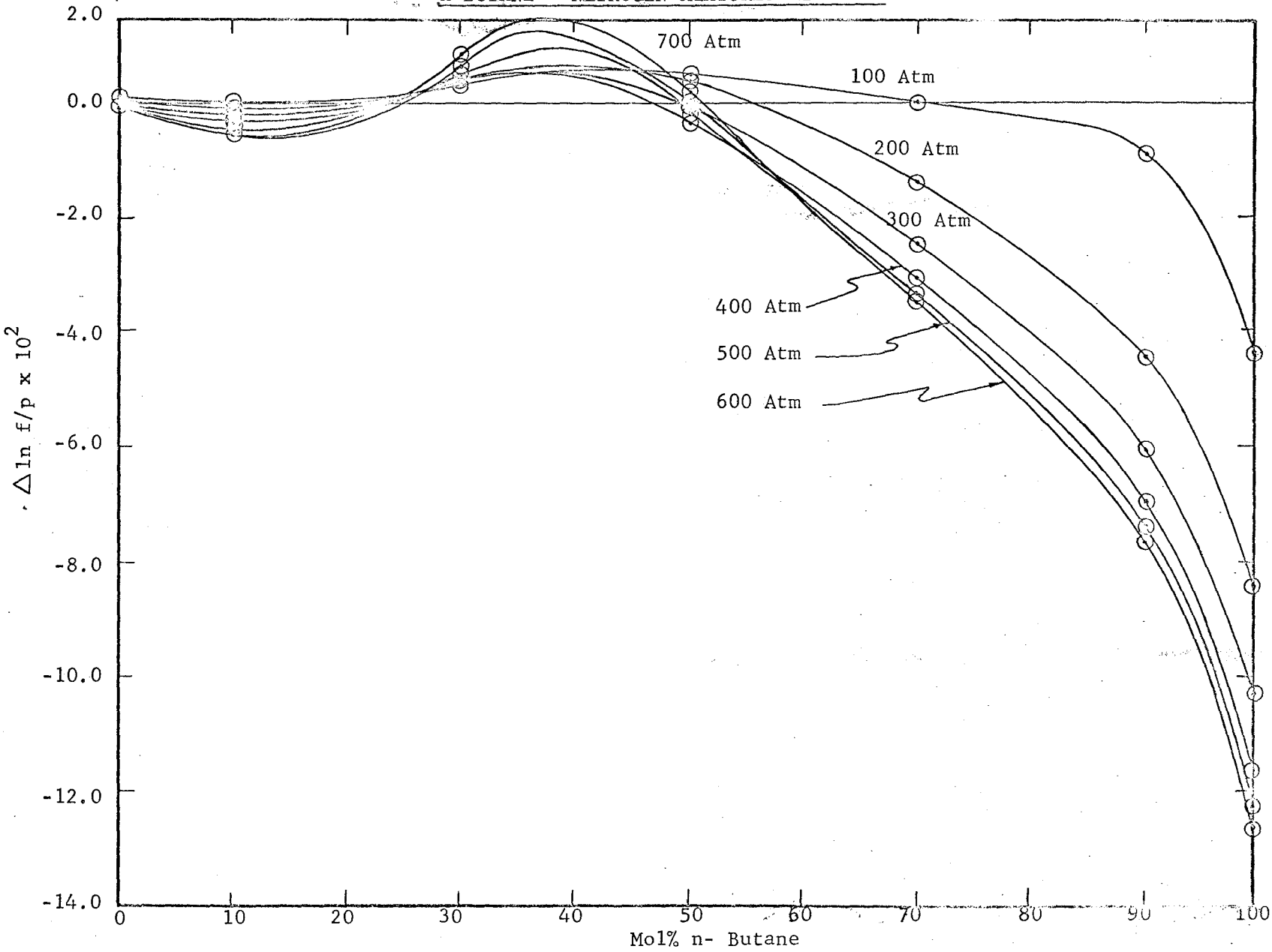


FIGURE 12

ACTIVITY COEFFICIENTS FOR n-BUTANE

n-BUTANE - NITROGEN MIXTURES AT 310°F

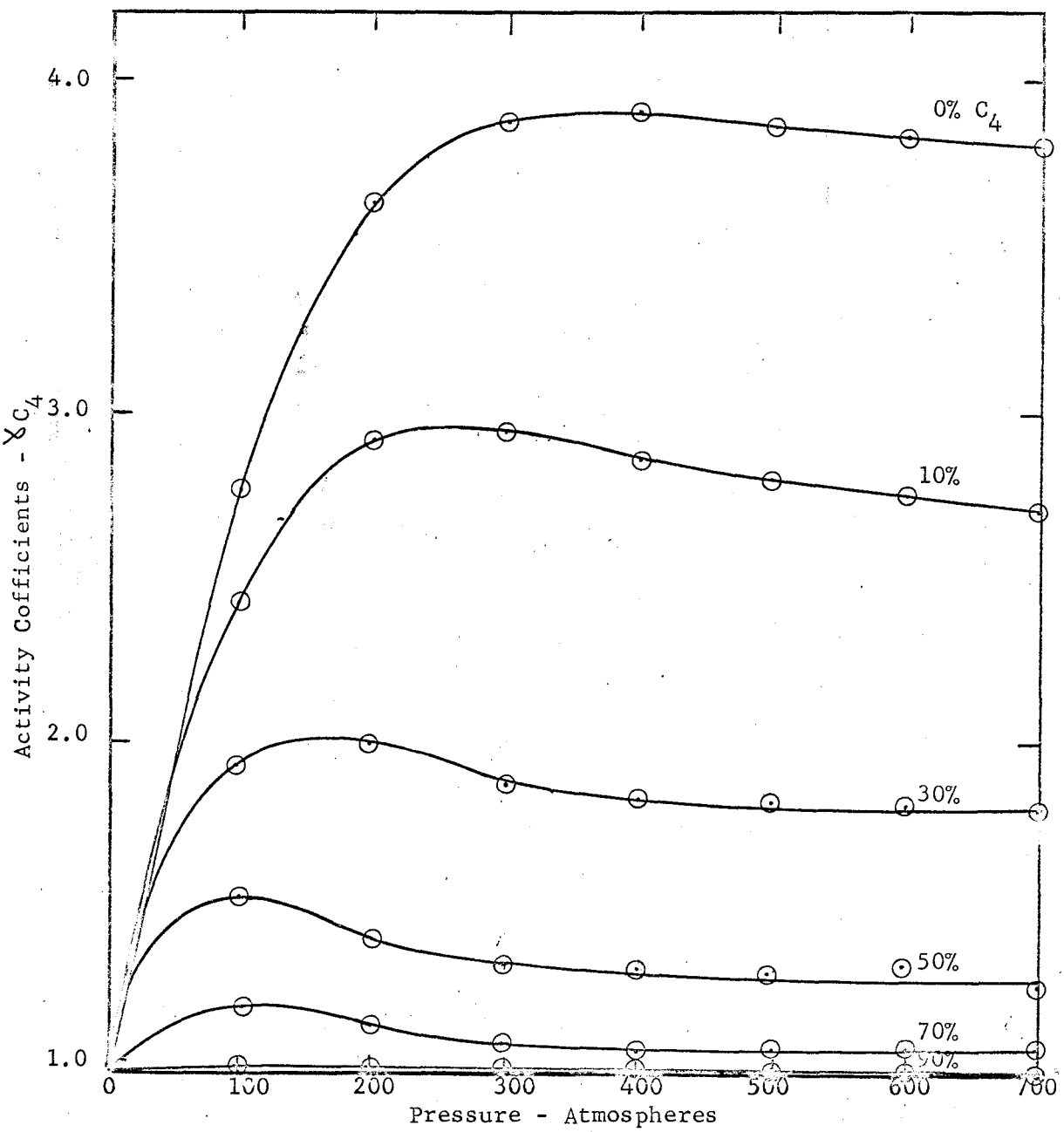


FIGURE 13

ACTIVITY COEFFICIENTS FOR NITROGEN

n-BUTANE - NITROGEN MIXTURES AT 310°F

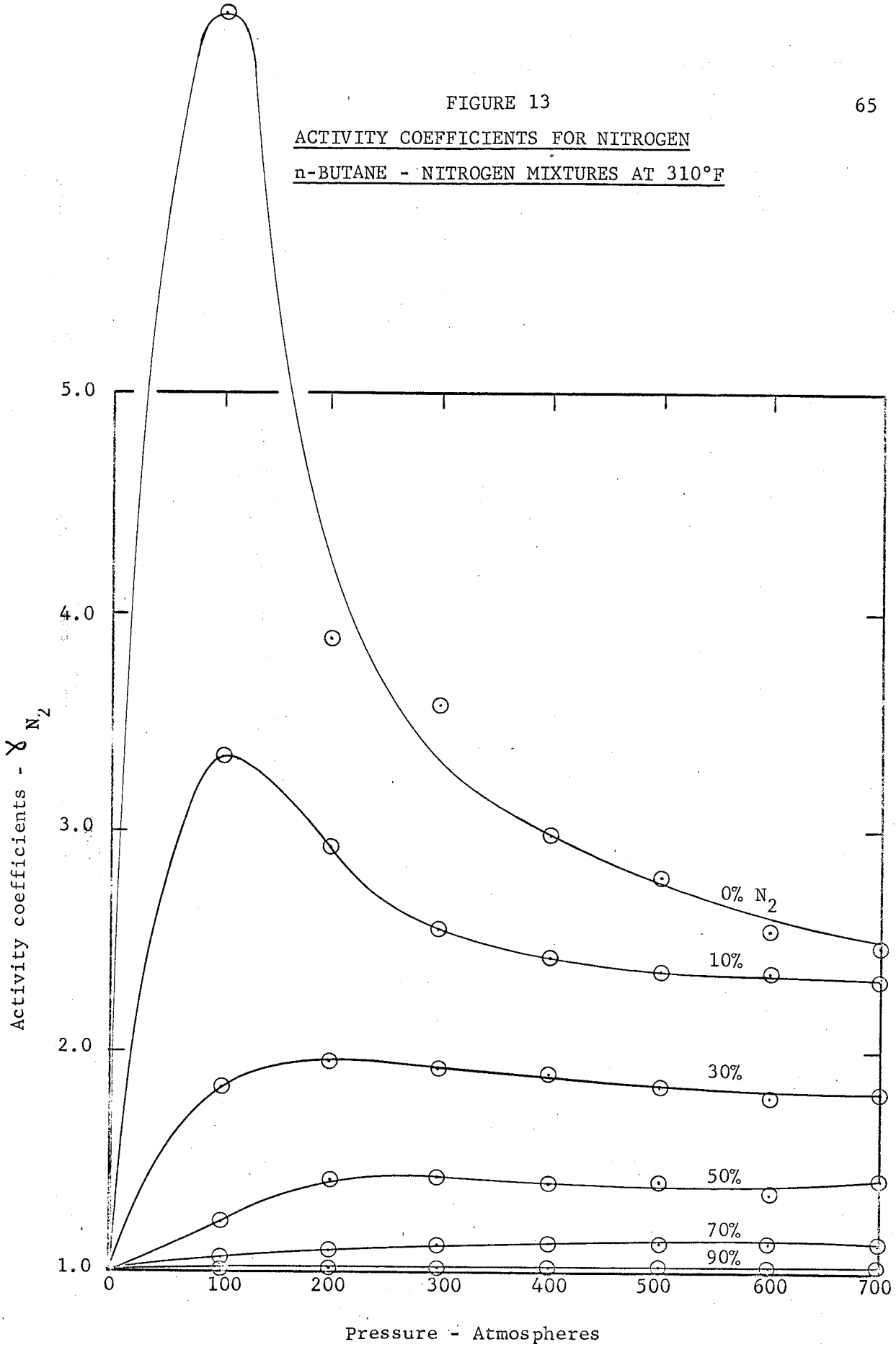


FIGURE 14

ACTIVITY COEFFICIENTS FOR n-BUTANE

n-BUTANE - NITROGEN MIXTURES AT 340°F

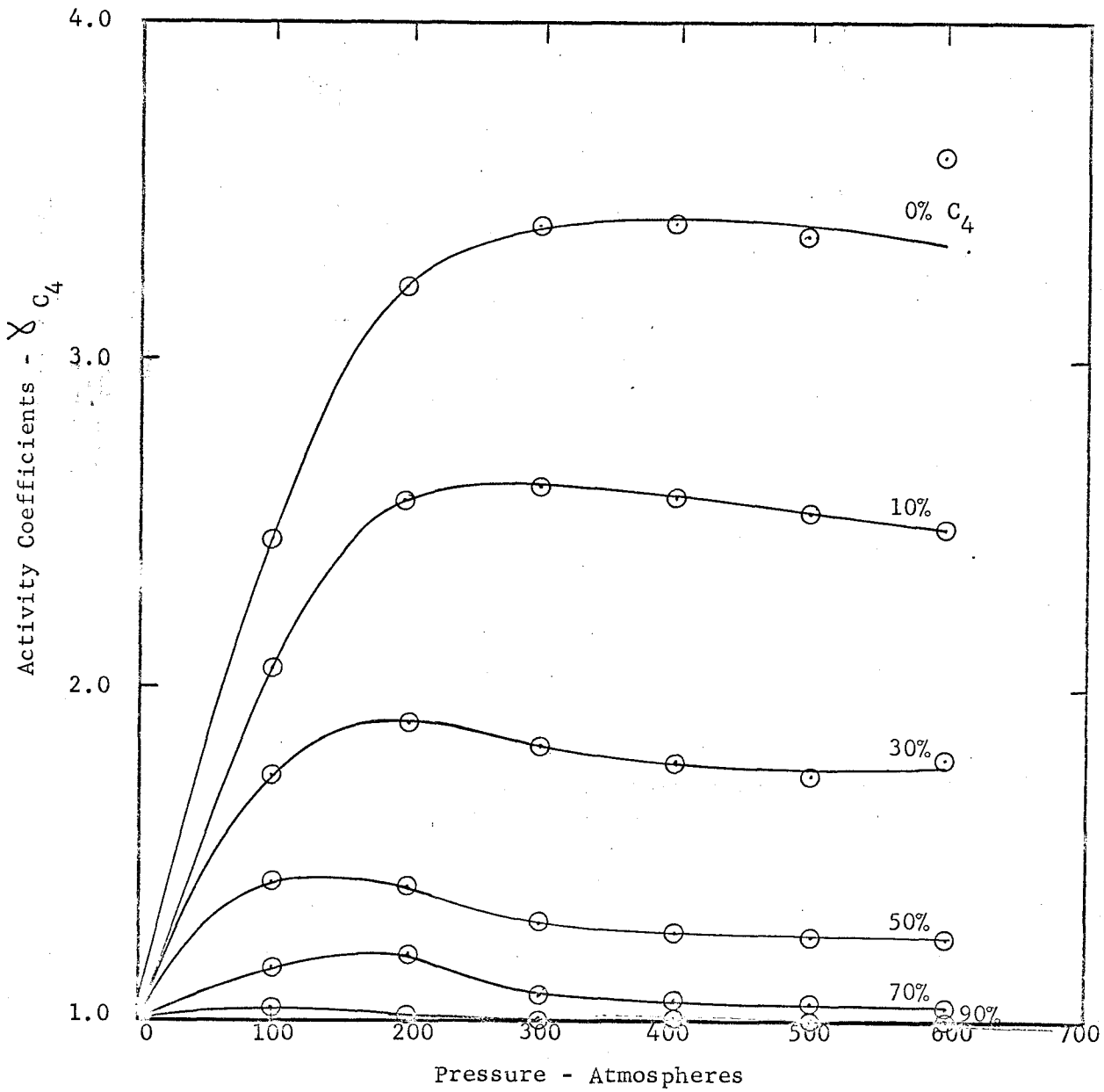


FIGURE 15

ACTIVITY COEFFICIENTS FOR NITROGEN

n-BUTANE - NITROGEN MIXTURES AT 340°F

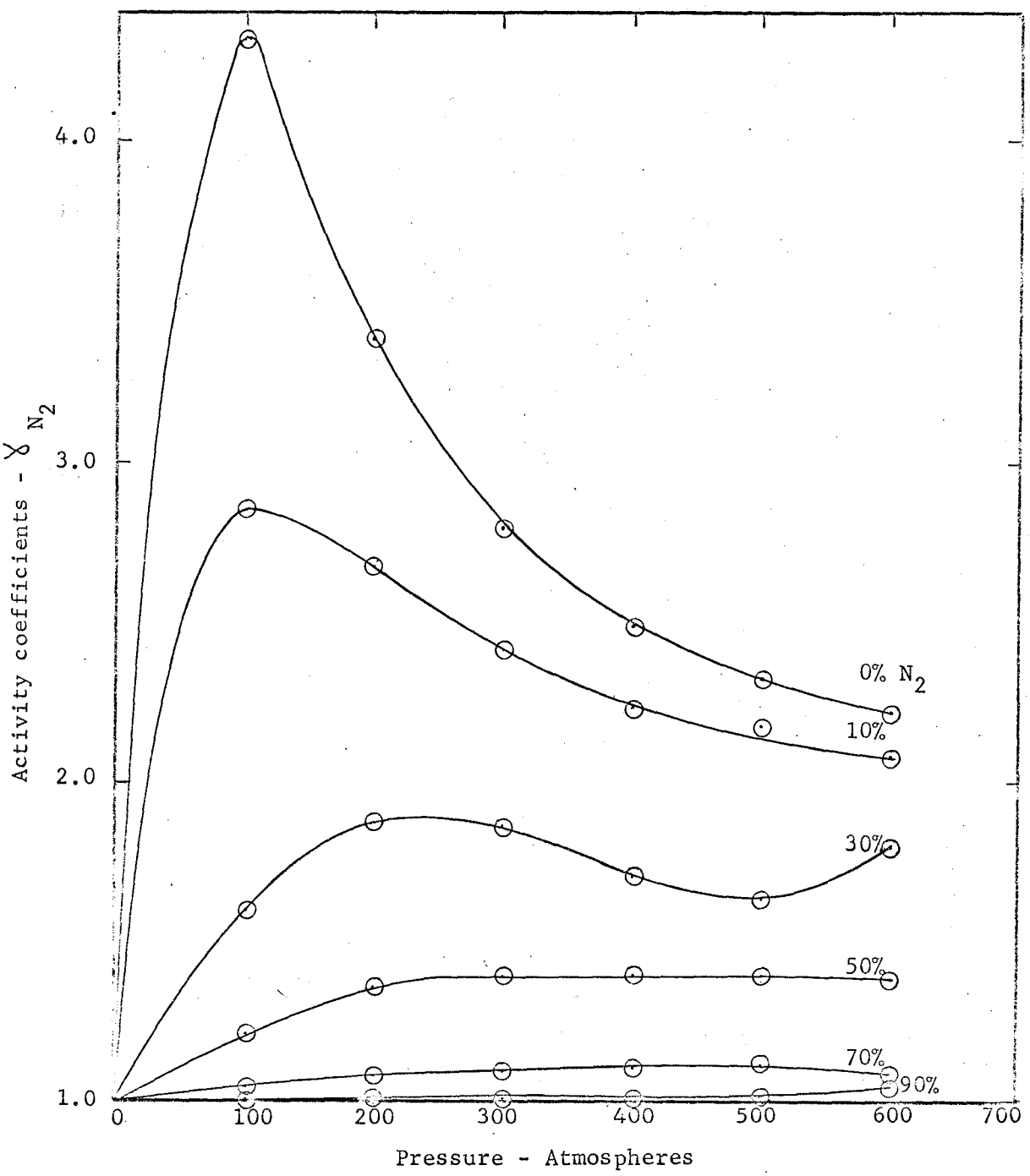


FIGURE 16

ACTIVITY COEFFICIENTS FOR n-BUTANE

n-BUTANE - NITROGEN MIXTURES AT 370°F

