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VAPOUR-LIQUID EQUILIBRIA IN THE SYSTEMS CARBON TETRACHLORIDE-TOLUENE AND N-PENTANE-BENZENE

by

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ABSTRACT

A modified recirculation Dvorak and Boublik still was used in the equilibrium determination. The vapour-liquid equilibria in the systems carbon tetrachloride-toluene were studied at five isothermal conditions. Liquid activity coefficients were evaluated. The values of γ were close to unity.

The vapour-liquid equilibria in the systems n-pentane-benzene were studied at four isothermal conditions. Liquid activity coefficients were also evaluated. Liquid-vapour equilibria at isobaric conditions were correlated using the data of heat of mixing at 25°C and the experimental $\ln \gamma$ values obtained from this work.

The $\ln \gamma$ values were correlated by means of the three-constant Redlich-Kister equation for the binary systems.

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NOMENCLATURE

B, C, D	=	constants
a, b, c	=	constants
β_{ii}	=	second virial coefficients of pure component
β_{12}	=	cross coefficient
f	=	fugacity
φ_i	=	fugacity coefficient
ΔH^E	=	heat of mixing
ΔG^E	=	excess free energy
L_i	=	partial molal enthalpy of pure component i
P	=	total pressure
p_i°	=	vapour pressure of pure component i
p_c	=	critical pressure
R	=	gas constant
T	=	absolute temperature, °K
T_c	=	critical temperature
T_r	=	reduced temperature
t	=	temperature, °C
V^L	=	liquid molal volume
V_c	=	critical molal volume
ω	=	Pitzer parameter
x_i	=	liquid mole fraction of component i
y_i	=	vapour mole fraction of component i
γ_i	=	liquid activity coefficient of component i
$\ln \gamma_i$	=	natural logarithm of liquid activity coefficient of component i
δ_{12}	=	interaction parameter
	=	$2\beta_{12} - \beta_{11} - \beta_{22}$

μ_i = chemical potential of component i

Subscripts

11, 22 = components

i, ii = components

I. INTRODUCTION

The composition of phases in equilibrium is very important in a great number of physical and chemical processes. The nature of equilibrium between phases may also be an important factor in many other problems; for example, in mixed-phase flow of liquids and gases in pipes. Many chemical reactions are carried out industrially at conditions where more than one phase exists. In these instances the equilibrium conditions are determined by the restriction of both physical equilibrium and chemical equilibrium.

Since the equilibrium relations of many systems can not be predicted from theoretical considerations, they may only be determined experimentally.

The experimental determination of vapour-liquid phase equilibria consists of the determination of the compositions of both the vapour and the liquid phase at equilibrium conditions. These determinations can be carried out either at constant temperature or at constant pressure.

The vapour-liquid equilibria of the carbon tetrachloride-toluene system have been previously investigated at isobaric condition [1-4]. Values reported by Ocon and Espantoso[1] differ only slightly from those reported by Carvey[2], but values of the latter set differ considerably from those reported by Smit and Ruyter[3] and by Rodger, Hsu and Furter[4]. From the area test[5, 6], Smit and Ruyter estimated that their data correspond to a heat of mixing of 110 ± 60 cal/mole while Carvey's data correspond to a heat of mixing of 800 cal/mole. The heat of mixing values recently reported by McGlashan, Stubley and Evatts[7] between 8° and 88.3°C. give a maximum value of only 11 cal/mole at the highest temperature, 88.3°C

which is approximately the average of the normal boiling points of the two pure components. This indicates that the thermodynamic consistency of the available isobaric data is uncertain. In order to avoid the uncertainty which is caused by the temperature effect on the liquid activity coefficients, it was decided to determine the vapour-liquid equilibrium data for the system carbon tetrachloride-toluene at isothermal conditions.

Vapour-liquid equilibrium data for aromatic-saturated hydrocarbon systems are of interest to petroleum and petrochemical industries. Equilibrium data for the binary system n-pentane-benzene have been previously investigated by Myers[8] at a constant pressure of 760 mm. Hg. Chao and Hougen[21] tested the data by means of their modified Redlich-Kister equation and calculated that the data are consistent. They suggested that the net area on a log (γ_1/γ_2) vs. x_1 plot for the system is due to the heat of mixing correction term and not to inconsistent measurements. On the other hand, Tao[22] tested the data by means of his "noise bound" and suggested that the consistency of the data is conditional. The difficulty in testing the data is due to large temperature range covered at the isobaric condition. In order to avoid the uncertainty which is caused by the temperature effect on the liquid activity coefficient, it was decided to determine the vapour-liquid equilibria of this system under isothermal conditions. Experimental equilibrium values were extrapolated to the isobaric condition of atmosphere pressure. The extrapolated data agree well with that reported by Myers.

II. THEORETICAL CONSIDERATIONS

Equilibrium implies a situation in which there is no change with respect to time. In thermodynamics, where attention is focused upon a particular quantity of material, this means no change in the properties of that material with respect to time. Actually, a true state of equilibrium is probably never reached owing to continual variations in the surroundings and to the retarding resistances. Equilibrium requires a balance of all potentials that may cause a change. However, the rate of change, and hence the rate of approach to equilibrium is proportional to the difference in potential between the actual state and the equilibrium state. Therefore the rate of change becomes very slow as equilibrium is approached.

1. Criterion of Equilibrium

A system is in equilibrium if only reversible processes can occur. Let us consider a closed system on which a constant pressure is acting as the only external force. In an infinitesimal reversible process at constant temperature, the Gibbs free energy of this system does not change, hence at equilibrium we have

$$dT = 0, \quad dP = 0, \quad dG = 0 \tag{1}$$

As applied to phase equilibrium, this criterion requires that the transfer of d(ni) moles of component i from phase (') to phase ('') must occur at equilibrium in such a way that

$$dG_{T,P} = (\bar{G}_i'' - \bar{G}_i') \, dni \tag{2}$$

if $dG_{T,P} = 0$, then $\bar{G}_i'' = \bar{G}_i'$ and this equality becomes a condition or criterion of phase equilibrium. This also can be written

$$\mu_i' = \mu_i'' \tag{3}$$

or

$$\hat{f}_i' = \hat{f}_i'' \tag{4}$$

where μ_i and f_i are the chemical potential and the fugacity of component i in a particular phase.

Thus, our criterion for equilibrium between simple phases are that:

(a) The temperature be uniform throughout the system.

(b) The pressure be uniform throughout the system.

(c) The chemical potential for each constituent be uniform throughout the system.

2. Activity Coefficients

Activity coefficients for both phases are useful for correlating the vapour-liquid equilibrium data. At constant temperature, a certain assumption may be made about the behaviour of the vapour phase which allows development of an accurate equation for the calculation of liquid phase activity coefficients from phase equilibrium data, since the activity coefficient is related to composition and is a precisely defined thermodynamics function. By definition

$$\gamma_i^L = \frac{\hat{f}_i^L}{x_i f_i^{\circ L}} \tag{5a}$$

$$\gamma_i^V = \frac{\hat{f}_i^V}{y_i f_i^{\circ V}} \tag{5b}$$

where f_i° is the reference fugacity at the standard state which is that of the system temperature and pressure. As a result of the criterion of equilibrium

$$\hat{f}_i^L = \gamma_i^L x_i f_i^{\circ L} = \gamma_i^V y_i f_i^{\circ V} = \hat{f}_i^V \tag{6a}$$

or

$$\gamma_i^L = \frac{y_i}{x_i} \frac{f_i^{\circ V}}{f_i^{\circ L}} \gamma_i^V = \frac{y_i}{x_i} \frac{f_i^{\circ V}/P}{f_i^{\circ L}/P} \gamma_i^V \tag{6b}$$

or

$$\ln \gamma_i^L = \ln \frac{y_i}{x_i} + \ln \frac{\varphi_i^V}{\varphi_i^L} + \ln \gamma_i^V \tag{6c}$$

where $\varphi_i = f_i^\circ/P$, is the fugacity coefficient. Since we are dealing with constant temperature and low pressure cases, we can take the simplest form of the virial equation of state to represent the volumetric behaviour of the vapour phase with more than adequate accuracy. Such that[9]

$$\ln \varphi_i^V = \frac{\beta_{ii} P}{RT} \tag{7}$$

The liquid phase $\ln \varphi_i^L$ must be calculated in two parts. At temperature, T, and at the vapour pressure of pure component i, the fugacity coefficient of the liquid phase is equal to the fugacity coefficient of the vapour phase and is therefore given by the same equation

$$\ln \varphi_i^\circ = \frac{\beta_{ii} P_i^\circ}{RT} \tag{8}$$

where the (°) indicates values at the saturated pressure. The change in $\ln \varphi_i^L$ in going from the vapour pressure, P_i°, to the solution P is given

$$\ln \varphi_i^L - \ln \varphi_i^\circ = \frac{1}{RT} \int_{P_i^\circ}^{P} (V_i^L - \frac{RT}{P}) \, d\, P$$

or

$$\ln \varphi_i^L = \frac{\beta_{ii} P_i^\circ}{RT} + \frac{1}{RT} \int_{P_i^\circ}^{P} V_i^L \, dP - \ln \frac{P}{P_i^\circ} \tag{9}$$

Since the volumes of liquids are insensitive to small changes in pressure, V_i^L may be taken as constant in the integration. Therefore

$$\ln \varphi_i^L = \frac{\beta_{ii} P_i^\circ}{RT} + \frac{V_i^L}{RT} (P - P_i^\circ) - \ln \frac{P}{P_i^\circ} \tag{10}$$

combining the equations for φ_i^V and φ_i^L, we have

$$\ln \frac{\varphi_i^V}{\varphi_i^L} = \ln \varphi_i^V - \ln \varphi_i^L = \frac{\beta_{ii}}{RT} (P - P_i^\circ) - \frac{V_i^L}{RT} (P - P_i^\circ) + \ln \frac{P}{P_i^\circ} \tag{11}$$