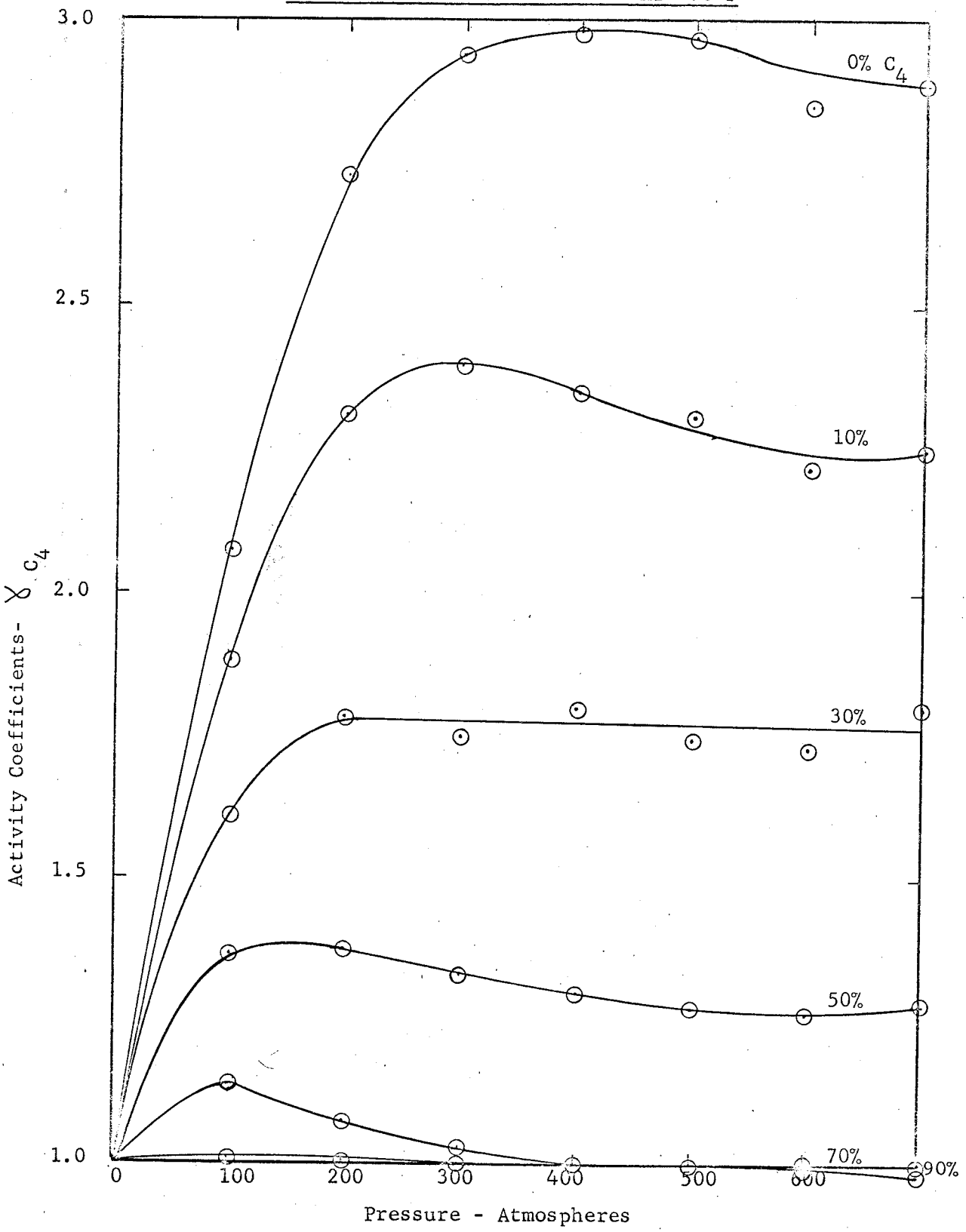


FIGURE 17

ACTIVITY COEFFICIENTS FOR NITROGEN

n-BUTANE - NITROGEN MIXTURES AT 370°F

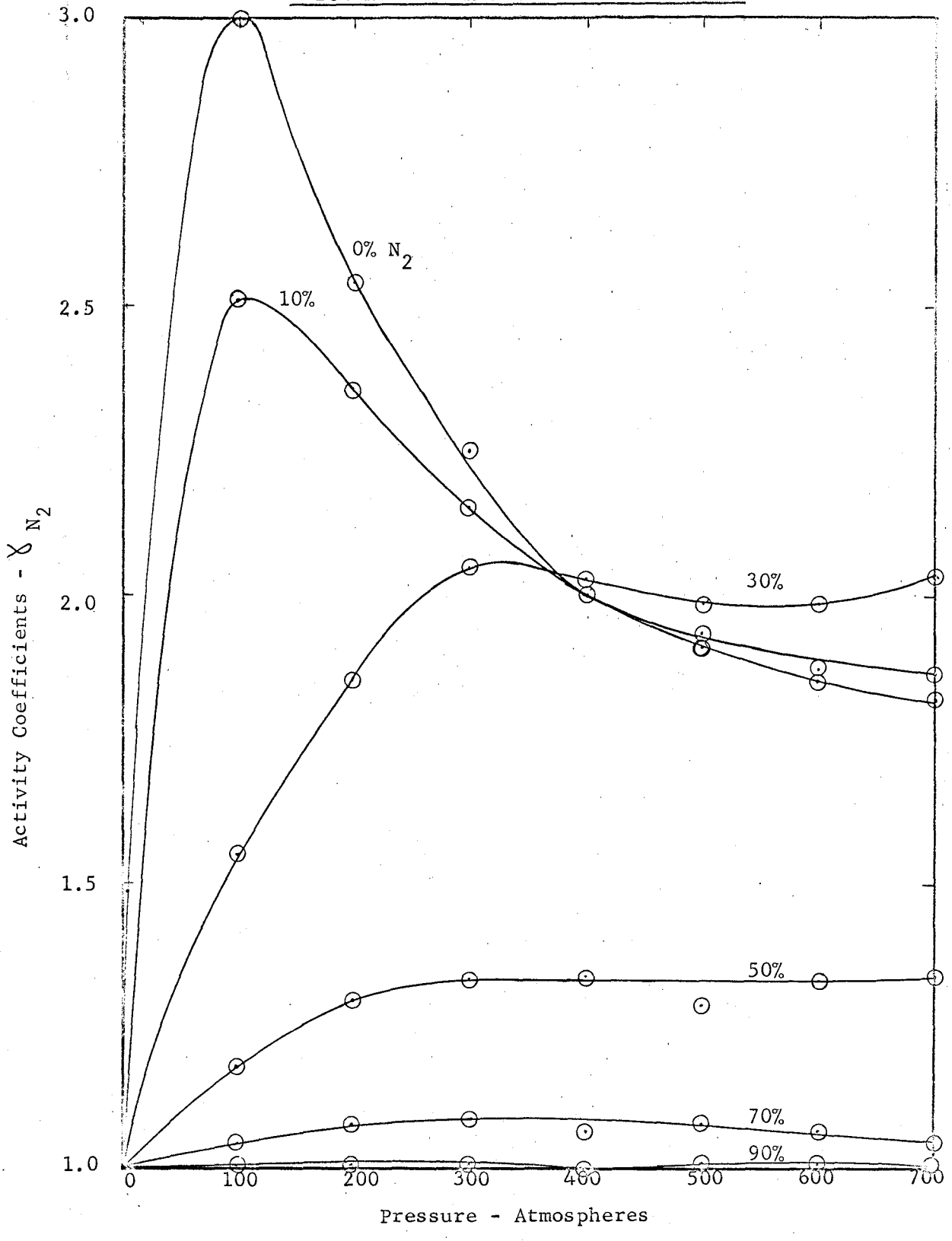


FIGURE 18

ACTIVITY COEFFICIENTS FOR n-BUTANE

n-BUTANE - NITROGEN MIXTURES AT 400°F

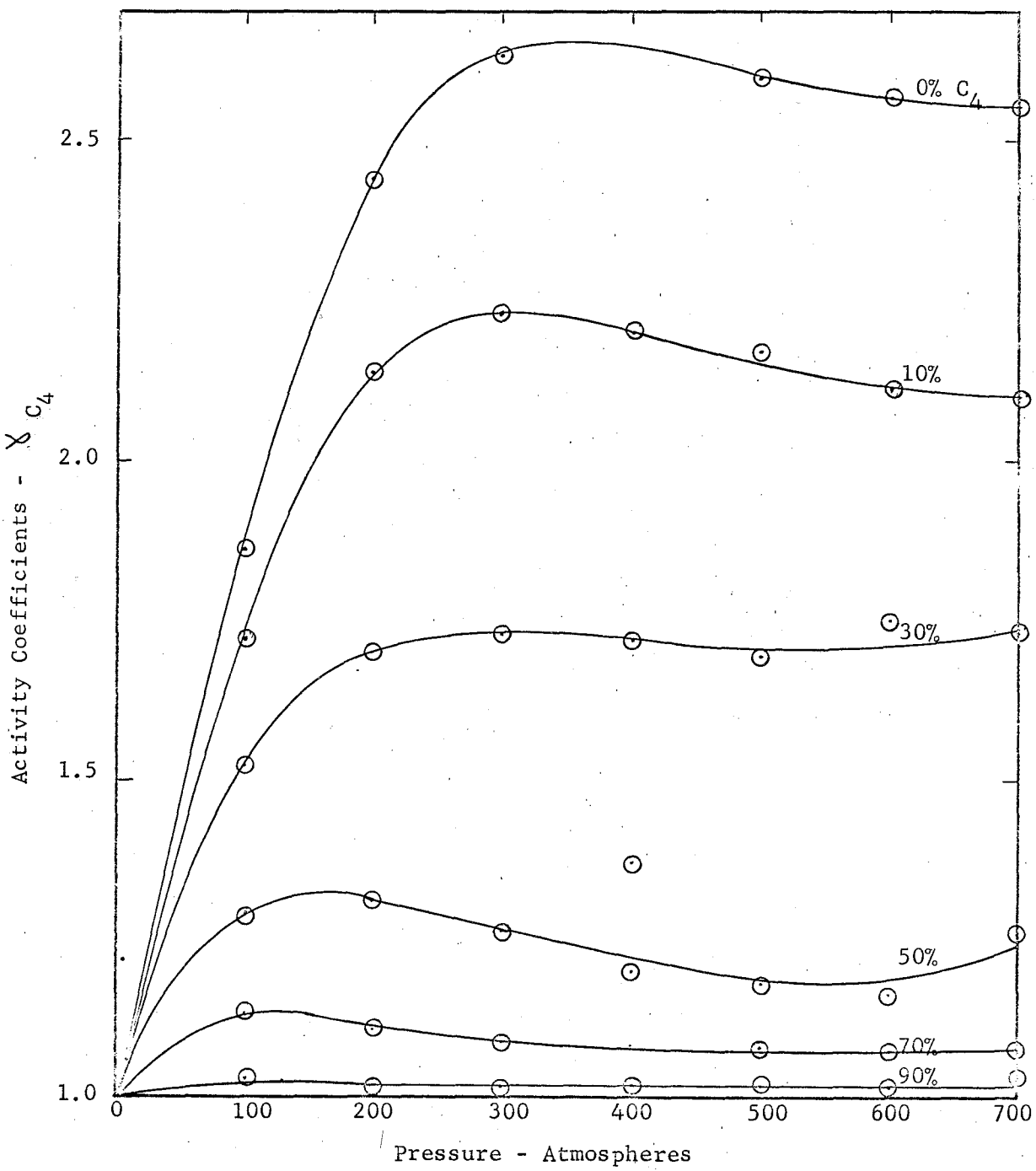


FIGURE 19

ACTIVITY COEFFICIENTS FOR NITROGEN

n-BUTANE - NITROGEN MIXTURES AT 400°F

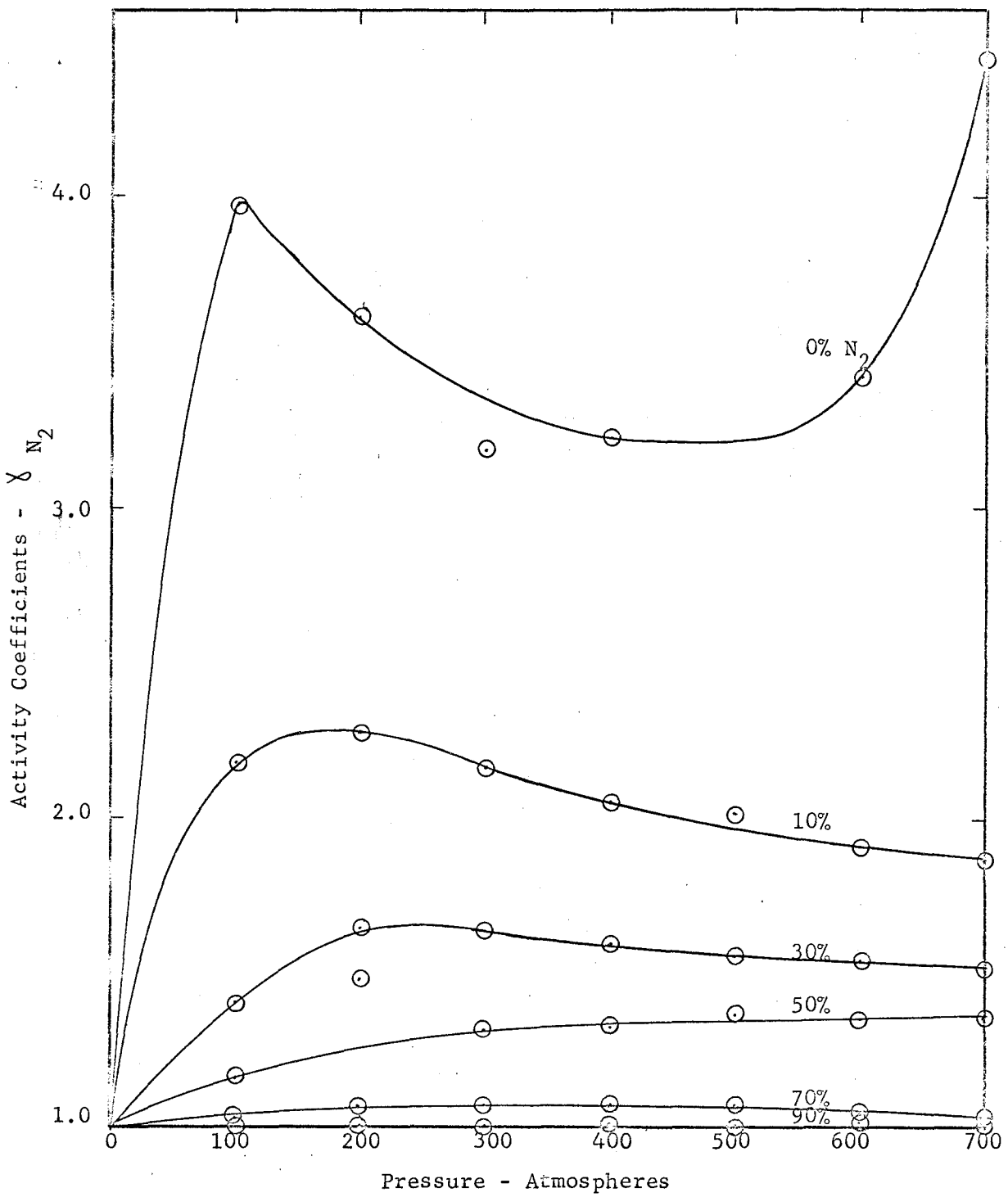


FIGURE 20

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 310°F and 100Atm

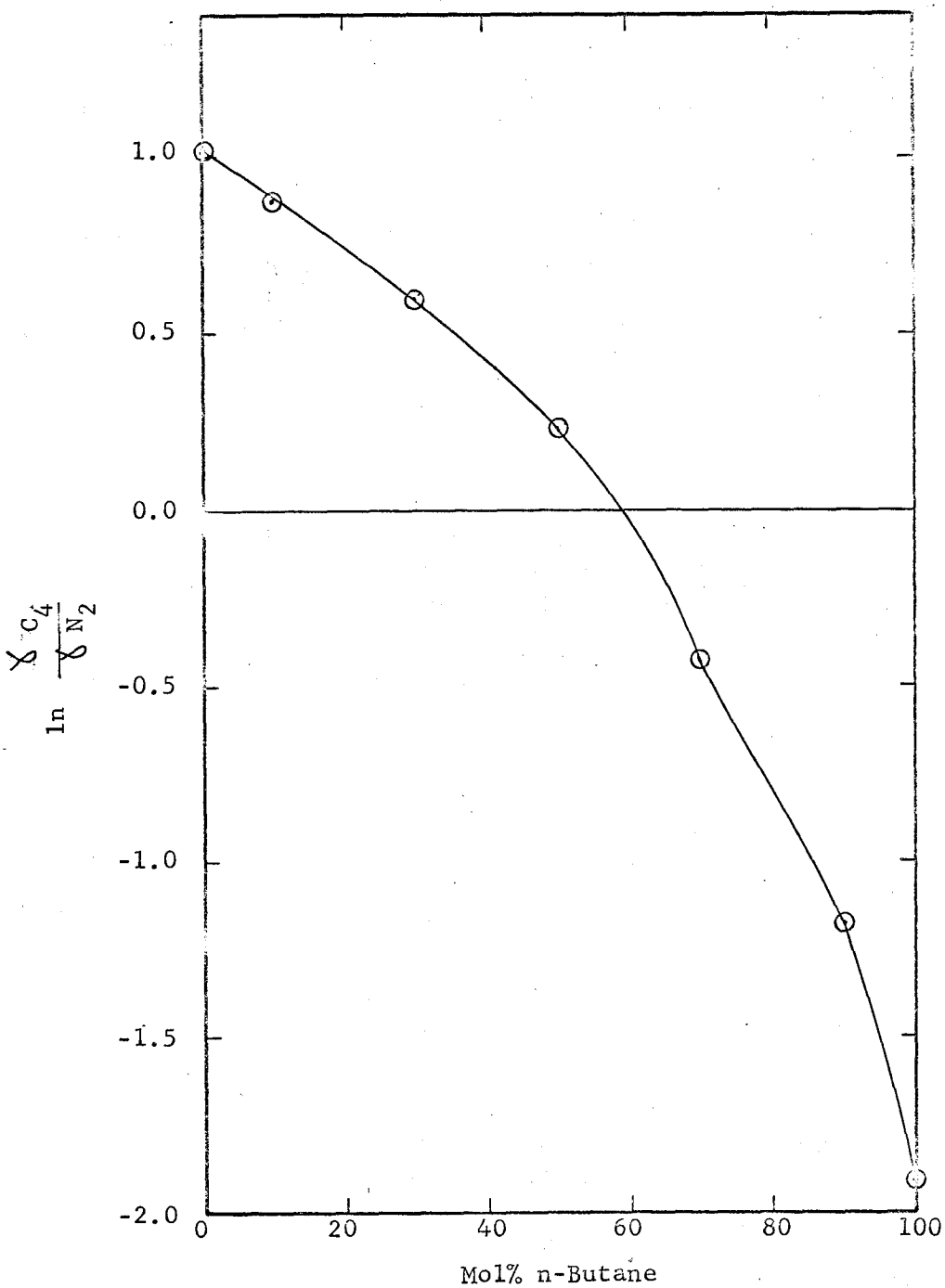


FIGURE 21

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 310°F and 200Atm

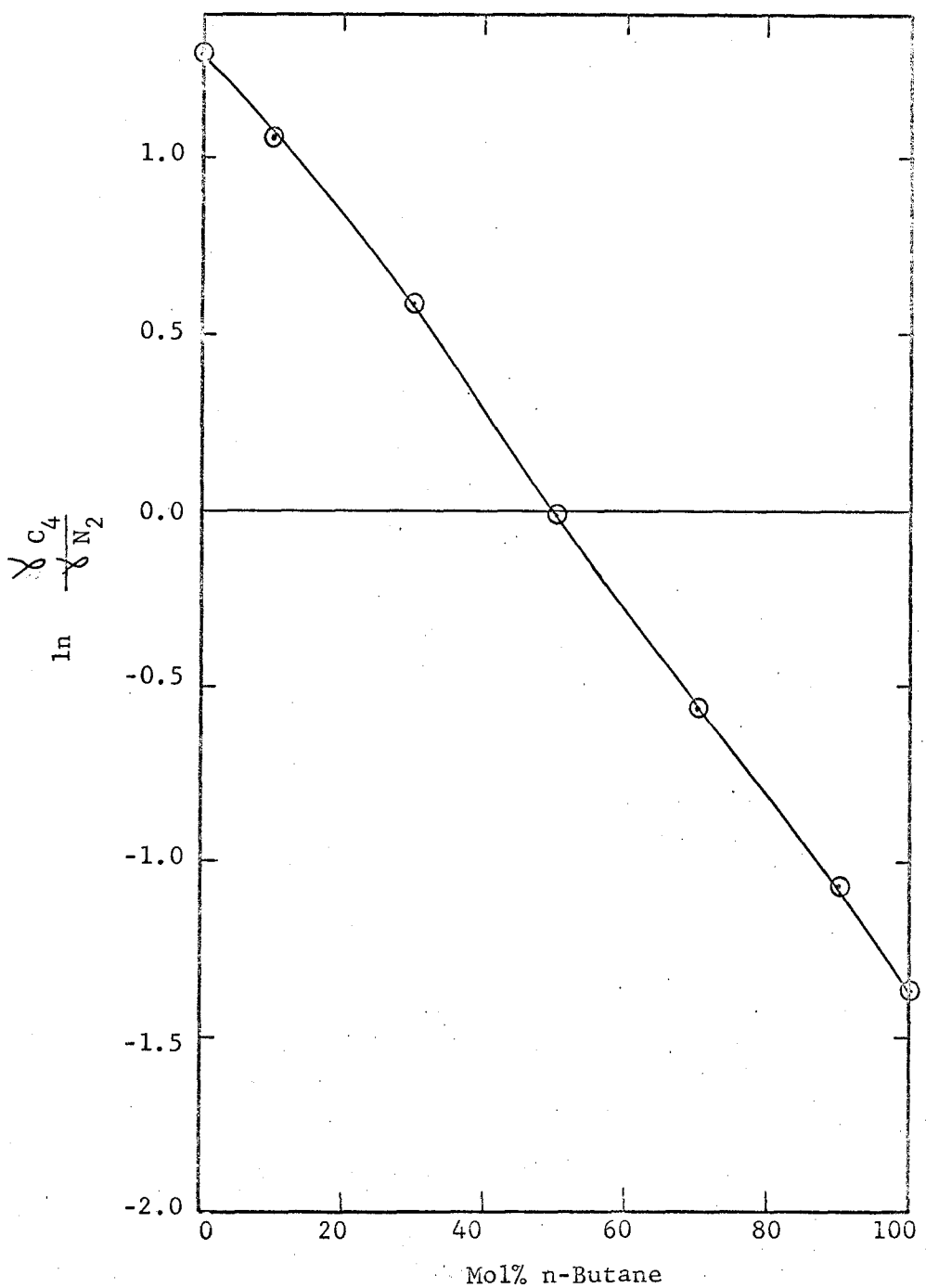


FIGURE 22

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 310°F and 300Atm

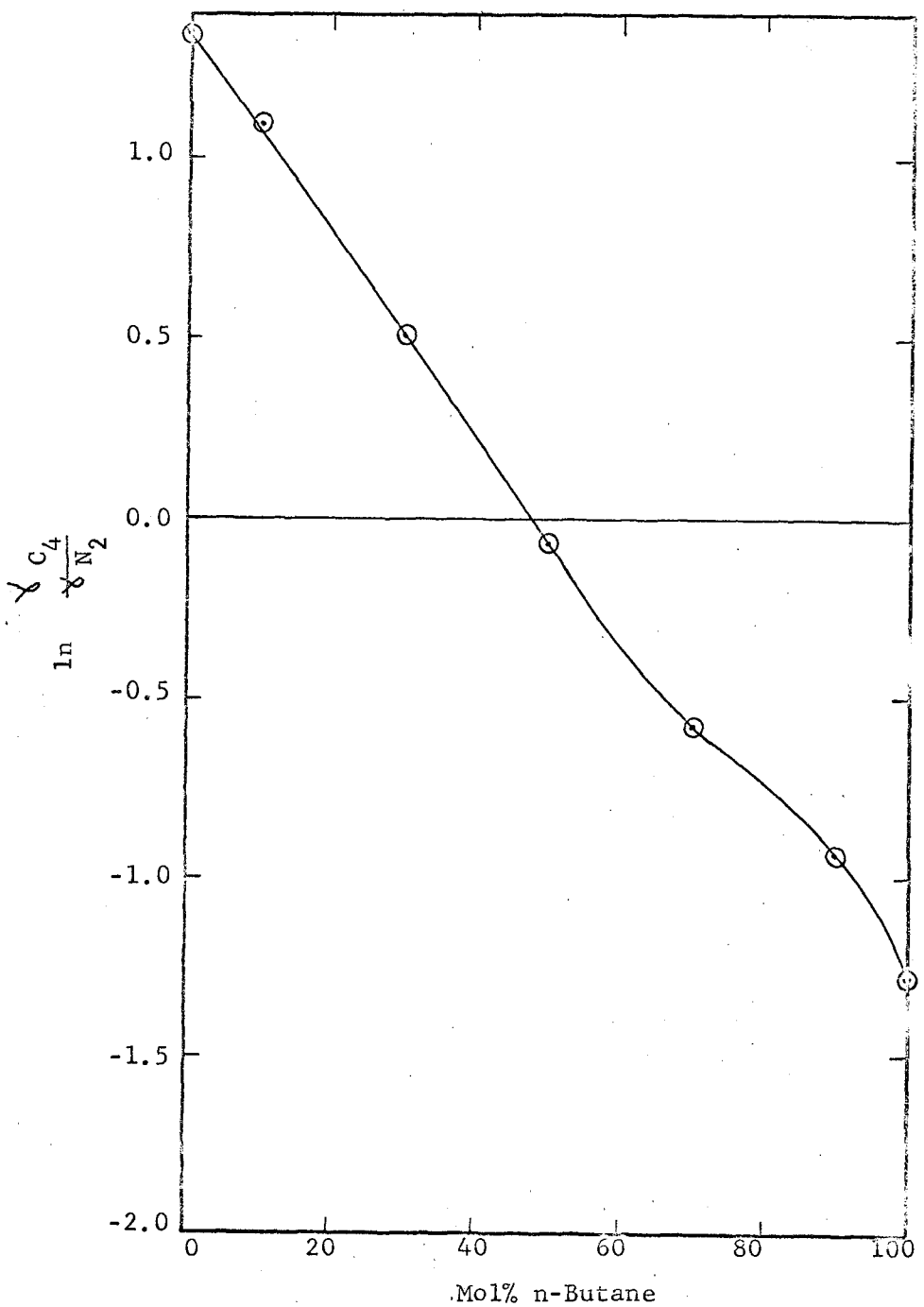


FIGURE 23

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 310°F and 400Atm

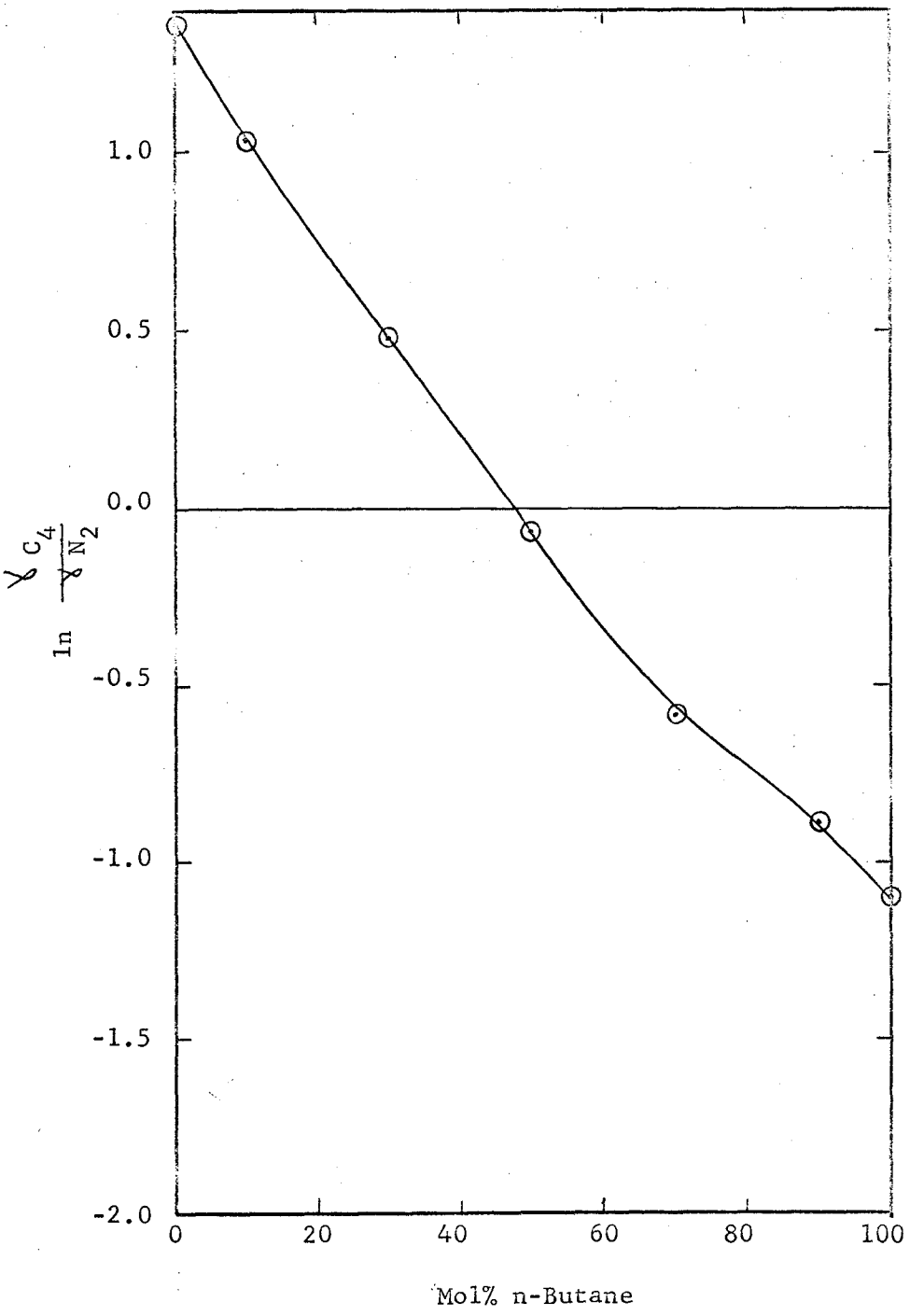


FIGURE 24

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 310°F and 500Atm

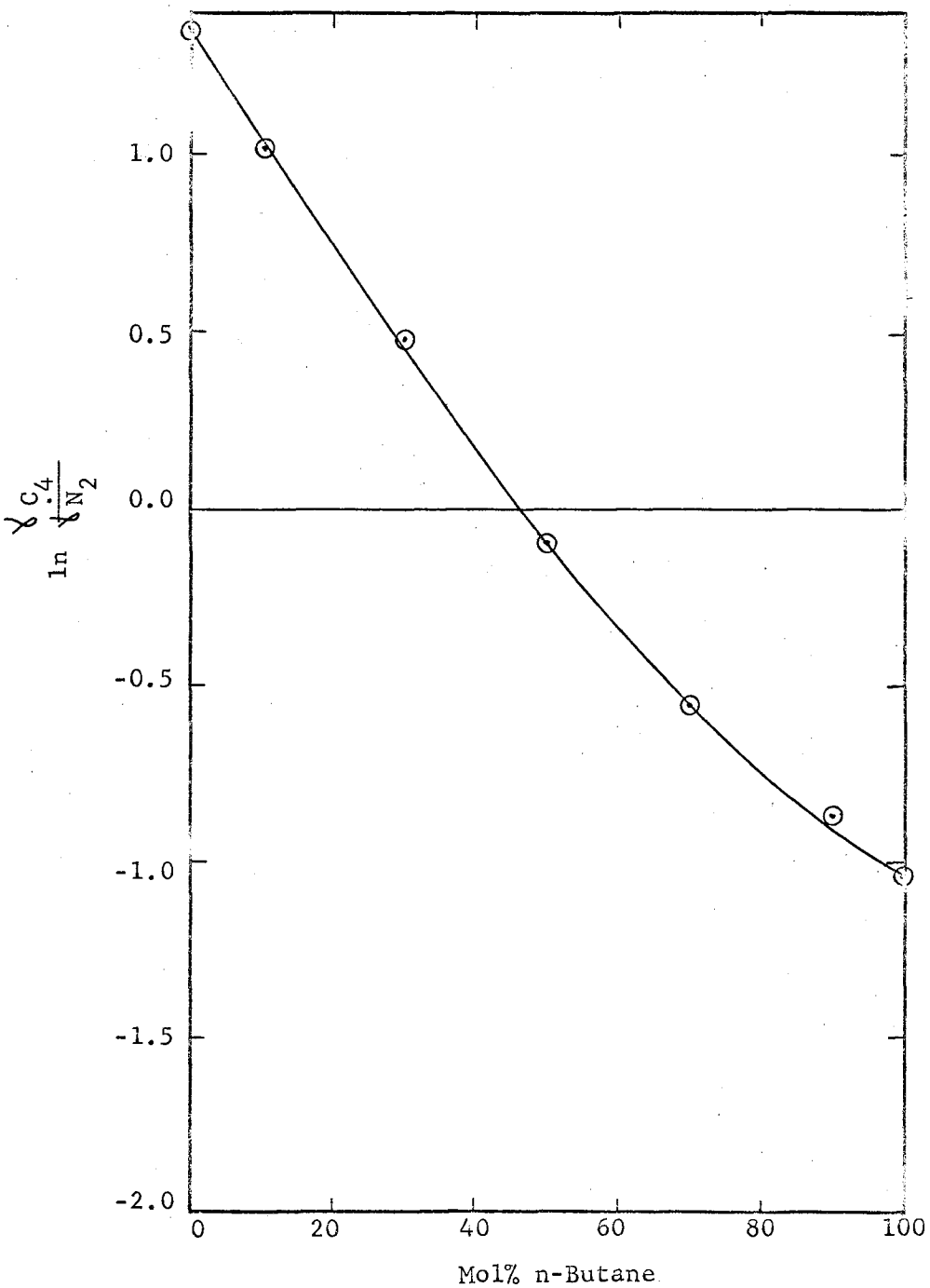


FIGURE 25

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 310°F and 600Atm

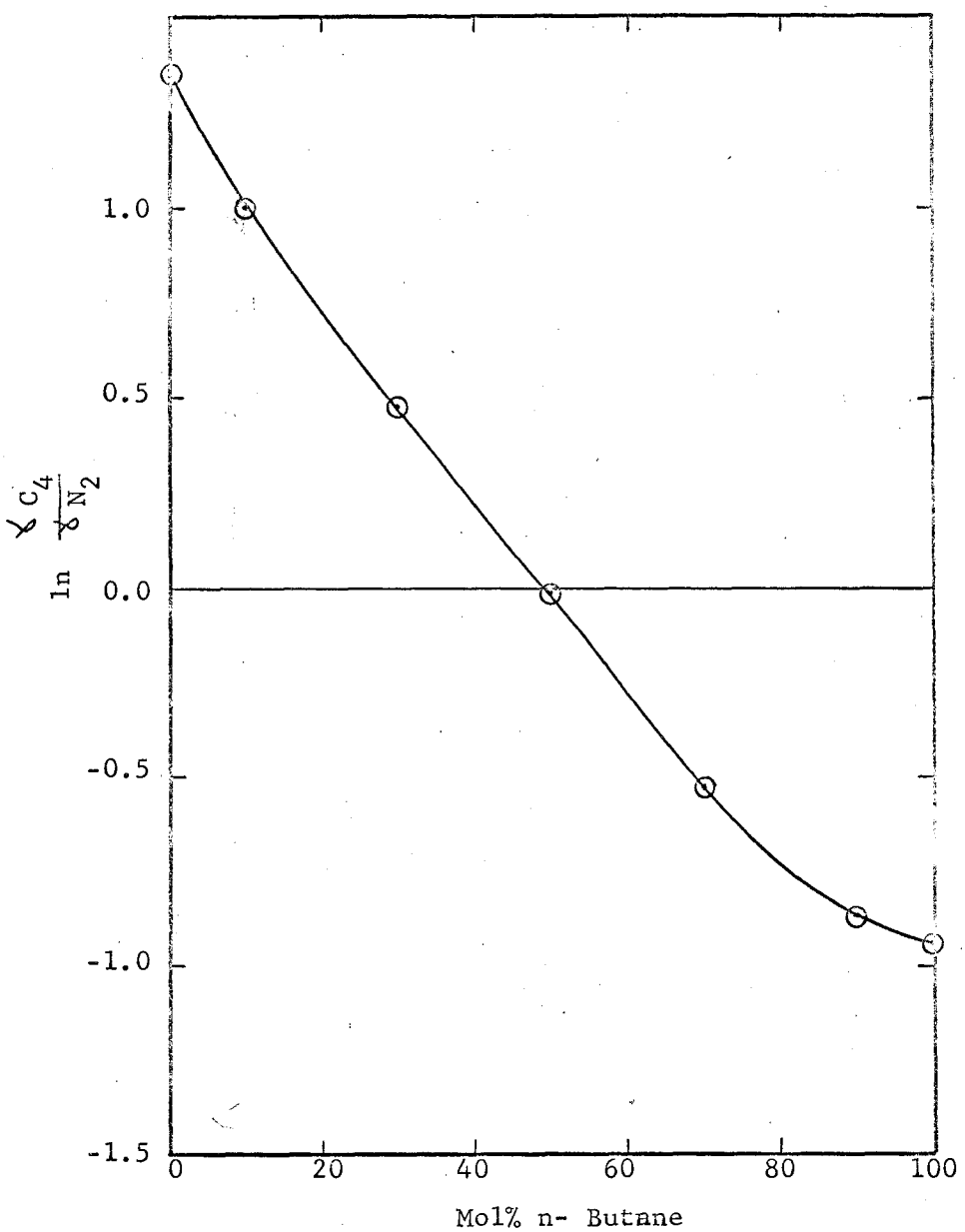


FIGURE 26

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 310°F and 700Atm

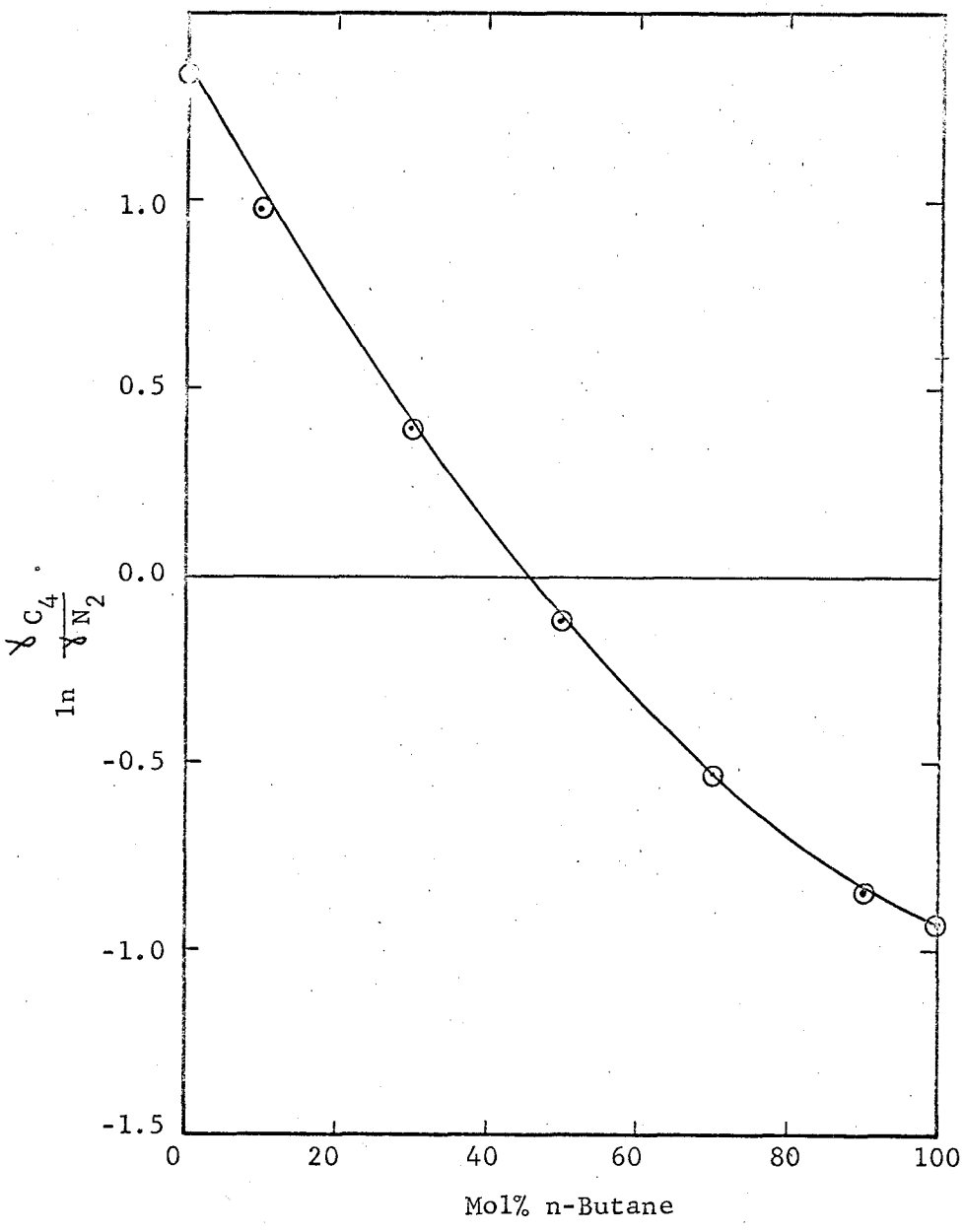