Substitution of equation 11 into equation 6 gives

$$\ln \gamma_i^L = \ln \frac{y_i P}{x_1 P_i^\circ} + \frac{(\beta_{ii} - V_i^L)(P - P_i^\circ)}{RT} + \ln \gamma_i^V \tag{12}$$

If the vapour phase is assumed to be an ideal solution (but not an ideal gas) then $\gamma_i^V = 1$, and the last term of equation 12 is zero. This introduced an additional approximation which is frequently not justified. For binary solutions we have the following two simple equations[11]

$$\ln \gamma_1^V = \frac{P \delta_{12} y_2^2}{RT} \tag{13}$$

$$\ln \gamma_2^V = \frac{P \delta_{12} y_1^2}{RT} \tag{14}$$

Thus for a binary solution at low pressure and constant temperature

$$\ln \gamma_1^L = \ln \frac{y_1 P}{x_1 P_1^\circ} + \frac{(\beta_{11} - V_1^L)(P - P_1^\circ)}{RT} + \frac{P \delta_{12} y_2^2}{RT} \tag{15}$$

$$\ln \gamma_2^L = \ln \frac{y_2 P}{x_2 P_2^\circ} + \frac{(\beta_{22} - V_2^L)(P - P_2^\circ)}{RT} + \frac{P \delta_{12} y_1^2}{RT} \tag{16}$$

where

y = mole fraction of component in the vapour phase

x = mole fraction of component in the liquid phase

P = total pressure

P_i° = vapour-pressure of the pure component i

V_i^L = molal volume of the liquid in the liquid state

β_{ii} = second virial coefficient

R = gas constant

T = temperature of the system

δ = interaction parameter

$= 2\beta_{12} - \beta_{11} - \beta_{22}$

β_{12} = cross second virial coefficient

γ_1^L, γ_2^L = activity coefficient (The superscript L herewith is omitted).

These equations allow the calculation of liquid phase activity coefficients for binary solutions at constant temperature from vapour-liquid equilibrium data and a minimum of volumetric information.

3. Temperature Effect on Liquid Activity Coefficients

For the constituent i in solution we write

$$\hat{a}_i = \frac{\hat{f}_i}{f_i^\circ} \tag{17}$$

clearly

$$\gamma_i = \frac{\hat{a}_i}{x_i} \tag{18}$$

The activity of a component in a nonideal solution is defined by

$$d\mu_i = RT\, d \ln \hat{a}_i \quad \text{(at constant T, P)} \tag{19}$$

where μ_i is the chemical potential of component i. Integrating this equation,

$$\mu_i = \mu_i^* + RT \ln \hat{a}_i \quad \text{(at constant T, P)} \tag{20}$$

where μ_i^* refers to the molar Gibbs free energy of pure component i as liquid at constant temperature and pressure of the solution. Substituting equation 18 into equation 20, and dividing both sides of the resulting equation by T, we obtain

$$\frac{\mu_i}{T} = \frac{\mu_i^*}{T} + R \ln x_i + R \ln \gamma_i \tag{21}$$

Partial differentiation of this equation with respect to temperature at constant pressure and constant composition gives

$$\frac{\partial (\mu_i/T)}{\partial T} = \frac{\partial (\mu_i^*/T)}{\partial T} + \frac{\partial \ln \gamma_i}{\partial T} \quad \text{(at constant P, x)} \tag{22}$$

or

$$-\frac{\bar{H}_i}{T^2} = -\frac{\tilde{H}_i}{T^2} + R\,\frac{\partial \ln \gamma_i}{\partial T} \quad \text{(at constant P, x)}$$

rearranging,

$$\frac{\partial \ln \gamma_i}{\partial T} = \frac{\tilde{H}_i - \bar{H}_i}{RT^2} = \frac{-L_i}{RT} \quad \text{(at constant P, x)} \qquad (23)$$

This is the expression for the temperature dependence of the activity coefficients. L_i is the partial molal enthalpy of component i in solution minus the enthalpy of the pure liquid at the same temperature.

From equation 23 it may be deducted that if L is a positive quantity (heat is absorbed) the activity coefficient decreases with temperature. On the other hand, when L is a negative quantity (heat is evolved), the activity coefficient increases with temperature. The magnitude of variation of activity coefficients with temperature depends on the quantity L.

4. Temperature Dependence of the Relative Partial Molar Enthalpy

In order to correlate the relative partial molar enthalpies L_1 and L_2 with temperature and therefore to determine the variation of activity coefficient with temperature, the knowledge of heats of mixing is essential. The quantity ΔH_N^M may be expressed as a function of temperature in the following manner.[11]

$$\Delta H_N^M = b'(n_1, n_2) + c'(n_1, n_2)\,T + d'(n_1, n_2)\,T^2 + \ldots \qquad (24)$$

where $b'(n_1, n_2)$, $c'(n_1, n_2)$, $d'(n_1, n_2)$ are functions of n_1 and n_2 only. Differentiating equation 24 with respect to n_1,

$$\frac{\partial (\Delta H_N^M)}{\partial n_1} = b(n_1, n_2) + c(n_1, n_2)\, T + d(n_1, n_2)\, T^2 + \ldots$$

$$= L_1 \qquad (25)$$

It is seen therefore the quantities L_1 and L_2 have the same temperature terms as the quantity ΔH_N^M. The simplest four temperature functions for ΔH_N^M are discussed here. For simplicity, only L_1 will be considered in cases 2 to 4.

Case I $\Delta H_N^M = 0$, therefore $L_1 = L_2 = 0$, and

$$\frac{\partial \ln \gamma_1}{\partial T} = \frac{\partial \ln \gamma_2}{\partial T} = 0$$

The activity coefficients are independent of temperature.

Case II At constant composition, ΔH_N^M = constant. Therefore L_1 = constant and

$$(\ln \gamma_1)_x = a + b/T \qquad (26)$$

This is the equation proposed by Yu and Coull[12]. If $a = 0$, equation 26 represents the condition proposed by White[13], Li and Coul[14] and Robinson and Gilliland[15].

Case III At constant composition, ΔH_N^M is a linear function of temperature.

$$\Delta H_N^M = b' + c' T \qquad (27)$$

Therefore

$$L_1 = b + c T \qquad (28)$$

and

$$(\ln \gamma_1)_x = a + b/T - c \ln T \qquad (29)$$

Case IV At constant composition

$$\Delta H_N^M = b' + c'T + d'T^2 \tag{30}$$

Therefore $L_1 = b + cT + dT^2$ (31)

$$(\ln \gamma_1)_x = a + b/T - c \ln T + dT \tag{32}$$

These equations were developed by Lu[11]. In many cases, over a moderate range of temperature and at constant liquid compositions that the quantity L is a linear function of temperature (equation 29) provides a good approximation. Therefore the activity coefficient for a component at constant composition should follow the temperature terms as indicated in equation 29.

5. Modification of the Redlich-Kister Equation[11]

Redlich and Kister proposed the following equation for representing the liquid activity coefficient at isothermal conditions.

$$\ln \gamma_1 = x_2^2 [B + C(4x_1 - 1) + D(2x_1 - 1)(6x_1 - 1) + \ldots] \tag{33}$$

$$\ln \gamma_2 = x_1^2 [B + C(4x_1 - 3) + D(2x_1 - 1)(6x_1 - 5) + \ldots] \tag{34}$$

The quantities B, C and D in equations 33 and 34 may be modified for representing isobaric conditions by including temperature terms as expressed by equation 29.

$$B = a + b/T - c \ln T \tag{35}$$

$$C = a' + b'/T - c' \ln T \tag{36}$$

$$D = a'' + b''/T - c'' \ln T \tag{37}$$

Therefore, equations 33 and 34 become

$$\ln \gamma_1 = (1 - x_1)^2 \left[a + b/T - c \ln T + (a' + b'/T - c' \ln T)(4x_1 - 1) + (a'' + b''/T - c'' \ln T)(2x_1 - 1)(6x_1 - 1) + \ldots\right] \quad (38)$$

$$\ln \gamma_2 = x_1^2 \left[a + b/T - c \ln T + (a' + b'/T - c' \ln T)(4x_1 - 3) + (a'' + b''/T - c'' \ln T)(2x_1 - 1)(6x_1 - 5) + \ldots\right] \quad (39)$$

6. Thermodynamic Consistency Test

The thermodynamic consistency of the binary system may be conveniently tested by the equation[5]

$$\int_{x_1 = 0}^{x_1 = 1.0} \ln \gamma_1/\gamma_2 \, d x_1 = 0 \quad \text{(constant T, P)} \quad (40)$$

This method is the so called area test which is attributed to Redlich-Kister. By plotting experimental data of $\ln \gamma_1/\gamma_2$, against x_1 from 0.0 to 1.0, the net area of the curve is equal to zero, or the area above the abscissa axis is equal to the area below that axis.

III. EXPERIMENTAL DETAILS

1. Description of Apparatus

A modified recirculation Dvorak and Boublik[16] still was used in the equilibrium determination. The still was made in pyrex glass. Details of the design are shown in Fig. 1. In the design, two modifications were made during this investigation:

(1) The circulation loop in the evacuated chamber (D in fig. 1) was shortened to reduce the pressure drop.

(2) A well for an electrical heater was made in the boiling vessel.

The Cottrell pump together with the circulation loop ensure the achievement of equilibrium. The long thermometer well (E) ensures good temperature measurement. Magnetic stirrers were placed in the liquid reservoir and the condensate reservoir. The stirring of the liquid prevents any possible density gradients occurring in the reservoirs.

A vacuum system connected to the condensate reservoir (G) and a Swietoslawski Ebuliometer[17] (Fig. 2) was employed to regulate the total pressure, therefore the temperature, of the system. The total pressure of the system was determined from the boiling temperature of the distilled water in the ebuliometer. Boiling temperature of the water was measured by means of a calibrated copper-constantan thermopile in conjunction with a Cambridge microstep potentiometer.