FIGURE 27

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 340°F and 100Atm

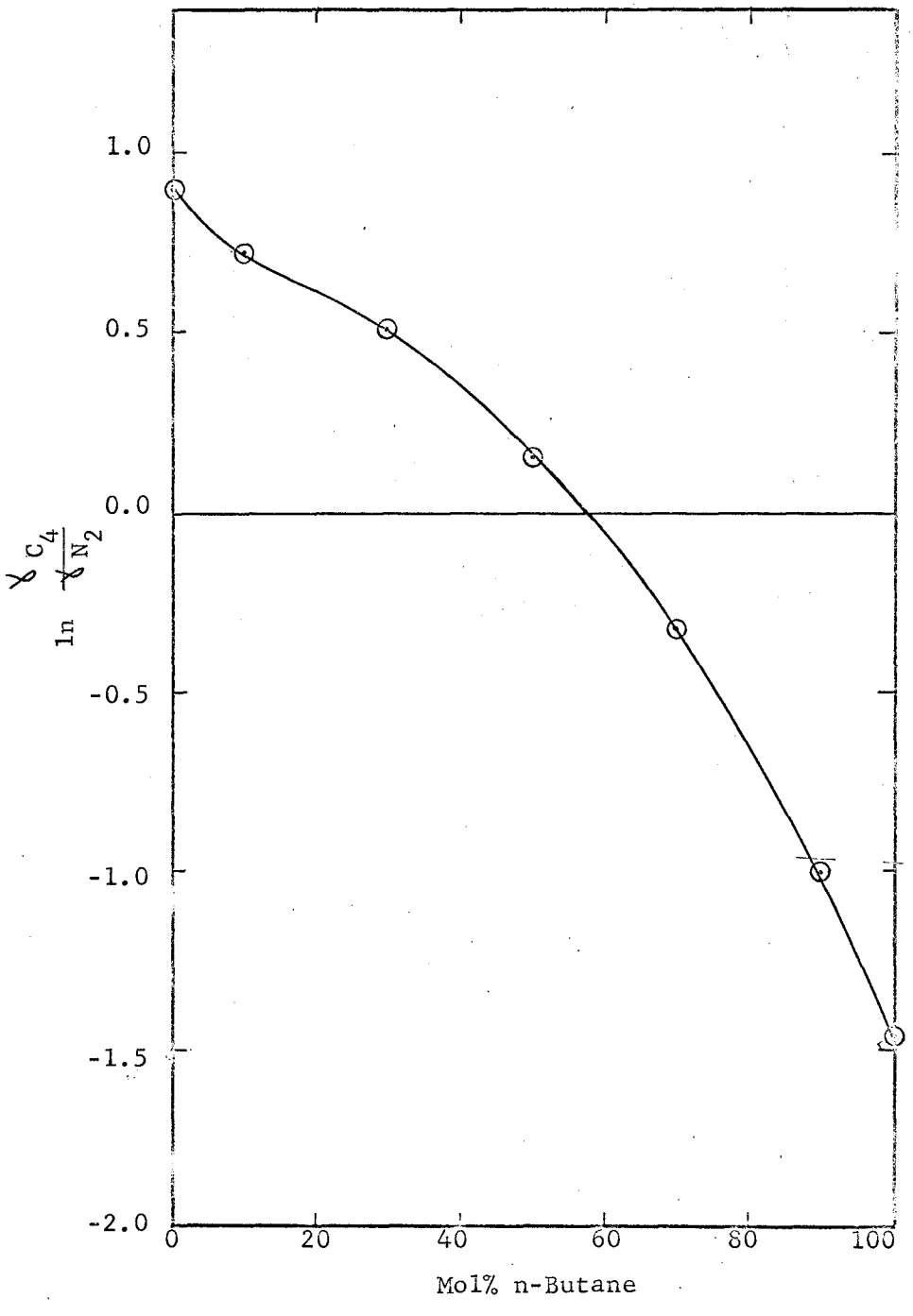


FIGURE 28

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 340°F and 200Atm

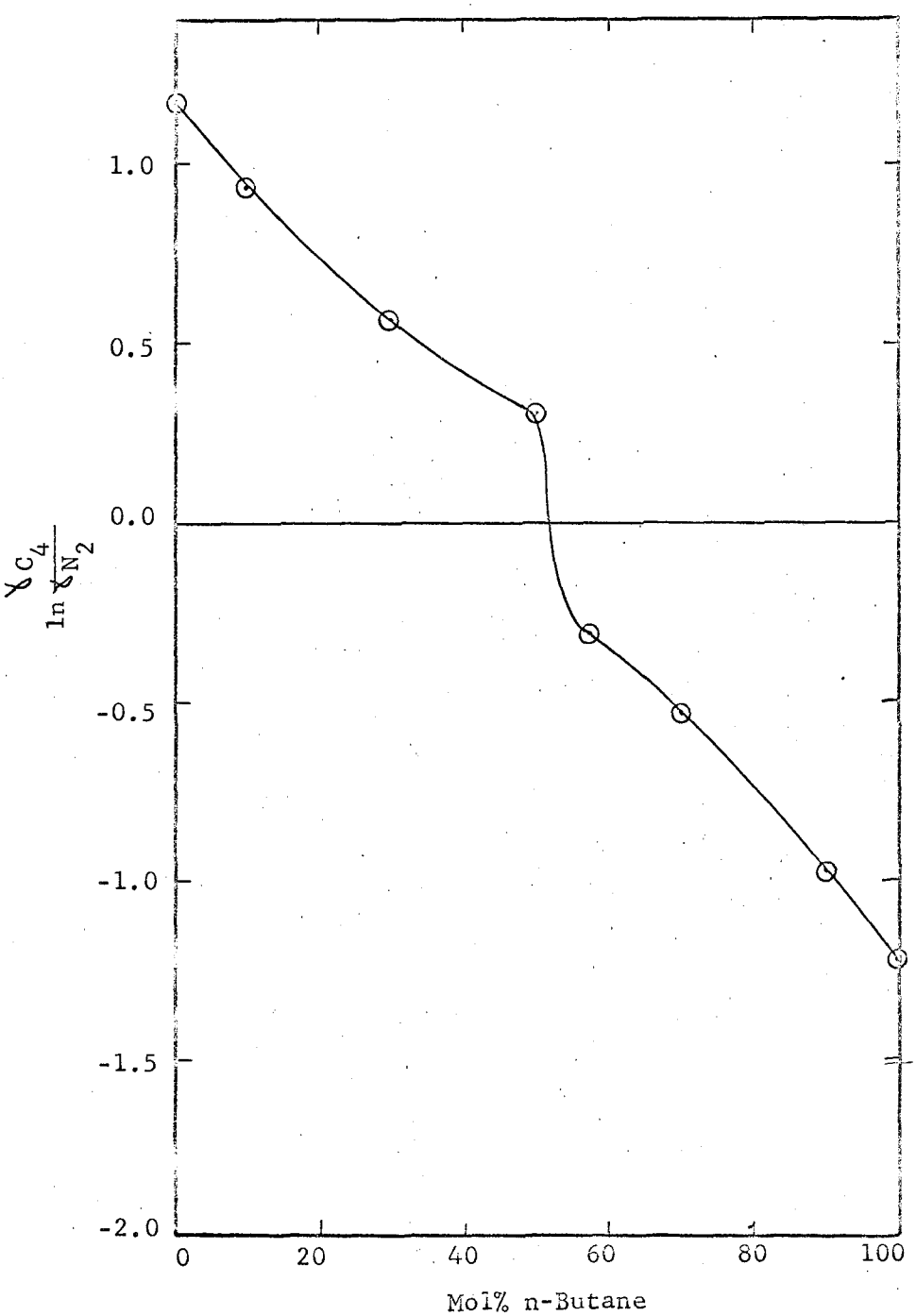


FIGURE 29

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 340°F and 300Atm

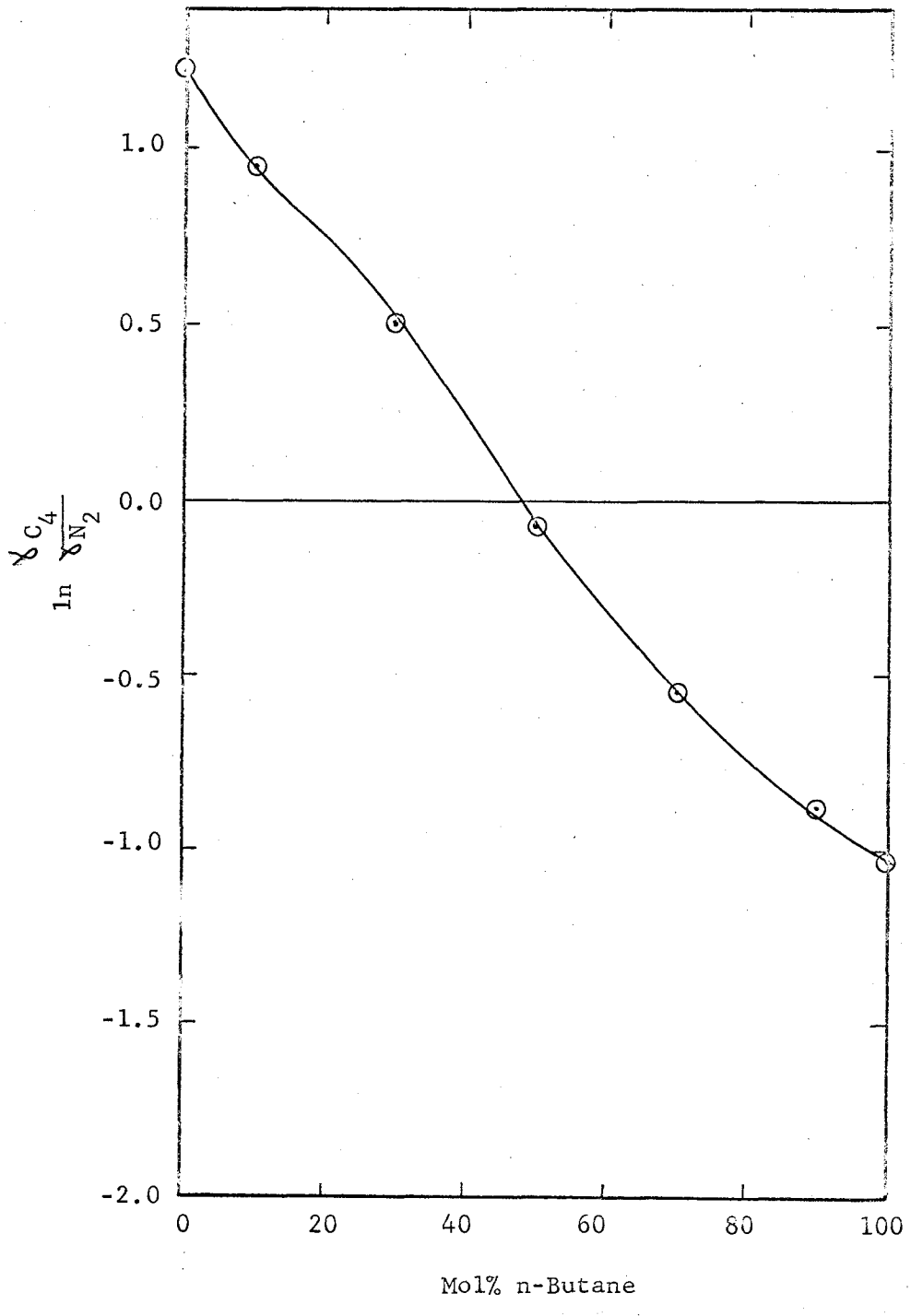


FIGURE 30

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 340°F and 400Atm

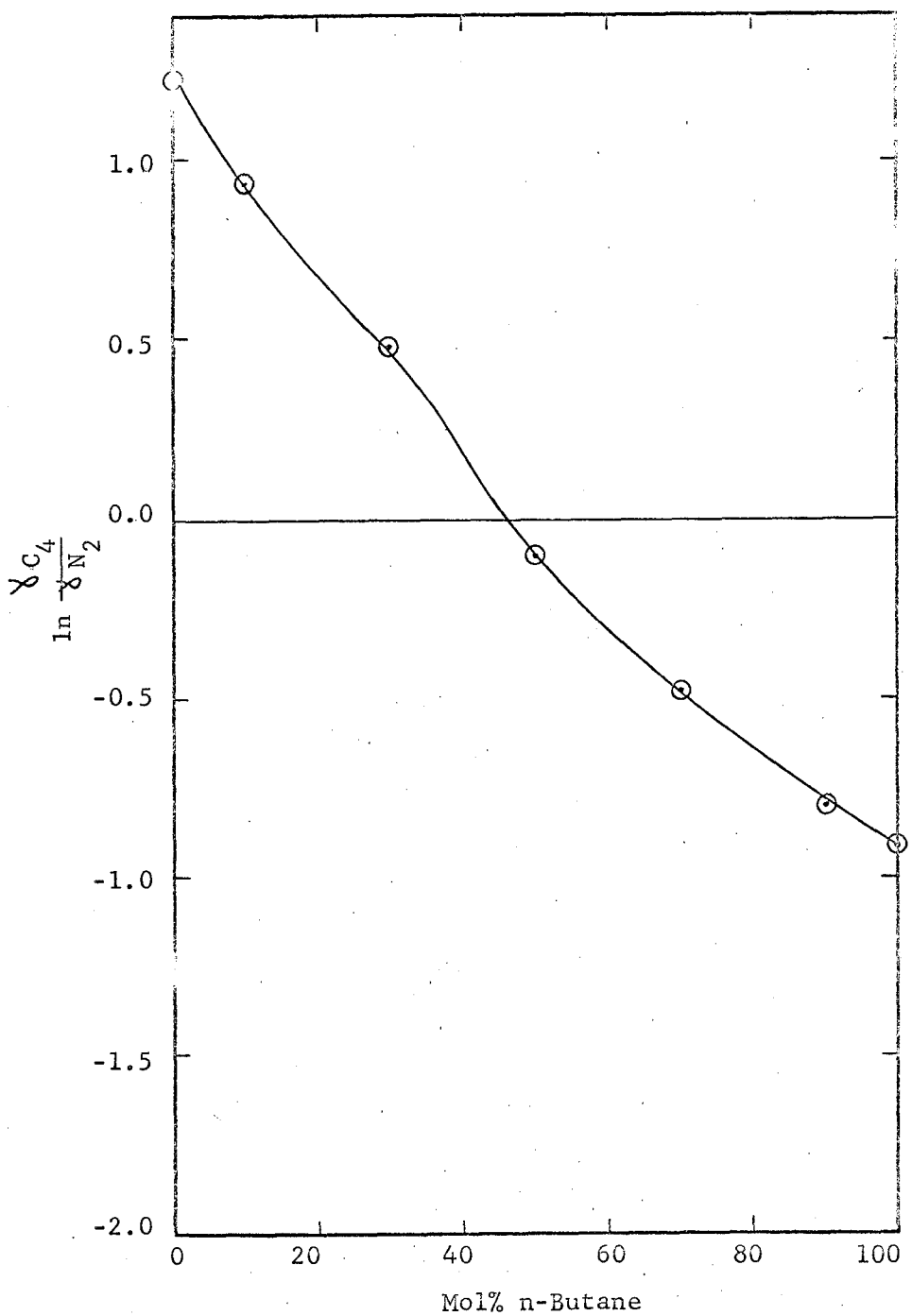


FIGURE 31

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 340°F and 500Atm

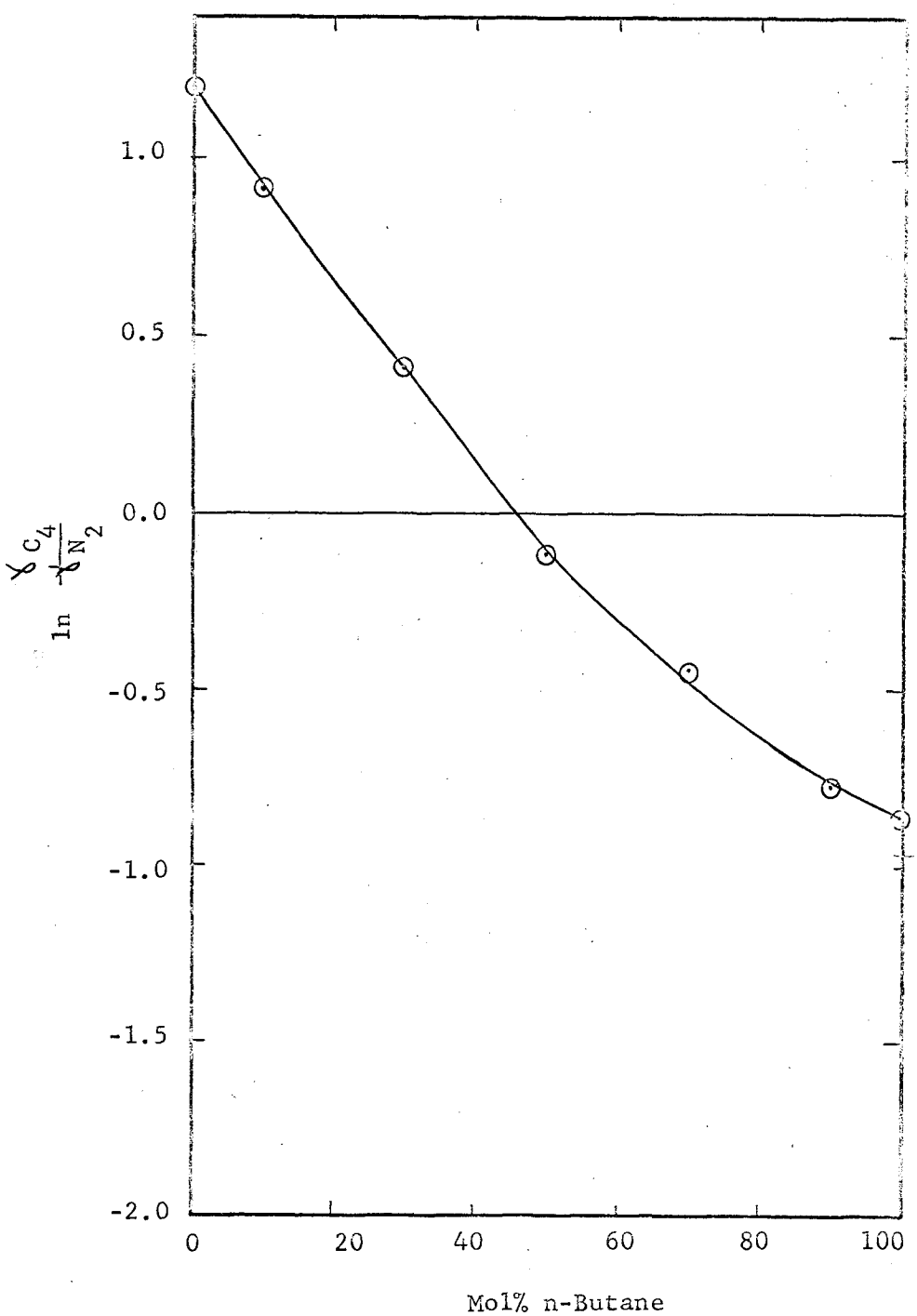


FIGURE 32

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 340°F and 600Atm

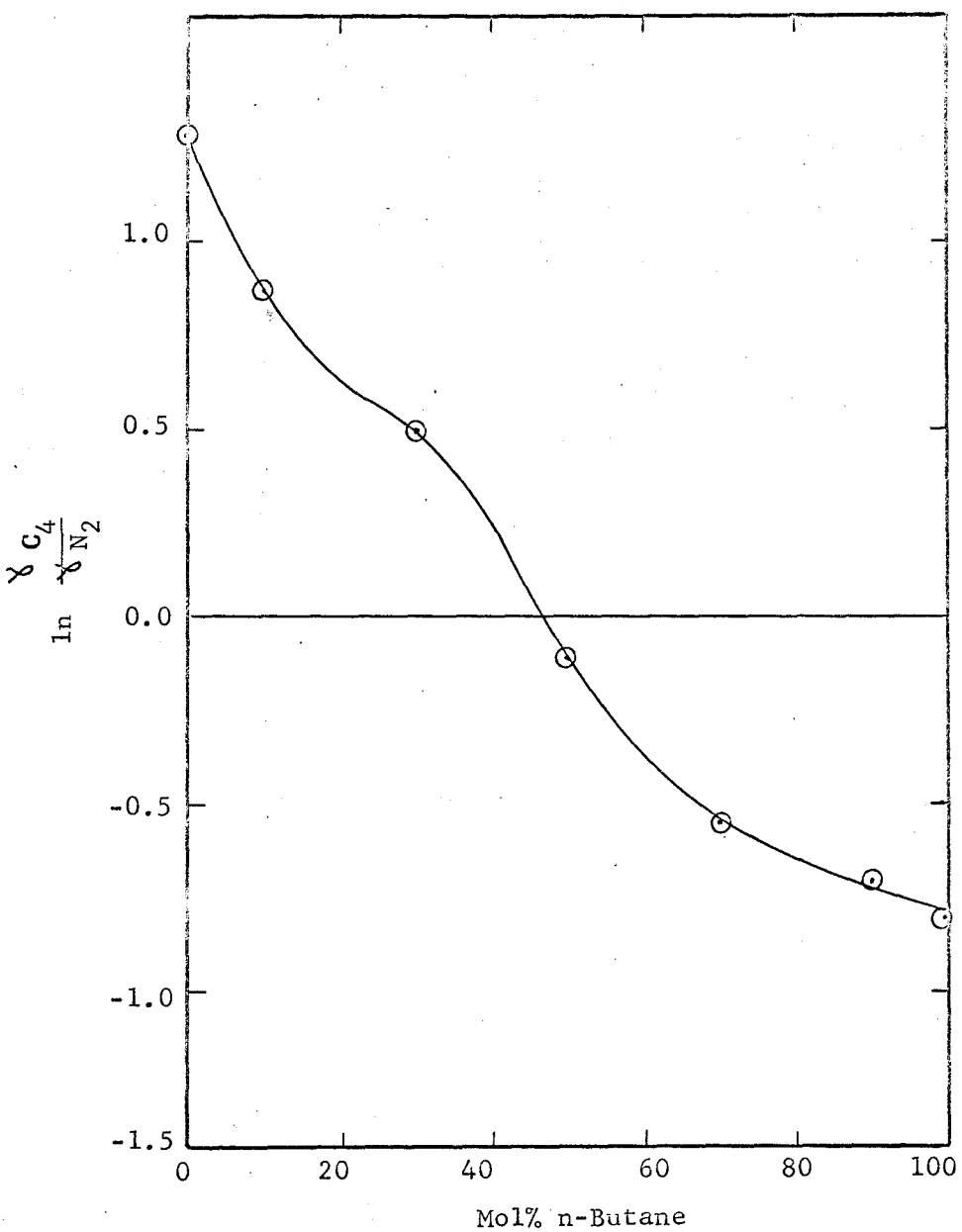


FIGURE 33

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 370°F and 100Atm

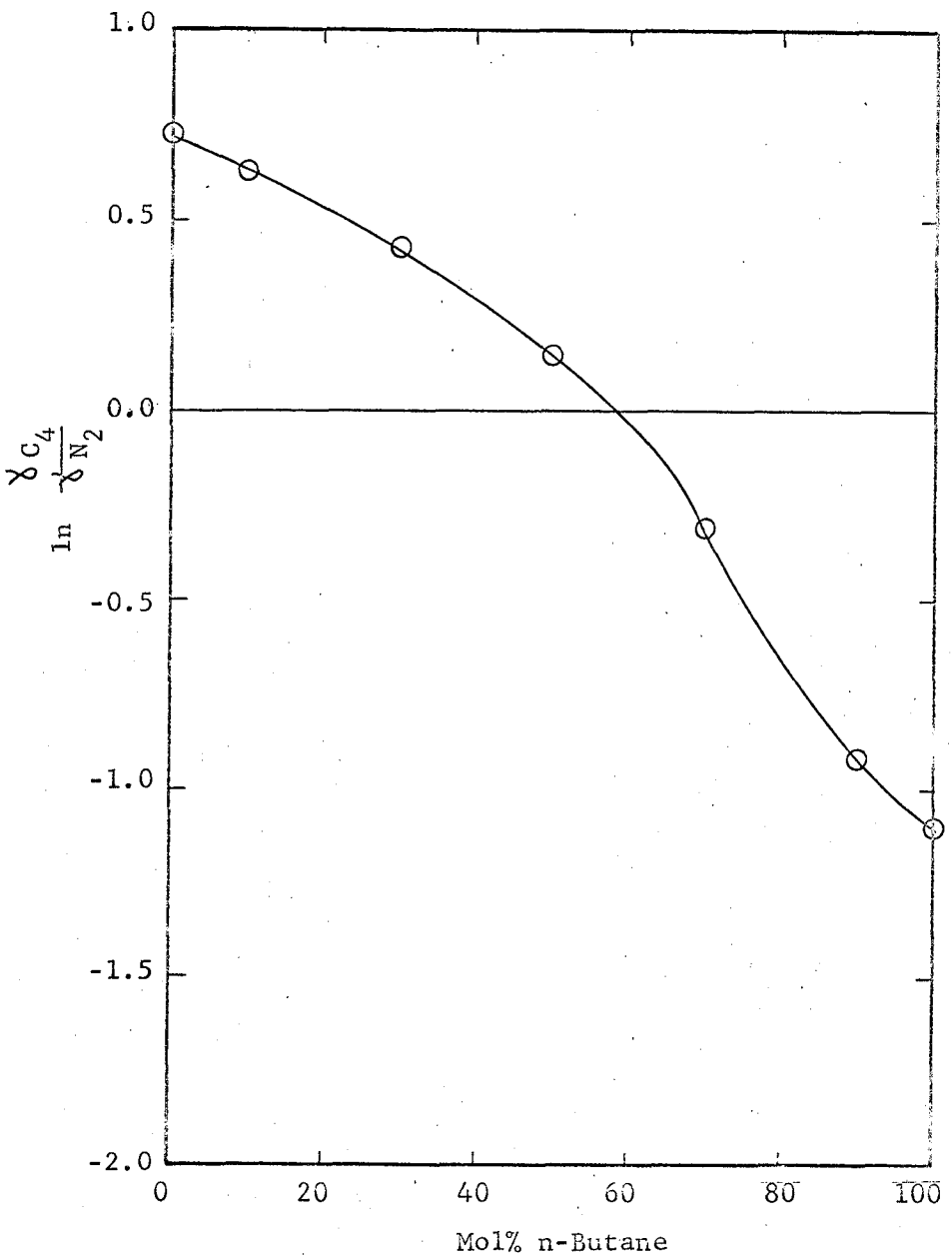


FIGURE 34

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 370°F and 200Atm

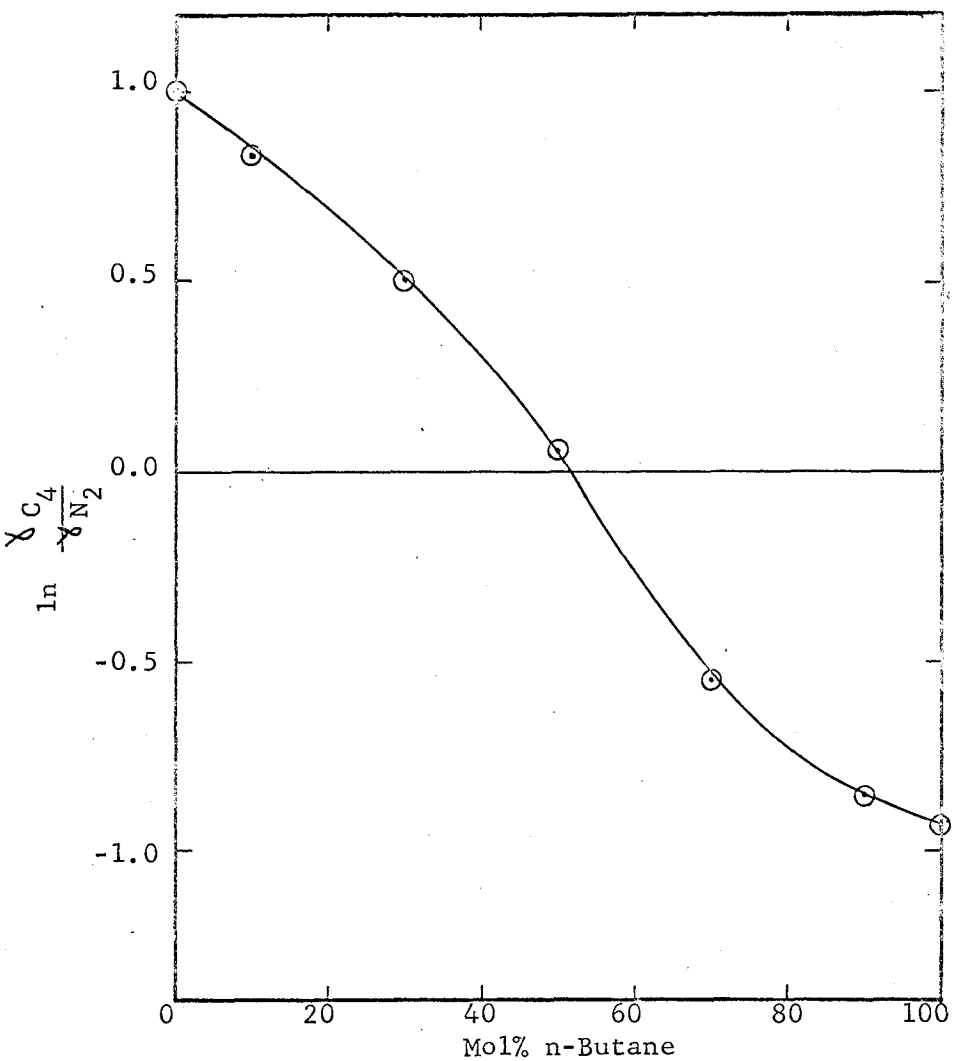


FIGURE 35

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 370°F and 300Atm

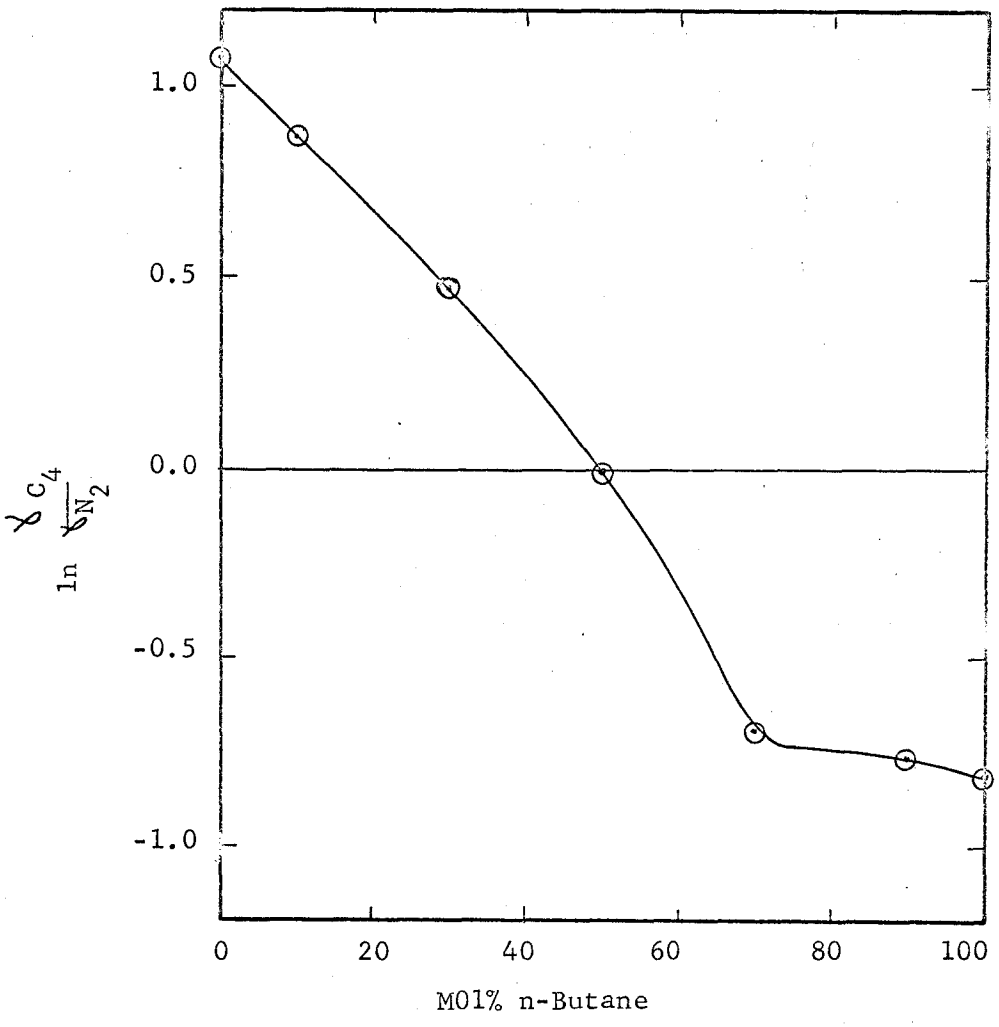


FIGURE 36

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 370°F and 400Atm

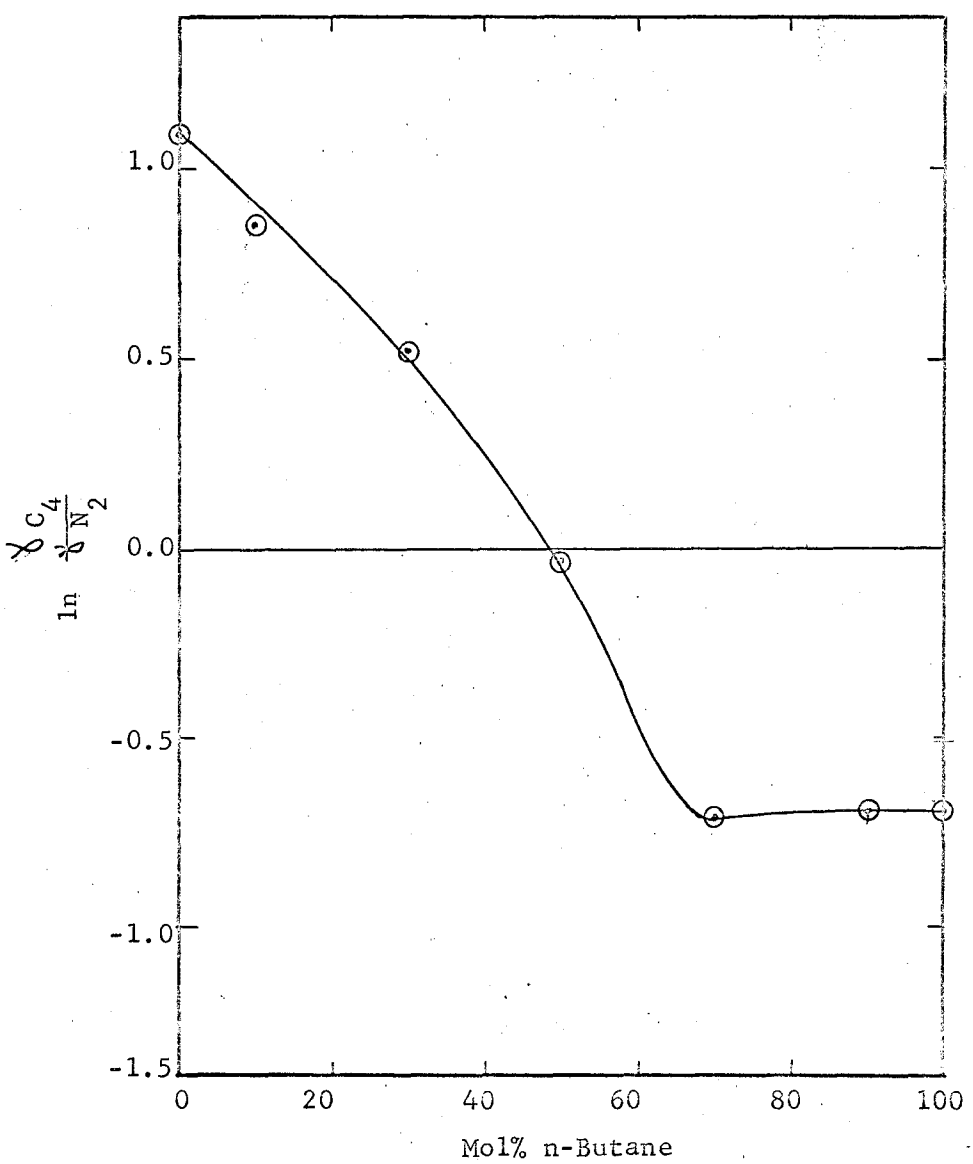


FIGURE 37