FIGURE 1

Modified Dvorak and Boublik Still

A	boiling vessel
B	liquid reservoir
C	vapour and liquid separator
D	evacuated chamber
E	thermometer well
F	condenser
G	condensate reservoir
H	mixing vessel
I	cooling jacket
J	heater well
K	Cottrell pump

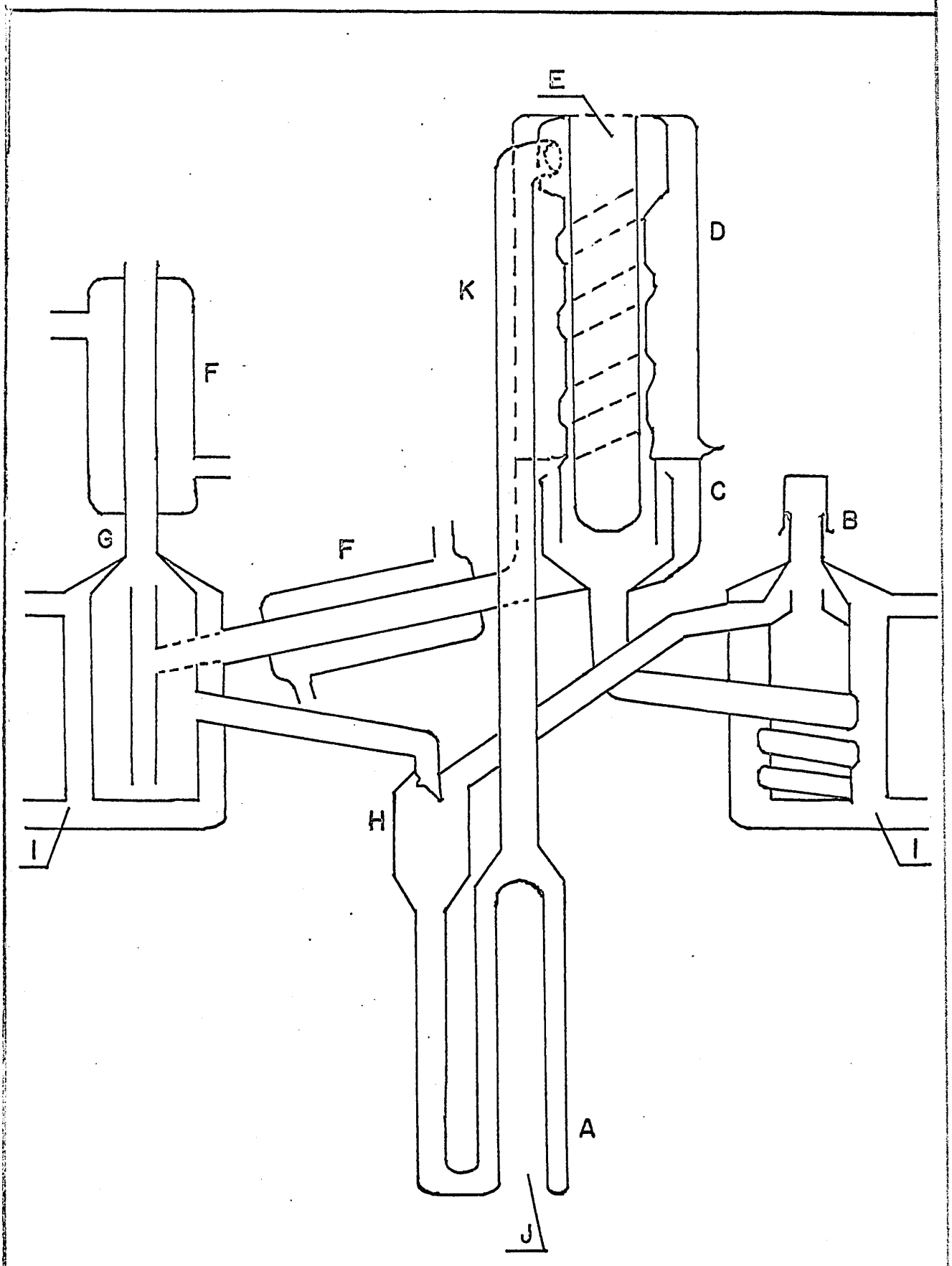

Fig. 1 Modified Dvorak and Boublik Still

FIGURE 2

Ebuliometer

A	boiling vessel
B	jacket
C	thermometer well
D	condenser
E	heater well

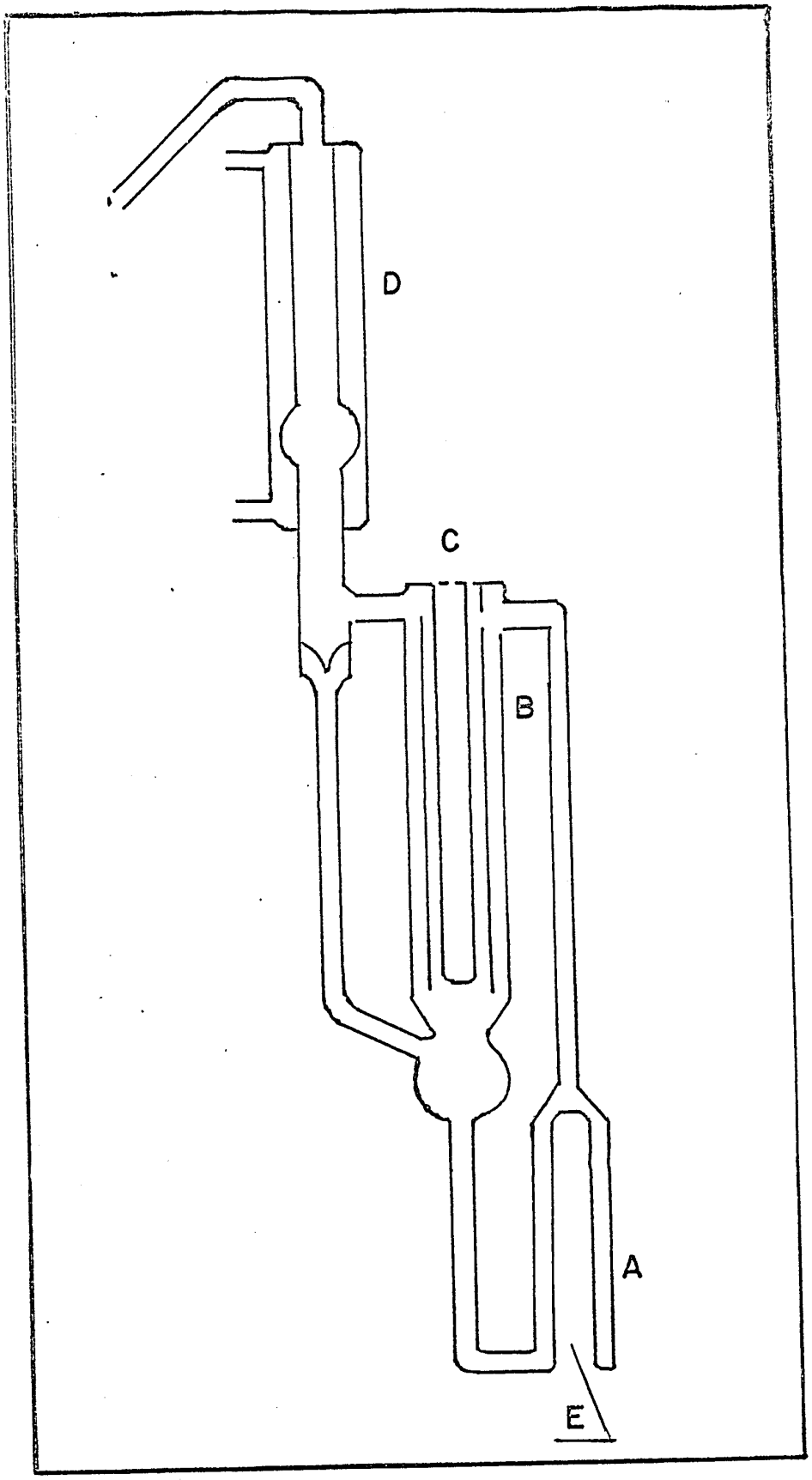

Fig. 2 Ebuliometer

2. Chemicals

The benzene and toluene were of research grade and were supplied by Phillips Petroleum Company. The carbon tetrachloride (99.9 mole % minimum) and n-pentane(99.9 mole % minimum) were supplied by Matheson, Coleman and Bell Company. They were used without further purification. Physical properties of the materials used are listed in Tables 2-6.

3. Procedure

Experimental procedure may be presented as follows:

A. Still - (1) Fill the liquid container, the condensate container and the boiling vessel to the positions marked on the necks of the vessels. The total amount of liquid required in the still is about 120 ml.

(2) Insert stirrers into the containers for the liquid phase and the condensate.

(3) Close the liquid phase container. Attach the condensate container to the vacuum system.

(4) Open cooling water and switch on the heater at low voltage.

B. Ebuliometer - (1) Fill the ebuliometer with distilled water up to the position marked on the boiling vessel.

(2) Open cooling water and switch on the heater at low voltage simultaneously with the still.

C. Still and Ebuliometer - (1) Regulate the system pressure as soon as the Beckmann thermometer in the thermometer well (E) of the still is steady at the required temperature. Maintain this

temperature for one and a half hours with steady circulation to ensure that the equilibrium is reached. Then the temperature is taken in the ebuliometer by means of a calibrated copper-constantan thermopile in conjunction with a Cambridge microstep potentiometer. The temperature taken is the boiling point of the distilled water in the ebuliometer at the existing pressure of the system. Therefore the system pressure may be calculated from the steam table at the known temperature.