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 370°F and 500Atm

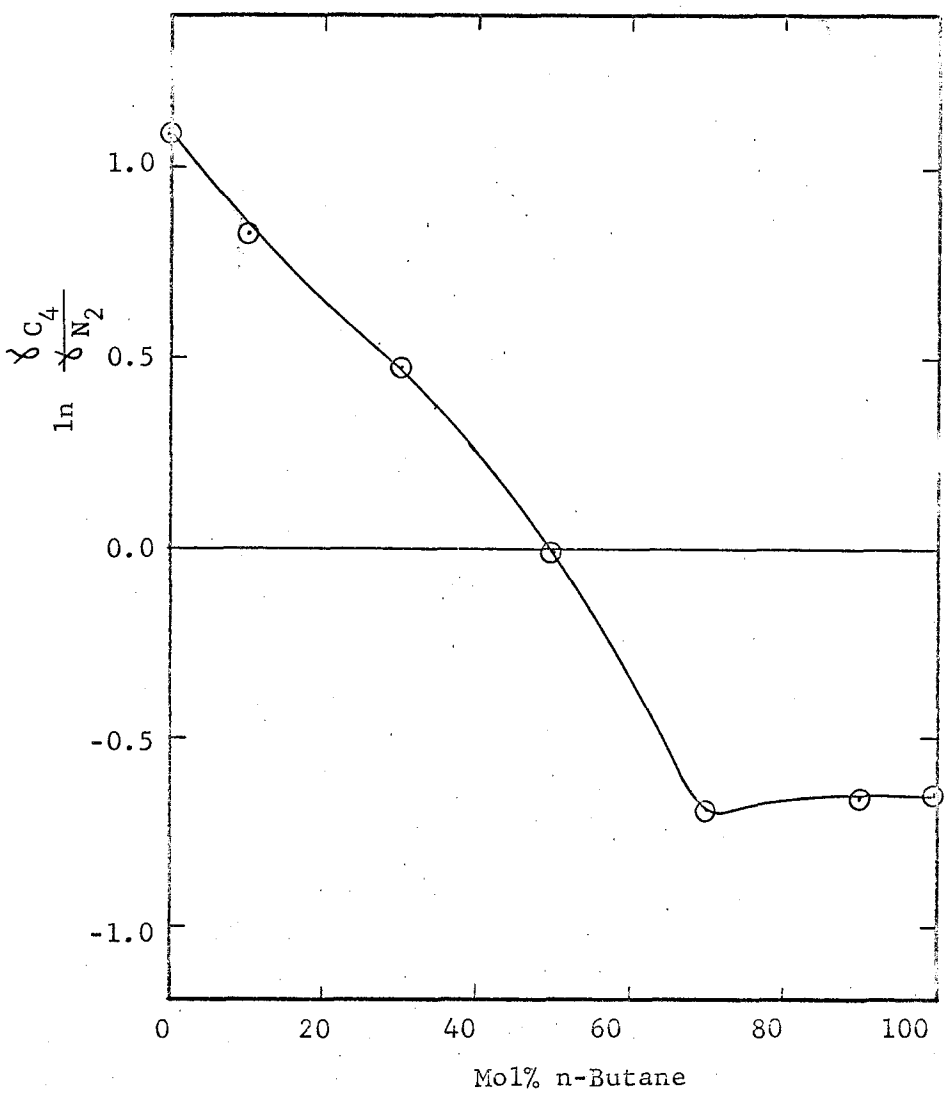


FIGURE 38

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 370°F and 600Atm

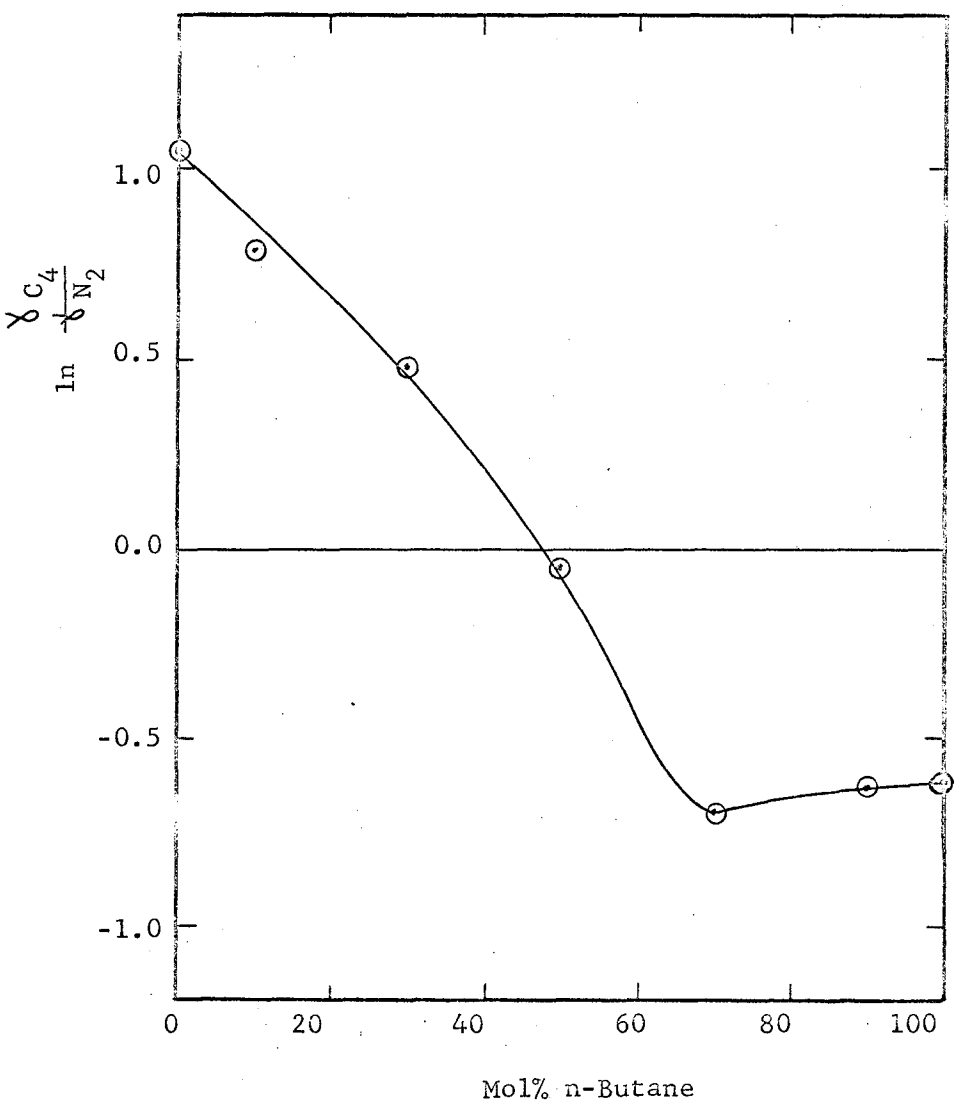


FIGURE 39

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 370°F and 700Atm

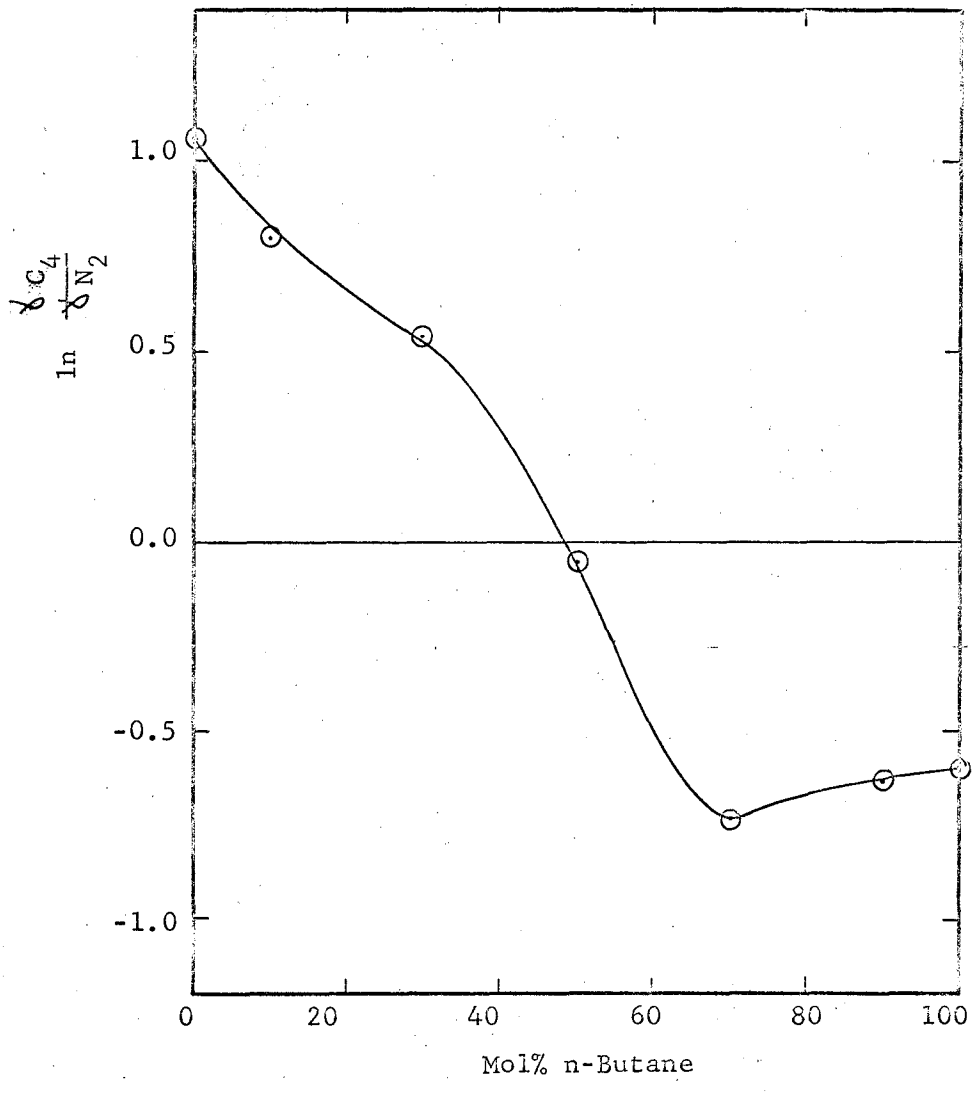


FIGURE 40

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 400°F and 100Atm

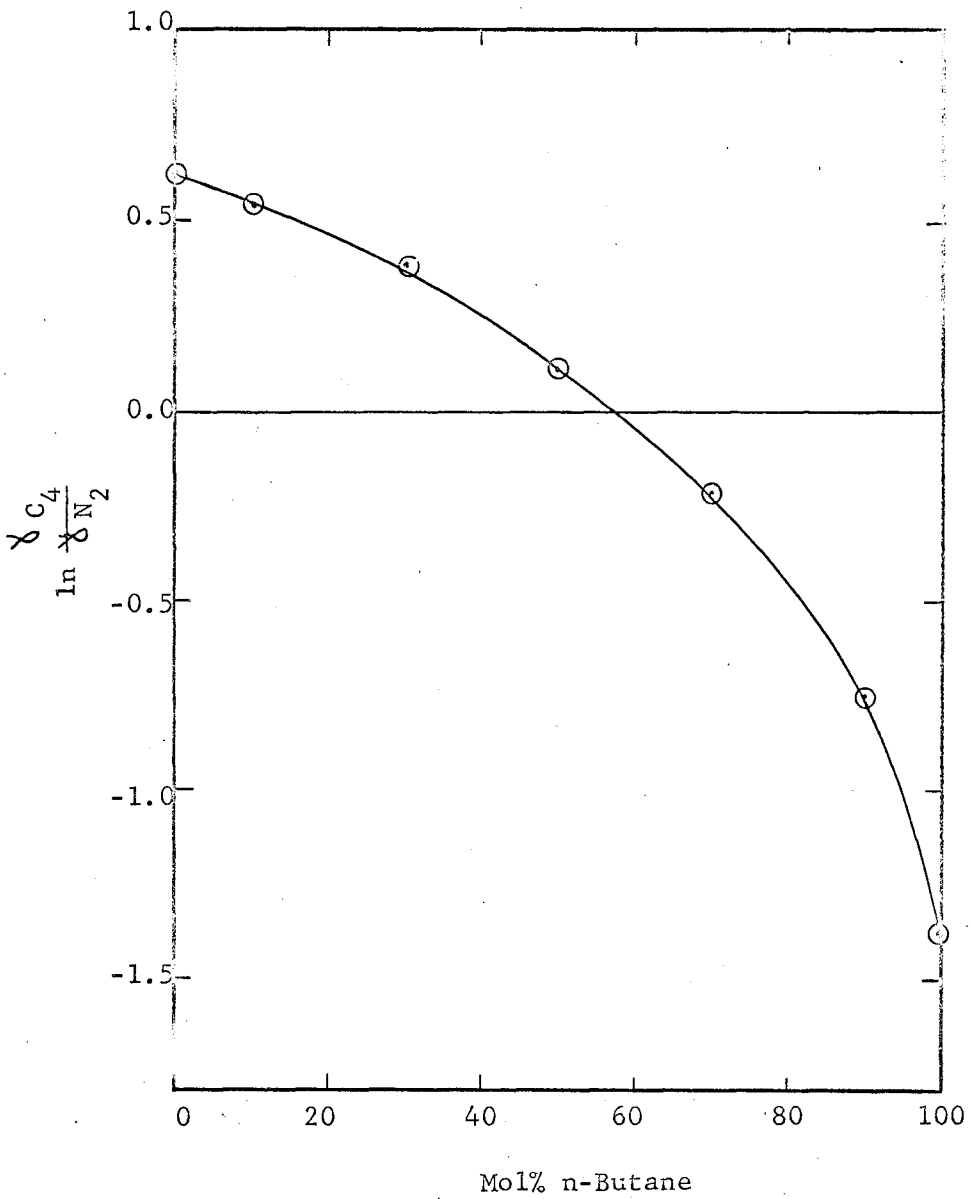


FIGURE 41

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 400°F and 200Atm

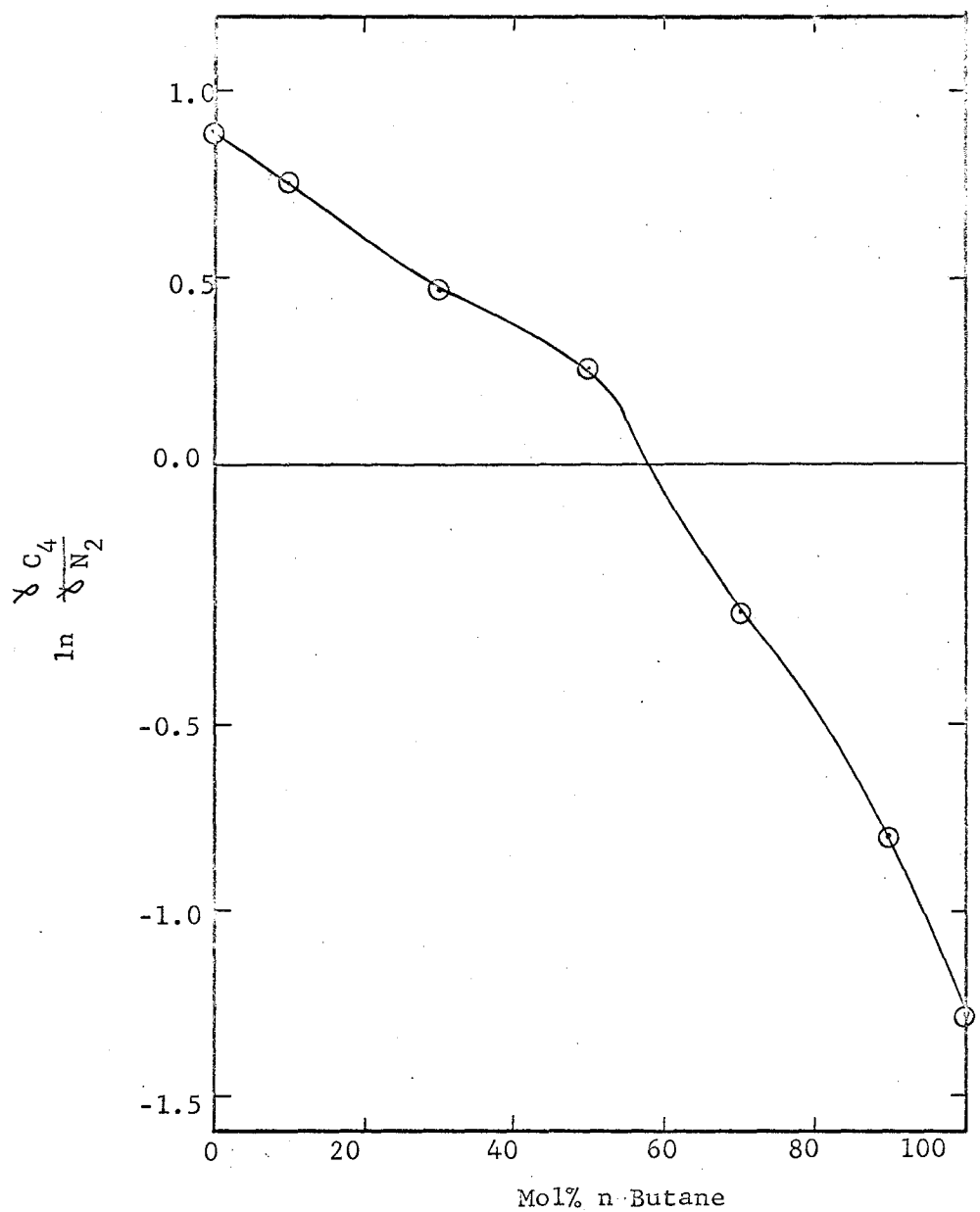


FIGURE 42

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 400°F and 300Atm

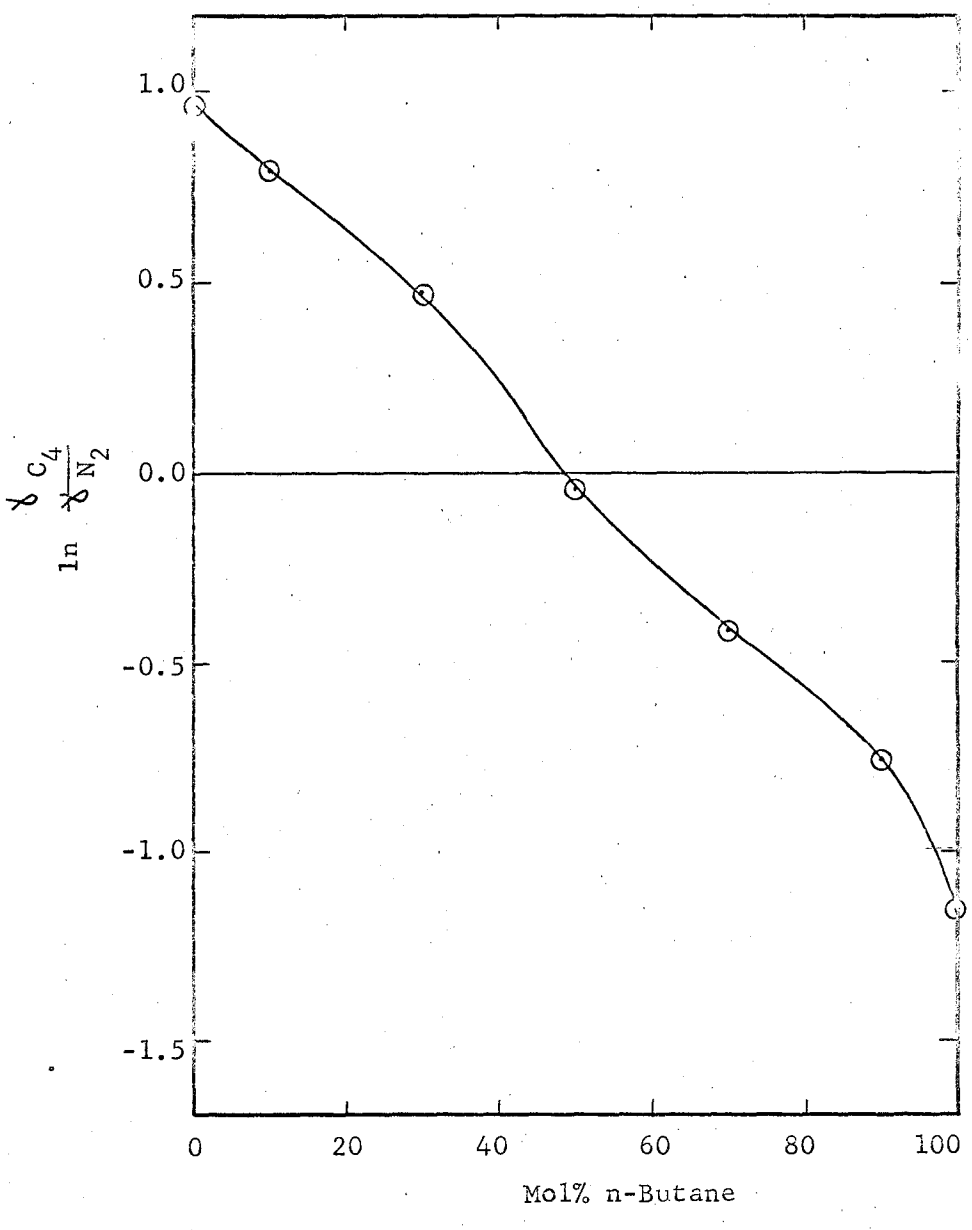


FIGURE 43

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 400°F and 400Atm

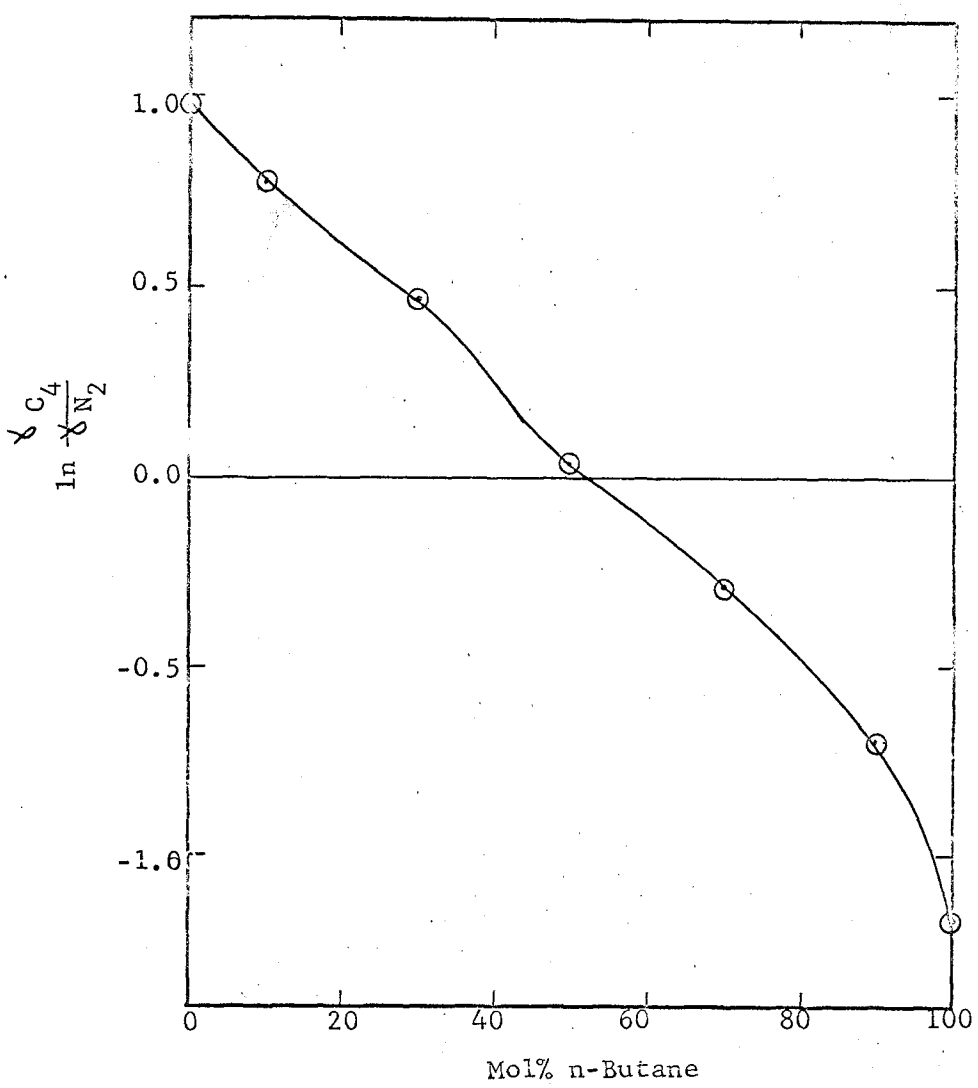


FIGURE 44

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 400°F and 500Atm

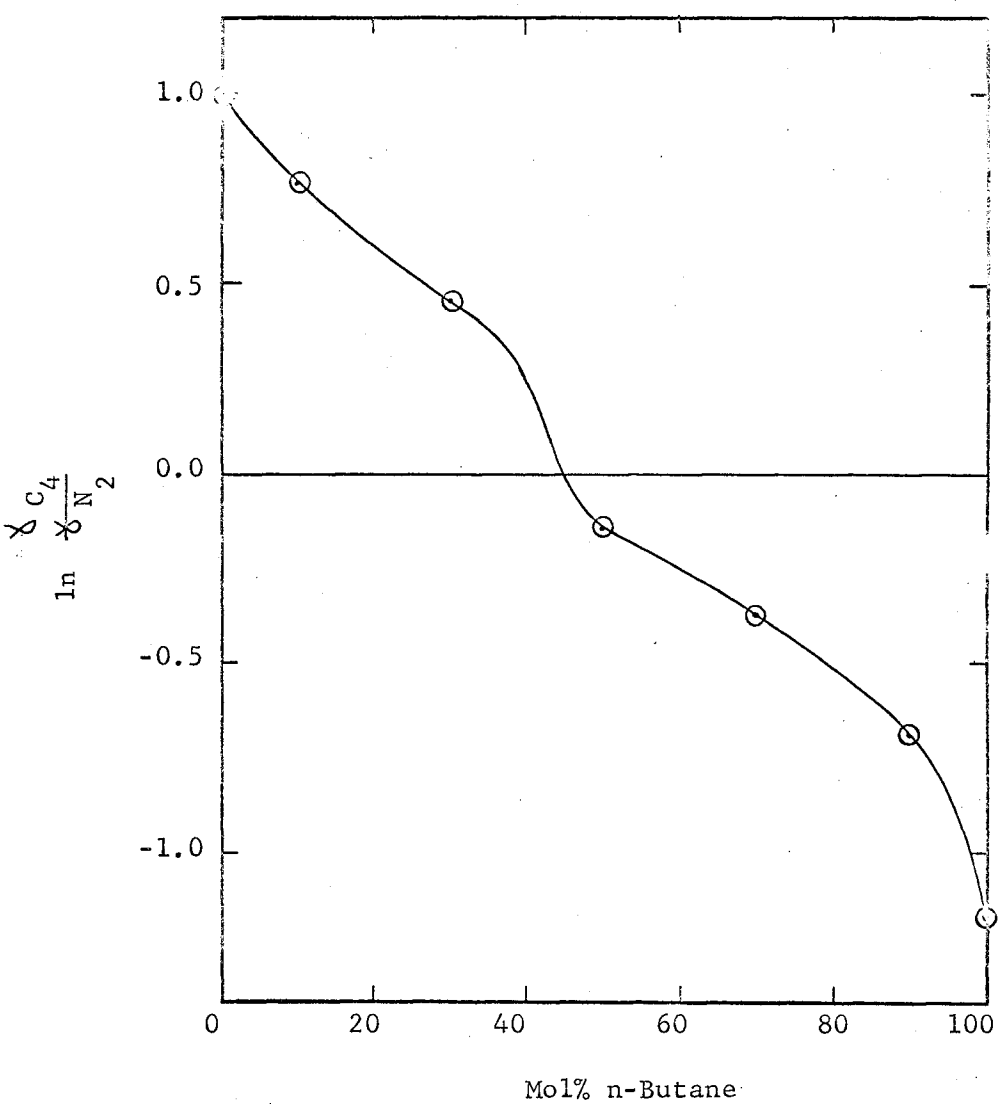


FIGURE 45

TEST FOR THERMODYNAMIC CONSISTENCY

n-BUTANE - NITROGEN MIXTURES AT 400°F and 600Atm

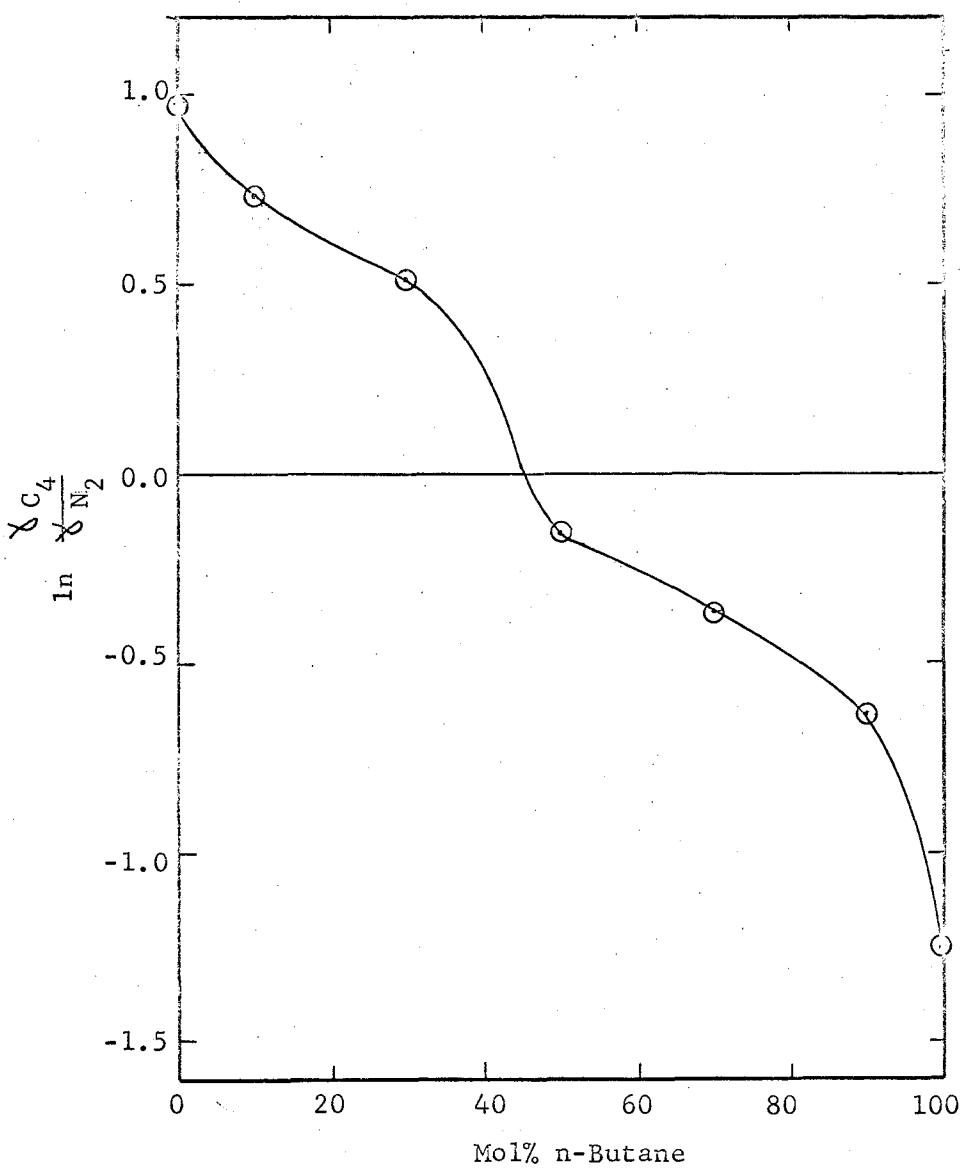
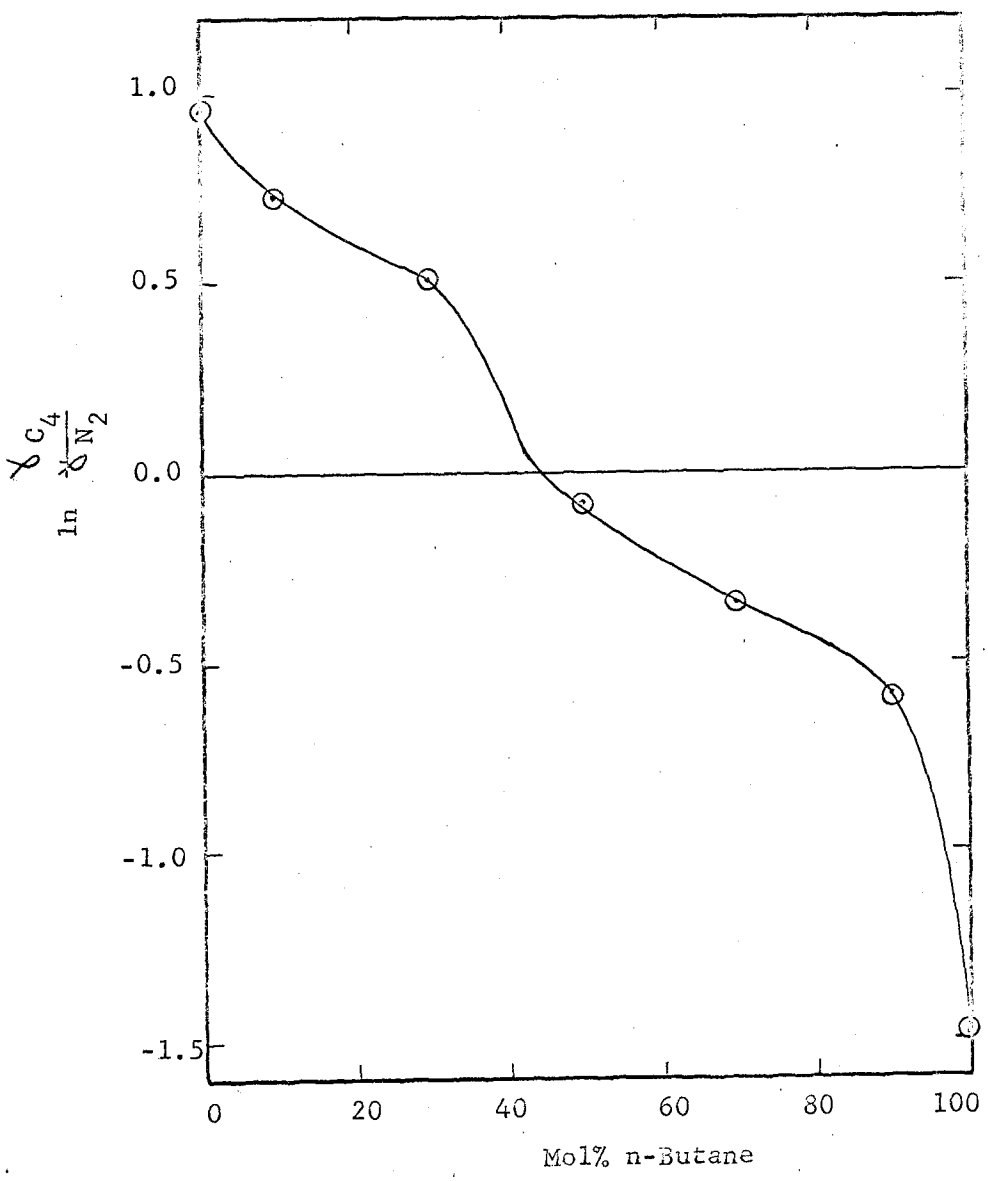


FIGURE 46

TEST FOR THERMODYNAMIC CONSISTENCY

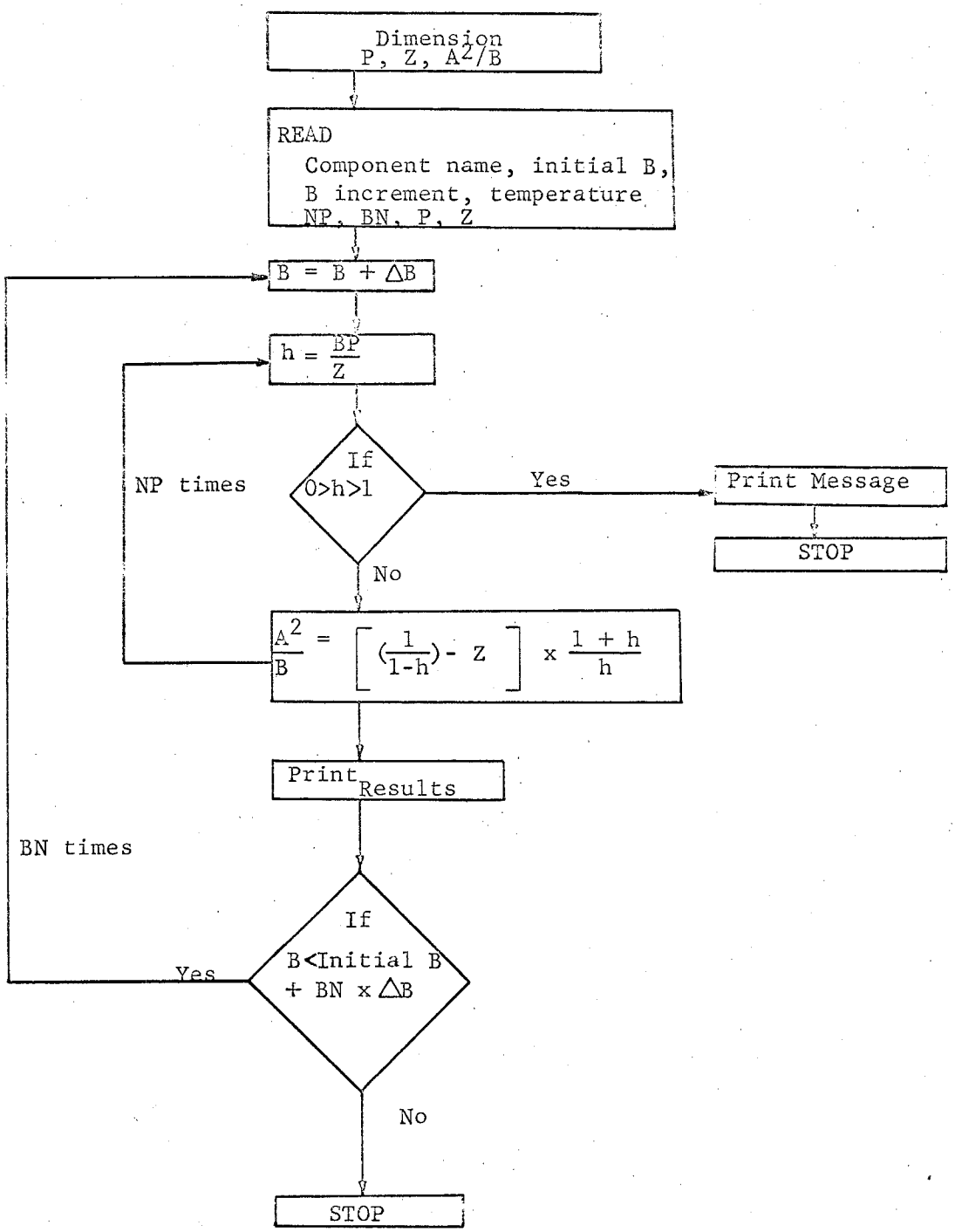
n-BUTANE - NITROGEN MIXTURES AT 400°F and 700 atm