(2) Switch off the heaters in the still and ebuliometer and introduce dry nitrogen to increase the system pressure to barometric pressure.

(3) Withdraw the samples of liquid and condensate phases from both containers by using syringes. In order to prevent liquid from vaporizing and changing the compositions of both samples caused by sudden rise in room temperature, keep the samples of both phases in a ice box.

D. Circulation Rate of the Still - The circulation rate of the still was optimized by changing the rate of circulation and measuring the reading in millivolt of the potentiometer at the normal boiling point of water. The following measurements were made in this investigation.

Circulation in drops/min	Reading in millivolt
28	214718
35	214727
38	214731
42	214732
46	214732
52	214732
56	214735

Circulation in drops/min	Reading in millivolt
60	214740
65	214755
70	214770

A graph of millivolt reading against circulation rate was plotted (Fig. 3). It showed that the best circulating rate of the still was 40-50 drops/ min. at which the temperature might be kept constant.

4. Calibration of Thermopile

The thermopile used in this investigation was a five-junction thermocouple made of copper constantan. The temperatures were calibrated against the vapour pressure of conducting grade distilled water. The calibration table prepared based upon the smoothed experimental measurements is given in Table 1.

5. Analysis of Samples

Prior to determination of the compositions of the vapour and liquid phases, a calibration of the refractive index-composition for the system under study was carried out by measuring the refractive indices of the binary mixtures of known compositions. The compositions were determined analytically by weighing samples individually with an analytical balance. The refractive indices were observed at 25°C by using a Bausch and Lomb Abbe 3-L precision refractometer. The results are summarized in Figures 7 and 8 and details are given in Tables 7 and 8. The reproducibility obtained in the calibration was accurate to $\pm$ 0.0003 mole fractions and the error in the reported equilibrium compositions is of the same magnitude. Prior to the measuring of the refractive index,

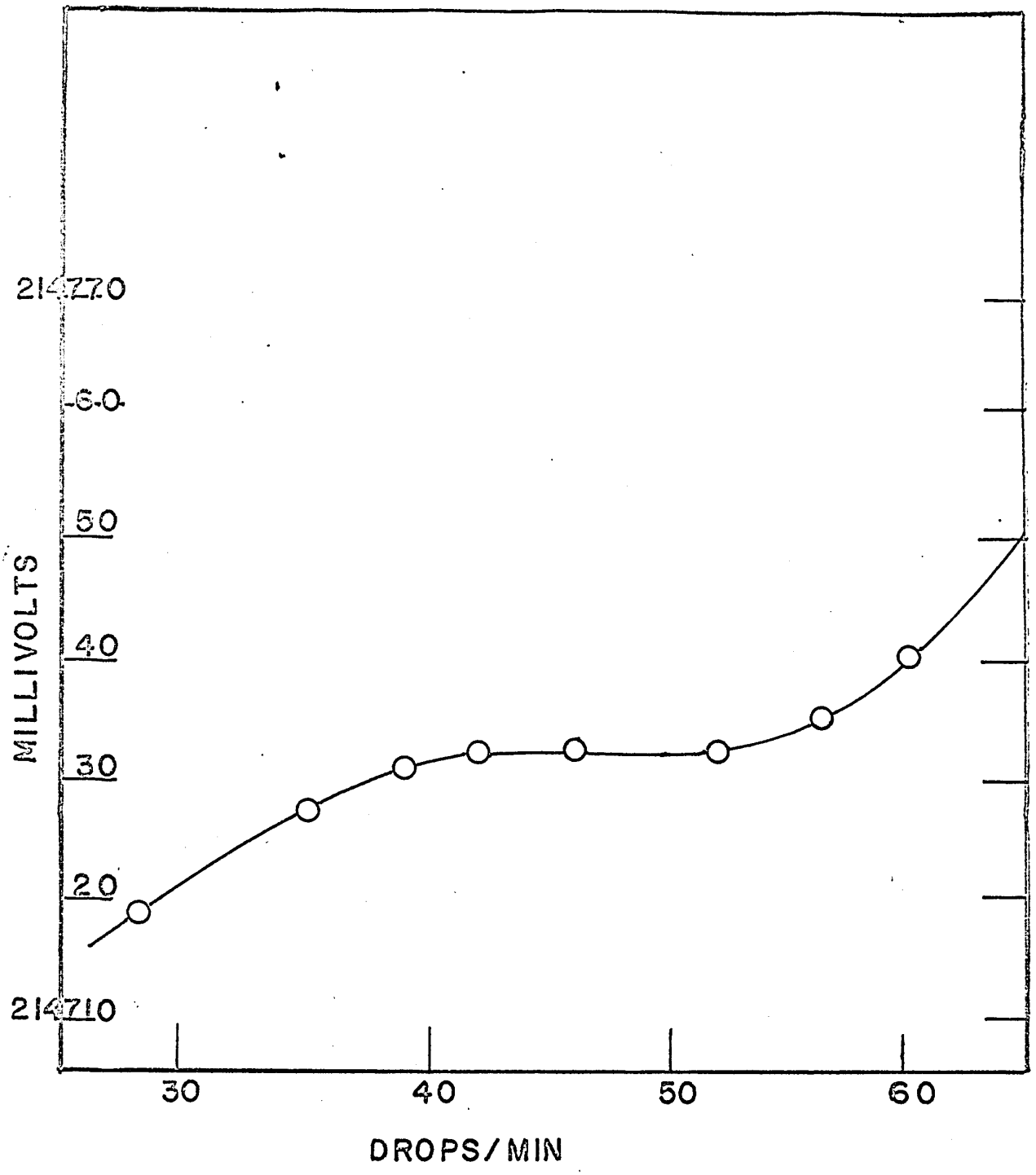

Fig. 3 Optimized Rate of Circulation of Still

the refractometer was allowed to half an hour after start-up to reach its operating temperature of 25°C. The refractometer was cleaned three times with acetone and was dried with compressed nitrogen gas. A few drops of sample were introduced into the refractometer and the index reading was then taken. By comparing the result with the calibration curve of index-composition of the system investigated, the composition was then obtained. A schematic diagram of the experimental apparatus is shown in Figure 4.

FIGURE 4

Schematic Diagram of Experimental Apparatus

1. Vacuum pump
2. three way stop cock
3. trap
4. two way stop cock
5. first reservoir
6. valve
7. magnetic valve
8. second reservoir
9. manostat
10. three way stop cock
11. ebuliometer
12. still
13. manometer

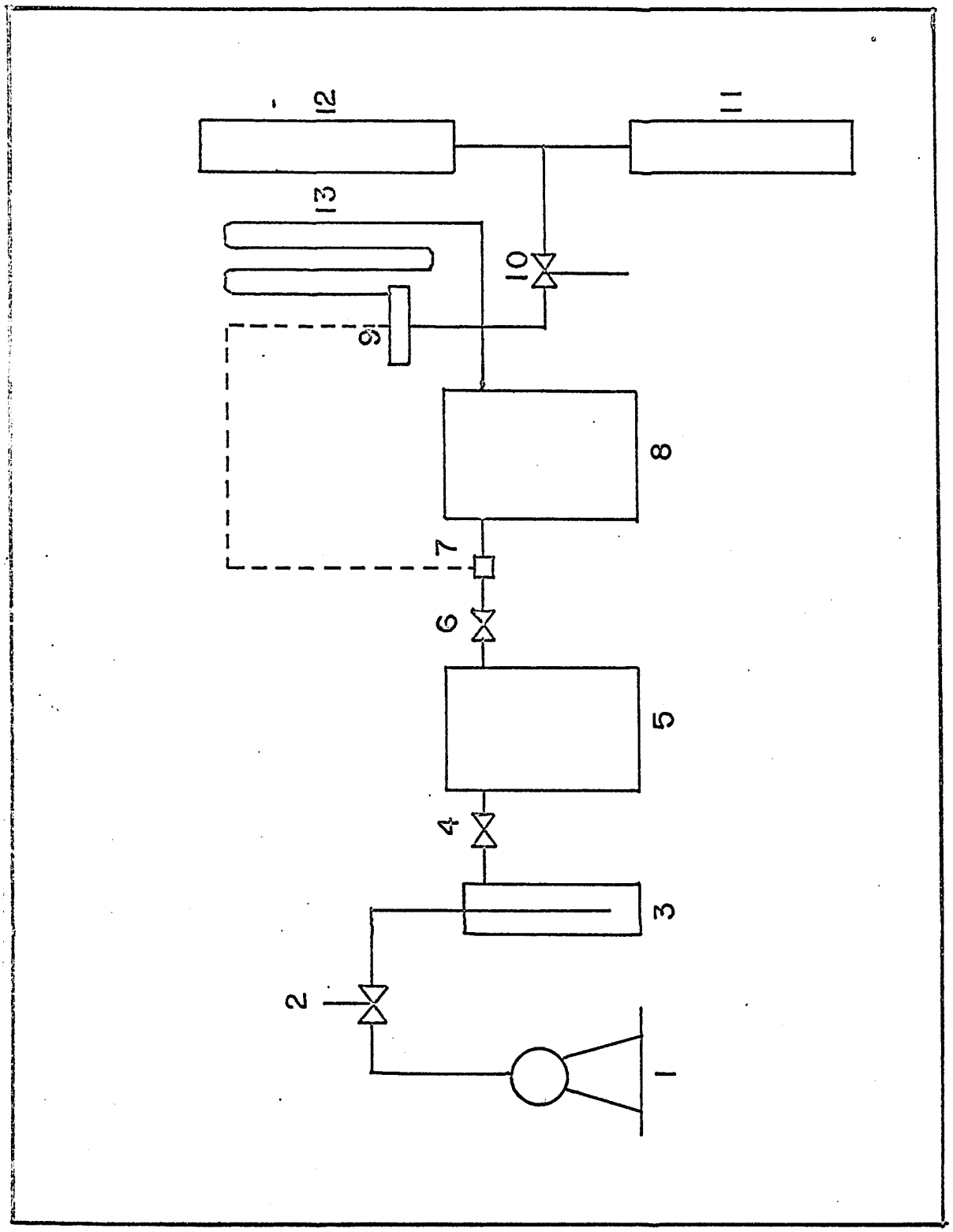

Fig. 4 Schematic Diagram of Experimental Apparatus

IV. RESULTS AND CORRELATIONS

The results of the physical properties of pure compounds and vapour-liquid equilibrium of the systems carbon tetrachloride-toluene and n-pentane-benzene investigated in this study are presented in this section. The correlation of the results is also included.

1. Physical Properties of the Pure Compounds

(a) Second Virial Coefficients

The second virial coefficients of the chemicals used β_{ii}, were calculated according to the equation of Pitzer and Curl[18].

$$\frac{B P_c}{R T_c} = (.1445 + .073\omega) - (.330 - .460\omega) T_r^{-1} - (.1385 + .500\omega) T_r^{-2} - (.0121 + .097\omega) T_r^{-3} - .0073\omega T_r^{-8} \quad (41)$$

The critical constants used in the calculation are listed in Table 2.

The second virial coefficients calculated from equation 41 at the temperatures investigated are tabulated in Table 3.

(b) Liquid Molal Volumes

Liquid molal volumes at 25°C were calculated from literature data[19]. The molal volumes at other temperatures were calculated from equation 42.

$$V^L = V_C / \left[1 + a\,(1 - T_r) + (1 + a)(1 - T_r)^{\frac{1}{3}} \right] \quad (42)$$

in which α was determined from the literature value at one temperature. Numerical values of molal volumes for pure components so calculated at temperatures desired are presented in Table 4. These values were checked experimentally for temperatures equal or below the room temperature. The agreements are excellent. However, at temperatures higher than the room temperature, the determination of density was difficult, all values were taken from the calculated results.

(c) Vapour Pressures

Vapour pressures of pure components were calculated from Antonine equation

$$\log_{10} P = A - \frac{B}{C + t^{\circ} C} \qquad (43)$$

the constants A, B, C in equation 43 are taken from the literature[19] and listed in Table 5. The numerical values of vapour pressure at desired temperatures are tabulated in Table 6.

2. Experimental Results

(a) The experimental total pressure-composition data at 35°C, 40°C, 45°C, 55°C and 65°C for the system of carbon tetrachloride-toluene, and also at 35°C, 40°C, 45°C and 50°C for the system of n-pentane-benzene are presented in Tables 9 to 17 and shown in Figures 9 and 20.

(b) Liquid activity coefficients for the system of carbon tetrachloride-toluene, evaluated by using equation 15 and 16 at five isotherms are listed in Tables 9 to 13, and shown in Figures 10 to 14.

(c) Liquid activity coefficients for the system of n-pentane-benzene at four isotherms are listed in Tables 14 to 17 and shown in Figures 21 to 24.

(d) Ratio of liquid activity coefficients for the system of carbon tetrachloride-toluene at five isotherms are listed in Tables 9 to 13 and shown in Figures 15 to 19.

(e) Ratio of liquid activity coefficients for the system of n-pentane-benzene at four isotherms are listed in Tables 14 to 17 and shown in Figures 25 to 28. The activity coefficients calculated from equations 33 and 34 using correlated constants B, C, D are also included in the Tables 9 to 13 for the system carbon tetrachloride-toluene and in the Tables 14 to 17 for the system n-pentane-benzene.

3. Correlation by Means of the Redlich-Kister Equation at Constant Temperature

The experimental activity coefficients data may be correlated by means of an integrated Gibbs-Duhem equation such as the Redlich-Kister equation[5]

$$\ln \gamma_1 = (1 - x_1)^2 \left[B + C\,(3x_1 - x_2) + D\,(x_1 - x_2)(5x_1 - x_2) + \ldots\right] \quad (33)$$

$$\ln \gamma_2 = (x_1^2) \left[B + C\,(x_1 - 3x_2) + D\,(x_1 - x_2)\,(x_1 - 5x_2) + \ldots\right] \quad (34)$$

Combining equations 33 and 34 gives

$$\ln \gamma_1/\gamma_2 = B\,(1 - 2x_1) + C\,(6x_1x_2 - 1) + D\,(1 - 2x_1)\,(1 - 8x_1x_2) \quad (44)$$

The constants B, C, and D were determined by means of the method of least squares. The constants obtained are listed in Table 18.

4. Thermodynamic Consistency Test

The method of area test was adopted in this work. The activity coefficients of carbon tetrachloride-toluene taken from Table 9 to 13 were integrated graphically over the whole concentration range for each isotherms. The results are presented in Table 19. It may be seen that the net area is less than $\pm 8 \times 10^{-3}$, which may be considered thermodynamically consistent.

Similar work was carried out for the system n-pentane-benzene for each isotherms. Results were also obtained and included in Table 19.

5. Correlation of Activity Coefficient in Terms of Temperatures for the System n-Pentane-Benzene

As discussed in the early section, the activity coefficients at constant compositions may be represented by equation 29.

$$\ln \gamma_j = a_j + b_j/T_i - c_j \ln T_i \qquad (29)$$

From the smoothed values of $\ln \gamma_j$ at different temperatures and the relative partial molal enthalpies L_j[20] at 25°C (Figure 29), the parameter a, b, c may be calculated by means of the method of least squares.

The values of a, b, c for first and second components are presented in Table 20 and Table 21.

Alternately the temperature dependence of the activity coefficients may also be represented by the modified Redlich-Kister equation as suggested by Lu[11] in which the constant B, C, D

are expressed in terms of temperatures, namely

$$B = a + b/T - c \ln T \tag{35}$$

$$C = a' + b'/T - c' \ln T \tag{36}$$

$$D = a'' + b''/T - c'' \ln T \tag{37}$$

From the characteristic points of the Redlich-Kister equation, B, C, D, can be solved by choosing three suitable points

at $x = 0.2959$

$$\ln \gamma_1/\gamma_2 = .4082\,(B - 2D/3) + \frac{c}{4}$$

$$\ln \gamma_1/\gamma_2 = \Delta a_1 + \Delta b_1/T - \Delta c_1 \ln T$$

Therefore

$$.4082\,(B - 2D/3) + \frac{c}{4} = \Delta a_1 + \Delta b_1/T - \Delta c_1 \ln T \tag{45}$$

Similarly,

at $x_1 = 0.5$

$$c/2 = \Delta a_2 + \Delta b_2/T - \Delta c_2 \ln T \tag{46}$$

and

at $x_1 = 0.8536$

$$-.7071B - c/4 = \Delta a_3 + \Delta b_3/T - \Delta c_3 \ln T \tag{47}$$

where Δa_1, Δa_2, Δa_3, Δb_1, Δb_2, Δb_3, Δc_1, Δc_2, Δc_3 are constants which can be obtained by reading off from Figures 30, 31 and 32. The numerical values are listed below:

x_1	Δa_i	Δb_i	Δc_i
.2959	137.775	-6272.190	20.446
.5000	37.604	-1701.030	5.605
.8536	-181.900	8340.217	-26.933

Then B, C and D can be obtained by solving Equations 45, 46 and 47 simultaneously. Following two equations are then resulted

$$\ln \gamma_1 = (1-x_1)^2 \{230.545 - 1059.498/(t+273.16) - 34.1256 \ln (t+273.16) + [75.243 - 3401.168/(t+273.16) - 11.209 \ln (t+273.16)](4x - 1) + [-91.3603 + 4035.1378/(t+273.16) + 13.644 \ln (t+273.16)](2x_1 - 1) \times (6x_1 - 1)\} \ldots \quad (48)$$

$$\ln \gamma_2 = x_1^2 \{230.545 - 1059.498/(t+273.16) - 34.1256 \ln (t+273.16) + [75.243 - 3401.168/(t+273.16) - 11.209 \ln (t+273.16)](4x_1 - 3) + [-91.3603 + 4035.1378/(t+273.16) + 13.644 \ln (t+273.16)] \times (2x_1 - 1)(6x_1 - 5)\} \ldots \quad (49)$$

6. Prediction of Vapour-Liquid Equilibrium at Isobaric Condition

In the literature[8] Myers has reported vapour-liquid equilibrium data at one atmospheric pressure for the system n-pentane-benzene. Vapour-liquid equilibrium data at isothermal conditions have been investigated during the course of this work. Isothermal vapour-liquid equilibria data obtained in this investigation were correlated for obtaining isobaric equilibria values, which were then compared with the literature data.

In Equations 15 and 16, assuming $\frac{P \delta_{12} y_i^2}{RT} = 0$, and combining them, gives

$$P = x_1 \gamma_1 P_1^\circ \exp \frac{(\beta_{11} - V_1)(P - P_1^\circ)}{RT} + x_2 \gamma_2 P_2^\circ \exp \frac{(\beta_{22} - V_2)(P - P_2^\circ)}{RT} \quad (50)$$

Equation 50 may be used to estimate the system temperature by a trial and error procedure. This method was used in this work to predict the vapour-liquid equilibrium at 1 atm for the system n-pentane-benzene. Two sources of the activity coefficients were used in the calculation. The first set of γ's was calculated from equation 29 and using constants a, b, c taken from Table 20 and 21. The calculated temperatures are presented in Table 22. The second set of γ's was calculated from Equations 48 and 49. The results of the prediction were also presented in Table 23. In Table 25, the Myers' values are also included for comparison. It may be seen that the results calculated from both methods are satisfactory.