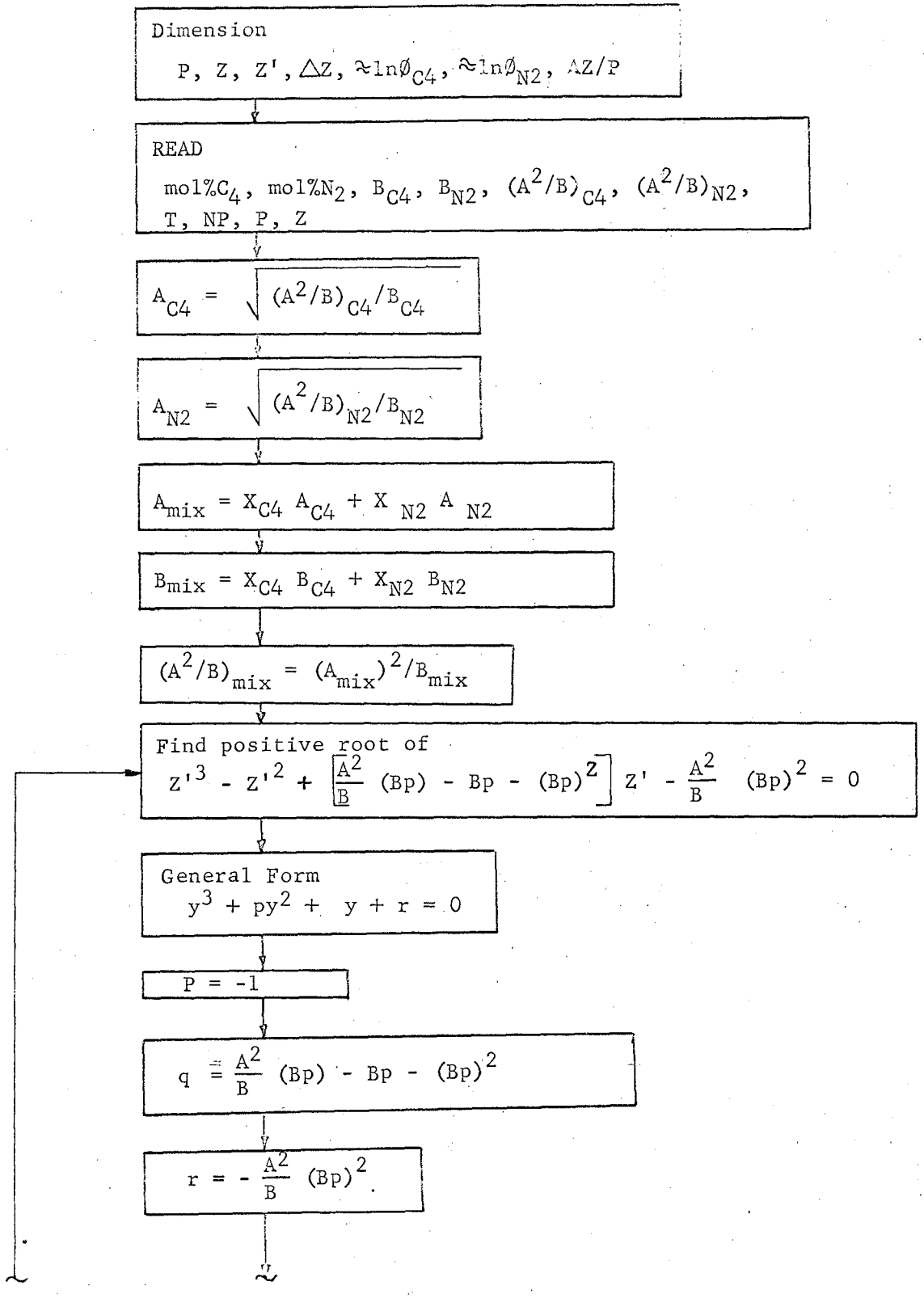
APPENDIX II

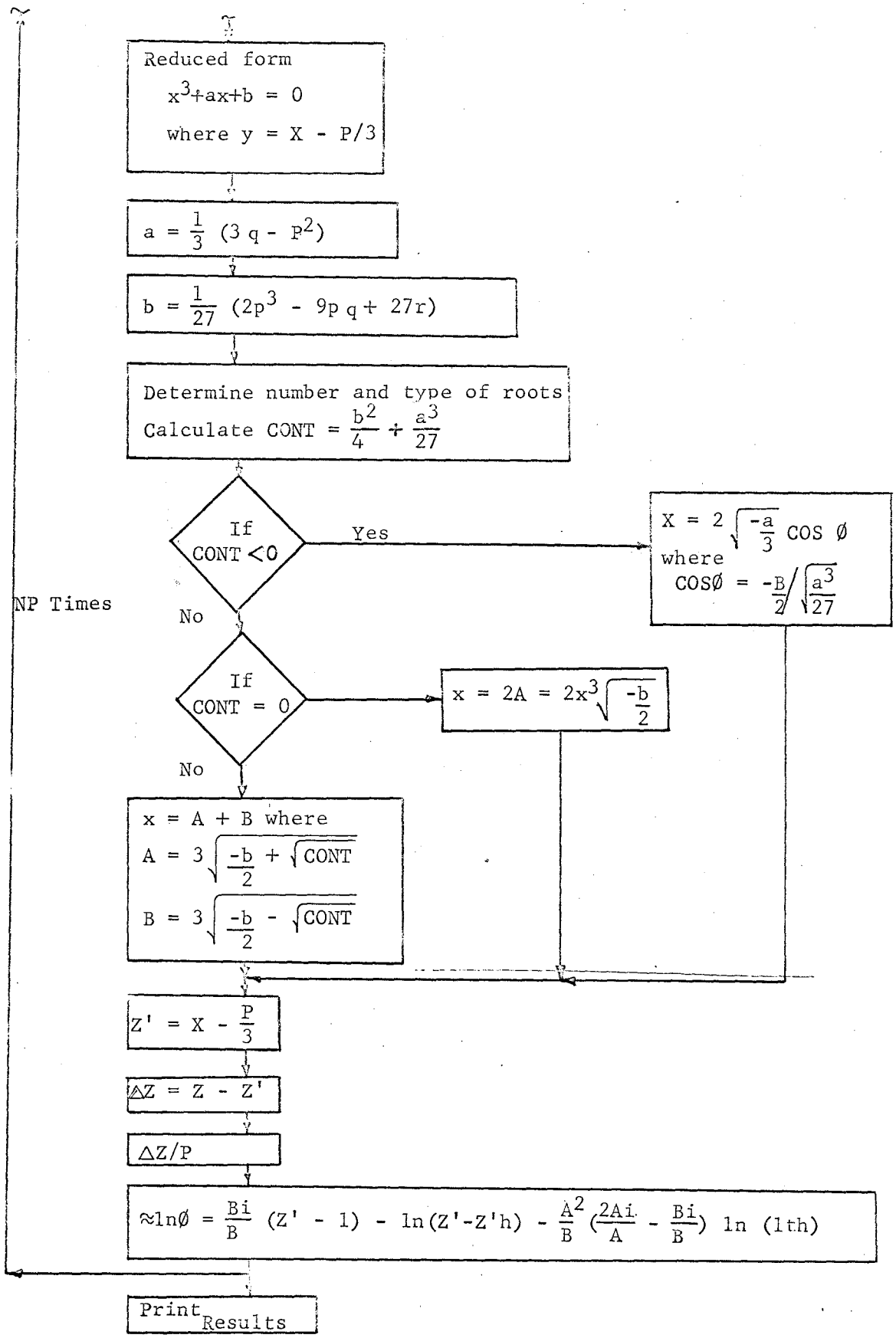
COMPUTER PROGRAMS

CALCULATION OF A^2/B CONSTANT
BLOCK DIAGRAM



CALCULATION OF Z', Z/P, AND lnØ
BLOCK DIAGRAM




Reduced form
$x^3+ax+b = 0$
where $y = X - P/3$
$a = \frac{1}{3}(3q - P^2)$
$b = \frac{1}{27}(2p^3 - 9pq + 27r)$
Determine number and type of roots
Calculate CONT = $\frac{b^2}{4} + \frac{a^3}{27}$
If CONT <0
Yes
$X = 2\sqrt{\frac{-a}{3}}\cos\phi$
where
$\cos\phi = -\frac{B}{2}\Big/\sqrt{\frac{a^3}{27}}$
NP Times
No
If CONT = 0
$x = 2A = 2x^3\sqrt{\frac{-b}{2}}$
No
$x = A + B$ where
$A = 3\sqrt{\frac{-b}{2} + \sqrt{CONT}}$
$B = 3\sqrt{\frac{-b}{2} - \sqrt{CONT}}$
$Z' = X - \frac{P}{3}$
$\Delta Z = Z - Z'$
$\Delta Z/P$
$\approx \ln\phi = \frac{Bi}{B}(Z' - 1) - \ln(Z'-Z'h) - \frac{A^2}{B}(\frac{2Ai}{A} - \frac{Bi}{B})\ln(1th)$
Print Results

APPENDIX III

DETAILED SAMPLE CALCULATION

DETAILED SAMPLE CALCULATION

The step-by-step procedure employed in calculating the constants for the Redlich and Kwong equation and then the fugacity and activity coefficients is illustrated by the following sample calculation.

Calculation of Redlich and Kwong Constants B and A^2/B

Constants are calculated by a trial procedure for the pure components of the mixture considered. To illustrate, one step of one trial is presented for n-butane at 310°F.

- Initial approximation of B; solution of equation 17.

$$B = 0.0867 \frac{T_c}{P_c T}$$

$$T_c = 305.6°F = 765.3°R$$

$$P_c = 37.5 \text{ Atm}$$

$$T = 310°F = 769.7°R$$

$$B = 0.0867 \frac{765.3}{37.5 \times 769.7}$$

$$B_{c4} = 0.002299$$

Similarly, the initial approximation of B for nitrogen at 310°F is calculated.

- Trail calculation of A^2/B; solution of equation 19.

$$\frac{A^2}{B} = \left(\frac{1}{1-h} - Z\right)\left(\frac{1+h}{h}\right)$$

$$n = \frac{Bp}{Z}$$

To illustrate the calculation assume B = 0.00227 for n-butane at 310°F. From experimental data the compressibility factor Z = 0.397 at 1500 psia (102.07 Atm).

$$h = \frac{Bp}{Z} = \frac{0.00227 \times 102.07}{0.397}$$

$$h = 0.5836$$

$$\frac{A^2}{B} = \left(\frac{1}{1 - 0.5836} - 0.397\right)\left(\frac{1 + 0.5836}{0.5836}\right)$$

$$\frac{A^2}{B} = 5.4396$$

This procedure is repeated for each pressure at which a compressibility factor is available. It has been programmed for computer calculation using Fortan IV language. The Fortran statements for this calculation are presented on page 100. A sample of the printout from this program is presented on page 102 for the trial when B = 0.00227 for n-butane.

Additional trial values of B are assumed until the value of A^2/B has a minimum variation; this determines the values of the constants for the Redlich and Kwong equation for n-butane at 310°F. Similarly, the constants for other temperatures and other components can be calculated. The constants used for the calculations are presented in Table 5.

- Calculation of A and B constants for gaseous mixtures; solution of equations 6 and 7.

  Basis: 30% n-Butane--- 70% Nitrogen at 310°F

  Constants for pure components at 310°F

	A	B	A^2/B
n-butane	0.1068	0.00227	5.0237
nitrogen	0.0220	0.00082	0.5900

$$A_{mix} = X_{c4} A_{c4} + X_{N2} A_{N2}$$

$$= 0.30 \times 0.1068 + 0.70 \times 0.0220$$

$$A_{mix} = 0.04744$$

$$B_{mix} = 0.001255$$

$$(A^2/B)_{mix} = \frac{A_{mix}^2}{B_{mix}}$$

$$= \frac{(0.04744)^2}{0.001255}$$

$$(A^2/B)_{mix} = 1.793$$

Calculation of Fugacity and Activity Coefficients

- Calculation of the compressibility as predicted by the Redlich and Kwong equation; solution of equation 4.

A form of the Redlich and Kwong equation is given by equation 4,

$$Z' = \frac{1}{1-h} - \left(\frac{A^2}{B}\right)\left(\frac{h}{1+h}\right)$$

where,

$$h = \frac{BP}{Z'}$$

Combining these equations and rearranging we obtain equation 20, i.e.,

$$Z'^3 - Z'^2 + \left[\frac{A^2}{B}(BP) - BP - (BP)^2\right] Z' - \frac{A^2}{B}(BP)^2 = 0$$

This can be put into ghe general form of the cubic equation, i.e.,

$$y^3 + py^2 + qy + r = 0$$

by letting

$$P = -1$$

$$q = \frac{A^2}{B}(BP) - BP - (BP)^2$$

and $r = -\frac{A^2}{B}(BP)^2$

The general form of the cubic can be reduced to

$$x^3 + ax + b = 0$$

by substituting $y = x - \frac{p}{3}$

$$a = \frac{1}{3}(3q - p^2)$$

$$b = \frac{1}{27}(2p^3 - 9pq + 27r)$$

The solutions of the reduced form are

$$x_1 = A + B \text{ and } x_2, x_3 = -\tfrac{1}{2}(A + B) \pm \frac{i\sqrt{3}}{2}(A - B)$$

where

$$A = \sqrt[3]{-\frac{b}{2} + \sqrt{\frac{b^2}{4} + \frac{a^3}{27}}}$$

$$B = \sqrt[3]{-\frac{b}{2} - \sqrt{\frac{b^2}{4} + \frac{a^3}{27}}}$$

If

① $\frac{b^2}{4} + \frac{a^3}{27} > 0$ there are one real root and two conjugate imaginary roots,

② $\frac{b^2}{4} + \frac{a^3}{27} = 0$ there are three real roots of which at least two are equal,

and ③ $\frac{b^2}{4} + \frac{a^3}{27} < 0$ there are three real and unequal roots

Since the desired solution will always be positive, there is only one unique solution applicable. For the first situation, which occurs most often, there is only one real solution which is the desired solution. For the second situation, this will almost never occur when utilizing computer accuracy and if it did occur, there is only one positive solution.

Should situation three occur the above solution is impractical. In this case, the roots are defined as,

$$x_1 = 2\sqrt{\frac{-a}{3}}\ \cos\ \phi$$

$$x_2 = 2\sqrt{-\frac{a}{3}}\ \cos\ (\frac{\phi}{3} + 120°)$$

$$x_3 = 2\sqrt{-\frac{a}{3}}\ \cos\ (\frac{\phi}{3} + 240°)$$

where, $\cos\ \phi = -\frac{b}{2}\Big/\sqrt{\frac{a^3}{27}}$

Here again only x_1 will yield a positive real number and is therefore the desired solution.

Application of this procedure and subsequent calculations are presented based on a 30% n-butane - 70% nitrogen mixture at 310°F and a pressure of 1500 psia (102.07 Atm).

From the previous section

$$A_{mix} = 0.04744$$

$$B_{mix} = 0.001255$$

$$(\frac{A^2}{B})_{mix} = 1.793$$

Therefore

$$P = -1$$

$$q = \frac{A^2}{B}(Bp) - Bp - (Bp)^2$$

$$Bp = 0.001255 \times 102.07$$

$$Bp = 0.1281$$

$$q = 1.793 \times 0.1281 - 0.1281 - (0.1281)^2$$

$$q = 0.0852$$

$$r = -\frac{A^2}{B}\ (Bp)^2$$

$$= -\ (1.793)\ x\ (0.1281)^2$$

$$r = -\ 0.0294$$

$$a = \frac{1}{3}\ (3q\ -(P)^2)$$

$$= \frac{1}{3}\ \left[3\ x\ 0.0852\ -\ (-1)^2\right]$$

$$a = -0.2481$$

$$b = \frac{1}{27}\left[2\ x\ (-1)^3\ -\ 9\ x\ (-1)\ x\ 0.0852\ +\ 27\ x\ (-0.0294)\right]$$

$$b = -\ 0.07507$$

$$\frac{b^2}{4} + \frac{a^3}{27} = \frac{(-0.07507)^2}{4} + \frac{(-0.2481)^3}{27}$$

$$\frac{b^2}{4} + \frac{a^3}{27} = 0.000843$$

$$A = \sqrt[3]{-\frac{b}{2} + \sqrt{\frac{b^2}{4} + \frac{a^3}{27}}}$$

$$= \sqrt[3]{-\frac{(-0.07507)}{2} + \sqrt{0.000843}}$$

$$A = 0.406$$

$$B = \sqrt[3]{0.03754\ -\ 0.02903}$$

$$B = 0.204$$

$$x = A + B$$

$$= 0.406 + 0.204$$

$$x = 0.610$$

$$x = 4\ -\ \frac{P}{3}$$

$$= 0.610\ -\ \frac{(-1)}{3}$$

$$y = 0.943$$

or equation compressibility $Z' = 0.943$

This calculation is repeated at each pressure for which experimental compressibility data are available. The procedure has been programmed using Fortran IV language, for the computer. It is part of the program presented on page 103 and sample results are given on page 107.

- Calculation of residuals

$$\triangle Z = Z - Z'$$

$$\triangle Z = 0.951 - 0.943$$

$$\triangle Z = 0.008$$

- Calculation of $\triangle Z/P$

$$\triangle Z/P = \frac{0.008}{102.07} = 0.00008$$

- Calculation of $\int_{P*}^{P} \frac{\triangle Z}{P} \, dP$

At each temperature and composition a plot of $\frac{\triangle Z}{P}$ was obtained. This plot was then graphically integrated, using a compensating polar planimeter in this instance. The plot is shown in Figure 3 and the integration is given below:

Pressure, Atm	in^2	$\triangle Z/P$ $\times 10^3$	$\triangle Z/P$ $\times 10^3$
0	0	0	0
100	3.43	9.8	9.8
200	2.56	7.31	17.11
300	2.03	5.80	22.91
400	1.90	5.43	28.34
500	2.26	6.46	34.80
600	2.43	6.94	41.74
700	2.33	6.66	48.40

$$0.7 \text{ in}^2 = 2 \times 10^{-3}$$

- Calculation of the analytical approximation of the fugacity coefficient; solution of equation 14.

$$\text{approx. } \ln\phi_i = \frac{B_i}{B}(Z'-1) - \ln(Z' - Z'h) - \frac{A^2}{B}\left(\frac{2A_i}{A} - \frac{B_i}{B}\right)\ln(1+h)$$

Solving for $\approx\ln\phi_{C4}$ where

$A_{C4} = 0.1068$

$A_{mix} = 0.04744$

$B_{C4} = 0.00227$

$B_{mix} = 0.001255$

$\left(\frac{A^2}{B}\right)_{mix} = 1.793$

$Z = 0.943$

$P = 102.07$ atm.

$h = \frac{Bp}{Z} = 0.1326$

$$\text{approx. } \ln\phi_{C4} = \frac{0.00227}{0.001255}(0.943 - 1) - \ln(0.943 - 0.943 \times 0.1326) - 1.793\left(\frac{2 \times 0.1068}{0.04744} - \frac{0.00227}{0.001255}\right) \times \ln(1 + 0.1326)$$

$$\text{approx. } \ln\phi_{C4} = -0.5137$$

Similarly, values of approx. $\ln\phi_{C4}$ and approx. $\ln\phi_{N2}$ are calculated over the desired temperature, pressure and composition range. This procedure has been programmed for computer using ~~Fortran IV language.~~ The Fortran statements are presented on pages 103 and 104 and a sample of the printout is given on pages 107, 108, and 109.

- Calculation of the graphical correction of the fugacity coefficient; solution of equation 15.

This correction factor is obtained by graphically differentiating using the method of intercepts, the curve of $\frac{\Delta z}{P}$ versus composition with parameters of pressure; Figures 8 through 11.

- Calculation of the fugacity coefficient; solution of equation 13.

The calculation of the fugacity coefficient of a component in the mixture is straightforward; the antilog of the summation of the results from the previous two sections. The analytically and graphically obtained values for $\ln\phi_i$ are presented in Tables 6 and 7 along with the respective values of the fugacity coefficients.

- Calculation of the activity coefficient; solution of equation 16.

This again is straightforward once values of the fugacity coefficient have been determined. The activity coefficient is the ratio of the fugacity coefficient of the component in the mixture and the fugacity coefficient of the pure component at the temperature and pressure of the system. Values for n-butane and nitrogen for our sample are given in Tables 6 and 7.

NOMENCLATURE

A	constant for the Redlich and Kwong equation
B	constant for the Redlich and Kwong equation
f	fugacity of gaseous mixture
fi	fugacity of pure component
h	defined as Bp/Z'
p	pressure in atmospheres
P_c	critical temperature of a component in atmospheres
P^*	zero pressure
T	absolute temperature of gas
T_c	critical temperature of a component in units consistent with T
Xi	mole fraction of component i in a gas mixture
Z	experimental compressibility factor of pure components or of the gas mixture
Z'	compressibility factor as calculated by an equation of state
γ_i	activity coefficient of component i
ϕ_i	fugacity coefficient of component i

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