V. DISCUSSION AND CONCLUSION

In this investigation the pressures were obtained indirectly through the temperature measurements. The boiling temperature of distilled water was measured by means of a calibrated copper-constantan thermopile in conjunction with a Cambridge microstep potentiometer. The accuracy of the calculated pressure was $\pm$ 0.05 mm. Hg. Equilibrium temperature were measured by means of the Beckmann Thermometers, which were adjusted to the desired temperature using a calibrated Leeds and Northrup Platinum Resistance Thermometer. The accuracy of the equilibrium temperature measurements is $\pm$ 0.05°C.

1. The experimental data were correlated by means of a three constants Redlich-Kister equation. Using these constants, calculated γ_i values are listed in Tables 9 to 13 and in Tables 14 to 17 respectively. The values of γ_i calculated by equations 15 and 16 are also listed in Tables 9 to 13 and in Tables 14 to 17 respectively. They are well represented by the Redlich-Kister equation. For the system of carbon tetrachloride-toluene, the values of γ_i, observed and calculated, are all close to unity, indicating that the carbon tetrachloride-toluene system may be considered as a nearly ideal one. No prediction of vapour-liquid equilibrium at isobaric condition for this system was made.

2. For the system n-pentane-benzene, the system pressure at 50°C is greater than 760 mm. Hg. when the mole fraction of n-pentane in the liquid phase, x_i reaches 0.5. This is above the normal operating pressure, 760 mm. Hg., of the equipment. In order to extend the concentration range, compressed nitrogen gas was introduced into the system. The highest operating pressure obtained

in this method was 960 mm. Hg. ; corresponding to the total system pressure for $x_1 = 0.6909$ at 50°C.

3. The method used for predicting the isobaric vapour-liquid equilibria data from isothermal data was very useful. The comparisons were made against literature data of Myers'. The deviations of temperatures, pressures and vapour compositions at constant liquid compositions are shown in Table 25.

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APPENDIX

SAMPLE CALCULATIONS

1. Second Virial Coefficient

For benzene at 35°C

(a) Accentric factor

$$\omega = -\log P_r - 1 \quad \text{at} \quad T_r = 0.7$$

$$T_c = 289.45°K^{(19)}$$

$$T = 0.7\, T_c = 0.7\,(289.45 + 273.16) = 393.827°K$$

$$t = 393.827 - 273.16 = 120.667°C$$

$$\log_P = 6.90565 - 1211.033/(t + 220.29)^{(19)}$$

$$P = \text{Exp}\,(6.90565 - 1211.033/(120.667 + 220.79))$$

$$= 2288.7 \text{ mm. Hg.}$$

$$P_c = 36936 \text{ mm. Hg.}^{(19)}$$

$$P_r = 2288.7/36936$$

$$\therefore \quad \omega = -\log P_r - 1$$

$$= \log {}^{36936}/_{2288.7} - 1$$

$$= 0.2088$$

(b) Second Virial Coefficient

$$B = R\,T_c/P_c\,(.1445 + .073\,\omega) - (.330 - .46\,\omega)\,T_r^{-1} - (.1385 + .5\,\omega)\,T_r^{-2}$$

$$- (.0121 + .097\,\omega)\,T_r^{-3} - .0073\,\omega\,T_r^{-8} \qquad (41)$$

$$= 62365.6 \times 289.45/36936\,[.1445 + 0.73\,(.2088)]$$

$$- (.330 - .46\,(.2088))\,(1.065)^{-1} - (.1385 + .5\,(.2088))\,(1.065)^{-2}$$

$$- (.0121 + .097\,(.2088))(1.065)^{-3} - (.0073\,(.2088))(1.065)^{-8}$$

$$= -1389.01$$

2. Liquid Molal Volume

$$V^L = V_C/(1+\alpha\,(1-T_r) + (1+\alpha)(1-T_r)^{\frac{1}{3}}) \qquad (42)$$

for n-pentane at 25°C

$$d = 0.62139;\quad V^L = 72 \div 0.62139 = 115.87$$

$$T_r = (273.16+25)/469.78 = 0.6347$$

$$V_c = 310.4$$

$$115.87 = 310.4 \div (1+\alpha(1-0.6347) + (1+\alpha)(1-0.6347)^{\frac{1}{3}})$$

$$\therefore \quad \alpha = 0.8936$$

at 35°C

$$T_r = (273.16+35) \div 469.78 = 0.6560$$

$$\therefore \quad V^L_{35} = 310.4/(1+0.8936\,(1-0.6560)+(1+0.8936)(1-0.6560)^{\frac{1}{3}})$$

$$= 117.86 \text{ ml/g-mole}$$

3. Liquid Activity Coefficient

For the system carbon tetrachloride-toluene at 35°C

$$\ln \gamma_1 = \ln \frac{y_1 P}{x_1 P_1^\circ} + \frac{(\beta_{11} - V_1)(P - P_1^\circ)}{RT} + \frac{P \delta_{12} (1-y_1)^2}{RT} \qquad (15)$$

where $x_1 = .0407$, $V_1 = 98.81$, $y_1 = .1384$, $R = 62365.6$, $P = 51.9$, $T = 273.16 + 35 = 308.16$

$P_1^\circ = 174.38 \qquad \delta_{12} = 1694.38$

$\beta_{11} = 2148.23$

$$\therefore \quad \ln \gamma_1 = \ln \frac{.1384 \times 5.19}{.0407 \times 174.38} + \frac{(-2148.38 - 98.81)(51.9 - 174.38)}{62365.6 \times 308.16}$$

$$+ \frac{51.9 \times 1694.33 \times (1 - 0.1384)^2}{62365.6 \times 308.16} = 0.0264$$

$$\gamma_2 = \exp(\ln \gamma_1) = \exp(0.0264) = 1.0268$$

Similarly; $\ln \gamma_2 = -.0009$

$\gamma_2 = .9991$

4. Temperature Calculation at Total Pressure

760 mm. Hg. for the system n-pentane-benzene at concentration x = 0.8

Try t = 39.99°C, then physical constants can be fixed

$\beta_{11} = -1071$

$V_1 = 118.9$

$\log P_1 = 6.85221 - 1064.63/(39.99 + 232) = 2.93799$

$\therefore \quad P_1 = 865.72$

$\ln \gamma_1 = -86.373 + 4078.171/(273.16 + 39.99)$

$+ 12.764 \ln (273.16 + 39.99)$

$= 0.0121$

$\therefore \quad \gamma_1 = 1.0122$

$\beta_{22} = -1334$

$V_2 = 91.26$

$$\log P_2 = 6.90565 - 1211.033/(39.99 + 220.79) = 2.2608$$

$$\therefore \quad P_2 = 182.28$$

$$\ln \gamma_2 = 78.707 - 3461.376/(39.99 + 273.16) + 11.698 \ln (39.99 + 273.16) = 0.4148$$

$$\gamma_2 = 1.514$$

$$E_1 = \text{Exp} \frac{(\beta_{11} - V_1)(760 - P_1^\circ)}{RT}$$

$$= \text{Exp} \frac{(-1071 - 118.9)(760 - 865.72)}{62356.6 \times 313.15} = 1.0065$$

$$E_2 = \text{Exp} \frac{(\beta_{22} - V_2)(760 - P_2^\circ)}{62365.6 \times 313.15}$$

$$= \text{Exp} \frac{(-1334 - 91.26)(760 - 182.28)}{62365.6 \times 313.15} = .9592$$

$$P = x_1 \gamma_1 P_1 E_1 + x_2 \gamma_2 P_2 E_2$$

$$\therefore \quad P = (.8)(1.0122)(865.72)(1.0065) + (.2)(1.514)(182.28)(.9592)$$

$$= 760.43 \approx 760$$

Therefore, $t = 39.99°C$ is the required temperature for this system at $x = 0.8$ mole fraction n-pentane at 1 atm.

5. Vapour Composition

$$y_1 = \left(x_1 \gamma_1 P_1 \text{ Exp} \frac{(\beta_{11} - V_1)(P - P_1)}{RT}\right) / P$$

for $x = 0.8$ mole fraction $n\text{-}C_5H_{12}$

$\gamma_1 = 1.0122$

$\beta_{11} = -1071$

$V_1 = 118.9$

$P = 760.43$

$P_1^\circ = 865.72$

$R = 62365.5$

$T = 39.99 + 273.16 = 313.15°K$

$$\therefore \quad y_1 = \left((.8)(1.0122)(865.72) \exp \frac{(-1071 - 118.9)(760 - 865.72)}{62365.6 \times 313.15}\right) / 760.43$$

$$= 0.9241$$

6. Activity Coefficient Calculated using Equation Proposed by Lu[11]

$$\ln \gamma_1 = (1 - x_1)^2 \{ 230.545 - 1059.498/(t + 273.16) - 34.1256 \ln (t + 273.16)$$
$$+ [75.243 - 3401.168/(t + 273.16) - 11.209 \ln (t + 273.16)](4x_1 - 1)$$
$$+ [-91.3603 + 4035.1378/(t + 273.16) + 13.644 \ln (t + 273.16)](2x_1 - 1)(6x_1 - 1) \} \quad (48)$$

for $x_1 = 0.3$, $t = 54°C$

Substitute values of x_1 and t into equation 48.

$\therefore \quad \ln \gamma_1 = 0.2540$

Similarly, by applying equation 49

$\ln \gamma_2 = 0.0582$

TABLE 1

CALIBRATION TABLE FOR 5-JUNCTION COPPER CONSTANTAN THERMOPILE

°C / Millivolt °C	0	·1	·2	·3	·4	·5	·6	·7	·8	·9
31	6219.	6239.	6260.	6281.	6301.	6322.	6343.	6364.	6385.	6405.
32	6426.	6447.	6468.	6488.	6509.	6530.	6551.	6572.	6592.	6613.
33	6634.	6655.	6676.	6696.	6717.	6738.	6759.	6780.	6801.	6822.
34	6842.	6863.	6884.	6905.	6926.	6947.	6968.	6989.	7009.	7030.
35	7051.	7072.	7093.	7114.	7135.	7156.	7177.	7198.	7219.	7239.
36	7260.	7281.	7302.	7323.	7344.	7365.	7386.	7407.	7428.	7449.
37	7470.	7491.	7512.	7533.	7554.	7575.	7596.	7617.	7638.	7659.
38	7680.	7701.	7722.	7743.	7764.	7785.	7806.	7827.	7848.	7869.
39	7891.	7912.	7933.	7954.	7975.	7996.	8017.	8038.	8059.	8080.
40	8101.	8123.	8144.	8165.	8186.	8207.	8228.	8249.	8270.	8292.
41	8313.	8334.	8355.	8376.	8397.	8419.	8440.	8461.	8482.	8503.
42	8524.	8546.	8567.	8588.	8609.	8630.	8652.	8673.	8694.	8715.
43	8737.	8758.	8779.	8800.	8822.	8843.	8864.	8885.	8907.	8928.
44	8949.	8970.	8992.	9013.	9034.	9056.	9077.	9098.	9119.	9141.
45	9162.	9183.	9205.	9226.	9247.	9269.	9290.	9311.	9333.	9354.
46	9375.	9397.	9418.	9439.	9461.	9482.	9504.	9525.	9546.	9568.
47	9589.	9611.	9632.	9653.	9675.	9696.	9718.	9739.	9760.	9782.
48	9803.	9825.	9846.	9868.	9889.	9911.	9932.	9954.	9975.	9996.
49	10018.	10039.	10061.	10082.	10104.	10125.	10147.	10168.	10190.	10211.
50	10233.	10254.	10276.	10297.	10319.	10341.	10362.	10384.	10405.	10427.
51	10448.	10470.	10491.	10513.	10535.	10556.	10578.	10599.	10621.	10642.
52	10664.	10686.	10707.	10729.	10750.	10772.	10794.	10815.	10837.	10859.
53	10880.	10902.	10924.	10945.	10967.	10988.	11010.	11032.	11054.	11075.
54	11097.	11119.	11140.	11162.	11184.	11205.	11227.	11249.	11270.	11292.
55	11314.	11336.	11357.	11379.	11401.	11422.	11444.	11466.	11488.	11510.

(TABLE 1)... continuation...

°C / millivolt	0	·1	·2	·3	·4	·5	·6	·7	·8	·9
56	11531.	11553.	11575.	11597.	11618.	11640.	11662.	11684.	11705.	11727.
57	11749.	11771.	11793.	11814.	11836.	11858.	11880.	11902.	11924.	11945.
58	11967.	11989.	12011.	12033.	12055.	12076.	12098.	12120.	12142.	12164.
59	12186.	12208.	12230.	12251.	12273.	12295.	12317.	12339.	12361.	12383.
60	12405.	12427.	12449.	12471.	12493.	12514.	12536.	12558.	12580.	12602.
61	12624.	12646.	12668.	12690.	12712.	12734.	12756.	12778.	12800.	12822.
62	12844.	12866.	12888.	12910.	12932.	12954.	12976.	12998.	13020.	13042.
63	13064.	13086.	13108.	13130.	13152.	13174.	13196.	13218.	13241.	13263.
64	13285.	13307.	13329.	13351.	13373.	13395.	13417.	13439.	13461.	13483.
65	13506.	13528.	13550.	13572.	13594.	13616.	13638.	13661.	13683.	13705.
66	13727.	13749.	13771.	13793.	13816.	13838.	13860.	13882.	13904.	13926.
67	13949.	13971.	13993.	14015.	14038.	14060.	14082.	14104.	14126.	14149.
68	14171.	14193.	14215.	14237.	14260.	14282.	14304.	14327.	14349.	14371.
69	14393.	14416.	14438.	14460.	14482.	14505.	14527.	14549.	14572.	14594.
70	14616.	14639.	14661.	14683.	14705.	14728.	14750.	14772.	14795.	14817.
71	14839.	14862.	14884.	14907.	14929.	14951.	14974.	14996.	15018.	15041.
72	15063.	15086.	15086.	15130.	15153.	15175.	15198.	15220.	15242.	15265.
73	15287.	15310.	15332.	15355.	15377.	15399.	15422.	15444.	15467.	15489.
74	15512.	15534.	15557.	15579.	15601.	15624.	15646.	15669.	15691.	15714.
75	15736.	15759.	15781.	15804.	15826.	15849.	15872.	15894.	15917.	15939.
76	15962.	15984.	16007.	16029.	16052.	16074.	16097.	16119.	16142.	16165.
77	16187.	16210.	16232.	16255.	16278.	16300.	16323.	16345.	16368.	16391.
78	16413.	16436.	16458.	16481.	16504.	16526.	16549.	16572.	16594.	16617.
79	16639.	16662.	16685.	16707.	16730.	16753.	16775.	16798.	16821.	16843.
80	16866.	16889.	16912.	16934.	16957.	16980.	17002.	17025.	17048.	17071.

(TABLE 1)... continuation...

°C / millivolt °C	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
81	17093.	17116.	17139.	17161.	17184.	17207.	17230.	17252.	17275.	17298.
82	17321.	17342.	17366.	17389.	17412.	17435.	17457.	17480.	17503.	17526.
83	17549.	17571.	17594.	17617.	17640.	17663.	17685.	17708.	17731.	17754.
84	17777.	17800.	17822.	17845.	17868.	17891.	17914.	17937.	17960.	17983.
85	18005.	18028.	18051.	18074.	18097.	18120.	18143.	18166.	18189.	18211.
86	18234.	18257.	18280.	18303.	18326.	18349.	18372.	18395.	18418.	18441.
87	18464.	18487.	18510.	18533.	18555.	18578.	18601.	18624.	18647.	18670.
88	18693.	18716.	18739.	18762.	18785.	18808.	18831.	18854.	18877.	18900.
89	18923.	18946.	18969.	18992.	19016.	19039.	19062.	19085.	19108.	19131.
90	19154.	19177.	19200.	19223.	19246.	19269.	19292.	19315.	19338.	19362.
91	19385.	19408.	19431.	. 9454.	19477.	19500.	19523.	19546.	19570.	19593.
92	19616.	19639.	19662.	19685.	19708.	19732.	19755.	19778.	19801.	19824.
93	19847.	19871.	19894.	19917.	19940.	19963.	19986.	20010.	20033.	20056.
94	20079.	20102.	20126.	20149.	20172.	20195.	20219.	20242.	20265.	20288.
95	20312.	20335.	20358.	20381.	20405.	20428.	20451.	20474.	20498.	20521.
96	20544.	20567.	02691.	20614.	20637.	20661.	20684.	20707.	20731.	20754.
97	20777.	20800.	20824.	20847.	20870.	20894.	20917.	20940.	20964.	20987.
98	21010.	21034.	21057.	21081.	21104.	21127.	21151.	21174.	21197.	21221.
99	21244.	21268.	21291.	21314.	21338.	21361.	21385.	21408.	21431.	21455.

TABLE 2

CRITICAL CONSTANTS FOR PURE COMPONENTS

Compound	T, °K[19]	$P_{mm\ Hg}$[19]	V_c ml/ g-mole[19]	ω
Carbon tetrachloride	556.26	34200	275.99	.14948
Toluene	593.96	30400	315.52	.24163
n-Pentane	469.78	25316	310.4	.2545
Benzene	562.61	36926	333.3	.2088

TABLE 3

CALCULATED SECOND VIRIAL COEFFICIENTS

OF PURE COMPONENTS

Compound	35°C	40°C	45°C	55°C	65°C
Carbon tetrachloride	-2148.23	-2043.8	-1948.4	-1780.2	-1636.9
Toluene	-1347.07	-1291.6	-1240.2	-1147.9	-1067.2

	35°C	40°C	45°C	50°C
n-pentane	-1115.23	-1071.9	-1031.4	-993.10
Benzene	-1389.01	-1327.7	-1271.37	-1219.02

TABLE 4

LIQUID MOLAL VOLUMES OF PURE COMPONENTS

Compound	Temperature °C	Molal Volume(ml/g-mole)	
		Expt'l	Calcd.
Carbon tetrachloride	20	96.01	95.99
	25	96.64	96.64
	35		97.91
	40		98.66
	45		99.36
	55		100.81
	65		102.33
Toluene	20	107.79	107.69
	25	108.26	108.26
	35		109.44
	40		110.04
	45		110.66
	55		110.92
	65		113.23
n-Pentane	20	114.88	114.87
	25	115.87	115.87
	35		117.86
	40		118.91
	45		119.99
	50		121.12
Benzene	20	88.74	88.94
	25	89.28	89.39
	35		90.69
	40		91.29
	45		91.91
	50		92.54

TABLE 5

CONSTANTS FOR ANTONINE EQUATION[19]

Compound	A	B	C
Carbon tetrachloride	6.93390	1242.43	230.
Toluene	6.95334	1343.943	219.377
n-Pentane	6.85221	1064.63	232.
Benzene	6.90565	1211.033	220.79

TABLE 6

VAPOUR PRESSURE OF PURE COMPONENTS (mm. Hg.)

Temp °C	Carbon tetrachloride		Toluene		n-Pentane		Benzene	
	Expt'l	lit[19]	Expt'l	lit[19]	Expt'l	lit[19]	Expt'l	lit[19]
35°	174. 35	174. 38	46. 7	46. 75	723. 23	732. 53	148. 3	148. 33
40°	213. 3	213. 23	59. 2	59. 15	867. 4	867. 15	182. 7	182. 78
45°	258. 57	258. 86	74. 25	74. 13		1024. 0	213. 47	213. 48
50°						1193. 95	271. 35	271. 32
55°	373. 3	373. 42	113. 8	113. 47				
65°	523. 9	523. 78	168. 9	168. 76				

TABLE 7

CALIBRATION OF REFRACTIVE INDEX vs. COMPOSITIONS FOR THE SYSTEM CARBON TETRACHLORIDE-TOLUENE AT 25°C

Refractive Index (at 25°C)	Mole Fraction CCl_4
1.49715	0
1.48966	.0845
1.48499	.1725
1.48109	.2542
1.47644	.3448
1.47177	.4338
1.46672	.5347
1.46213	.6239
1.45744	.7097
1.45298	.7998
1.44836	.8921
1.44399	.9749
1.44292	1.0000

TABLE 8

CALIBRATION OF REFRACTIVE INDEX vs. COMPOSITION FOR THE SYSTEM N-PENTANE-BENZENE AT 25°C

Refractive Index (at 25°C)	Mole Fraction $n\text{-}C_5H_{12}$
1.49791	0
1.49122	.0366
1.47998	.0999
1.46872	.1745
1.45744	.2422
1.44588	.3188
1.43475	.3911
1.42233	.4672
1.41132	.5489
1.40085	.6366
1.38882	.7199
1.37745	.8068
1.36686	.8999
1.35471	1.0000

TABLE 9

EXPERIMENTAL VAPOUR-LIQUID EQUILIBRIUM DATA FOR THE SYSTEM CARBON TETRACHLORIDE-TOLUENE AT 35°C

Total Pressure mm. Hg. P	Liquid mole fraction x_1	Vapour mole fraction y_1	Liquid Activity Coefficients						
			$\ln \gamma_1$	γ_1		$\ln \gamma_2$	γ_2		$\ln \gamma_1/\gamma_2$
				obs.	calc'd		obs.	calc'd	
51.9	.0407	.1384	.0264	1.0268	1.0284	-.0009	.9991	1.0001	.0273
55.8	.0712	.2247	.0237	1.0240	1.0254	-.0050	.9950	1.0003	.0287
64.4	.1381	.3770	.0210	1.0212	1.0205	.0009	1.0011	1.0008	.0201
72.5	.2001	.4839	.0173	1.0175	1.0173	.0019	1.0021	1.0015	.0154
81.4	.2701	.5804	.0139	1.0140	1.0147	-.0002	.9998	1.0022	.0161
95.0	.3762	.6915	.0106	1.0107	1.0120	.0017	1.0019	1.0035	.0089
99.4	.4111	.7215	.0091	1.0091	1.0113	.0021	1.0022	1.0040	.0070
109.6	.4943	.7831	.0058	1.0032	1.0097	.0065	1.0005	1.0053	-.0007
118.2	.5621	.8251	.0044	1.0014	1.0084	.0082	1.0042	1.0067	-.0036
124.7	.6145	.8533	-.0013	.9987	1.0074	.0089	1.0089	1.0082	-.0102
130.4	.6589	.8753	.0016	1.0018	1.0064	.0131	1.0132	1.0100	-.0115
140.1	.7346	.9094	.0015	1.0016	1.0046	.0157	1.0158	1.0142	-.0142
147.9	.7972	.9342	-.0010	.9990	1.0030	.0180	1.0182	1.0193	-.0190
158.6	.8834	.9646	-.0002	.9998	1.0012	.0243	1.0215	1.0295	-.0245

TABLE 10

EXPERIMENTAL VAPOUR-LIQUID EQUILIBRIUM DATA FOR THE SYSTEM CARBON TETRACHLORIDE-TOLUENE AT 40°C

Total Pressure mm. Hg. P	Liquid mole fraction x_1	Vapour mole fraction y_1	Liquid Activity Coefficients						
			$\ln \gamma_1$	γ_1		$\ln \gamma_2$	γ_2		$\ln \gamma_1/\gamma_2$
				obs.	calc'd		obs.	calc'd	
68.9	.0630	.1979	.0310	1.0315	1.0336	-.0006	.9994	1.0010	.0316
80.9	.1397	.3725	.0295	1.0263	1.0083	-.0007	.9993	1.0037	.0266
94.3	.2236	.5118	.0254	1.0257	.9964	.0010	1.0001	1.0063	.0244
101.3	.2731	.3755	.0135	1.0136	.9946	.0027	.9973	1.0068	.0108
110.8	.3342	.6443	.0131	1.0132	.9958	.0041	.9973	1.0063	.0090
120.8	.3995	.7051	.0100	1.0101	.9996	.0062	.9988	1.0041	.0038
131.9	.4719	.7618	.0076	1.0076	1.0046	.0010	1.0010	1.0001	.0066
136.1	.4897	.7744	.0178	1.0181	1.0059	.0119	1.0120	.9990	.0057
141.2	.5352	.8033	.0018	1.0018	1.0086	.0048	1.0048	.9961	-.003
144.3	.5498	.8129	.0082	1.0082	1.0094	.0082	1.0082	.9952	0
149.3	.5731	.8276	.0181	1.0183	1.0105	.0132	1.0133	.9939	-.0049
151.6	.6059	.8441	-.0028	.9972	1.0116	.0069	1.0077	.9923	.0097
159.5	.6428	.8626	.0097	1.0097	1.0123	.0299	1.0304	.9912	-.0067
161.2	.6664	.8751	-.0016	.9984	1.0124	.0134	1.0135	.9910	-.0150
169.8	.7224	.9011	-.0019	.9981	1.0116	.0152	1.0153	.9928	-.0171
172.5	.7299	.9273	.0035	1.0038	1.0114	.0162	1.0160	.9933	-.0125

(TABLE 10)... continuation...

Total Pressure mm. Hg. P	Liquid mole fraction x_1	Vapour mole fraction y_1	Liquid Activity Coefficients						
			ln γ_1	γ_1		ln γ_2	γ_2		ln γ_1/γ_2
				obs.	calc'd		obs.	calc'd	
179.3	.7858	.9273	-.0040	.9960	1.0093	.0206	1.0208	1.0000	-.0246
187.2	.8265	.9429	.0023	1.0024	1.0072	.0324	1.0329	1.0087	-.0301
193.1	.8772	.9611	-.0006	.9994	1.0044	.0249	1.0252	1.0255	-.0255
197.6	.9032	.9698	-.0003	.9997	1.0030	.0324	1.0329	1.0371	-.0327
197.7	.8956	.9677	.0015	1.0035	1.0034	.0245	1.0248	1.0355	-.0230

TABLE 11

EXPERIMENTAL VAPOUR-LIQUID EQUILIBRIUM DATA FOR THE SYSTEM CARBON TETRACHLORIDE-TOLUENE AT 45°C

Total Pressure mm. Hg. P	Liquid mole fraction x_1	Vapour mole fraction y_1	Liquid Activity Coefficients						
			$\ln \gamma_1$	γ_1		$\ln \gamma_2$	γ_2		$\ln \gamma_1 / \gamma_2$
				obs.	calc'd		obs.	calc'd	
81.0	.0382	.1238	.0311	1.0313	1.0281	-.0008	.9992	1.0000	.0319
88.4	.0771	.2278	.0269	1.0273	1.0272	-.0010	.9990	1.0001	.0279
98.6	.1317	.3483	.0242	1.0245	1.0254	.0005	1.0006	1.0003	.0237
112.6	.2081	.4799	.0202	1.0204	1.0225	.0010	1.0011	1.0009	.0192
122.0	.2587	.5498	.0159	1.0161	1.0202	.0022	1.0023	1.0015	.0137
136.8	.3396	.6421	.0144	1.0146	1.0165	.0038	1.0039	1.0031	.0106
147.5	.3982	.6971	.0092	1.0092	1.0139	.0054	1.0056	1.0046	.0038
157.1	.4502	.7395	.0076	1.0076	1.0116	.0072	1.0073	1.0063	.0004
165.8	.4973	.7739	.0095	1.0098	1.0096	.0090	1.0092	1.0081	.0005
178.9	.5715	.8198	-.0003	.9997	1.0069	.0103	1.0104	1.0113	-.0100
188.6	.6254	.8497	.0050	1.0058	1.0051	.0135	1.0136	1.0139	-.0085
196.8	.6689	.8728	-.0015	.9985	1.0039	.0152	1.0154	1.0161	-.0167
208.	.7321	.9022	.0028	1.0030	1.0024	.0159	1.0160	1.0196	-.0131
218.2	.7869	.9256	.0012	1.0015	1.0014	.0184	1.0186	1.0227	-.0162
232.3	.8679	.9563	-.0004	.9996	1.0005	.0251	1.0225	1.0274	-.0255

TABLE 12

EXPERIMENTAL VAPOUR-LIQUID EQUILIBRIUM DATA FOR THE SYSTEM CARBON TETRACHLORIDE-TOLUENE AT 55°C

Total Pressure mm. Hg. P	Liquid mole fraction x_1	Vapour mole fraction y_1	Liquid Activity Coefficients						
			$\ln \gamma_1$	γ_1		$\ln \gamma_2$	γ_2		$\ln \gamma_1/\gamma_2$
				obs.	calc'd		obs.	calc'd	
132.8	.0767	.2173	.0254	1.0256	1.0311	-.0026	.9974	1.0003	.0280
142.4	.1117	.2949	.0286	1.0290	1.0277	-.0001	.9999	1.0007	.0287
153.2	.1518	.3716	.0206	1.0207	1.0242	-.0017	.9983	1.0012	.0223
168.6	.2122	.4696	.0185	1.0187	1.0200	.0006	1.0003	1.0021	.0179
183.7	.2719	.5499	.0128	1.0129	1.0167	.0042	1.0043	1.0032	.0086
195.6	.3175	.6037	.0162	1.0163	1.0146	.0024	1.0025	1.0040	.0138
215.1	.3967	.6818	.0086	1.0086	1.0117	.0046	1.0047	1.0056	.0040
234.1	.4672	.7399	.0060	1.0060	1.0095	.0061	1.0062	1.0072	-.0001
252.8	.5423	.7924	.0086	1.0087	1.0076	.0078	1.0079	1.0092	.0008
270.5	.6111	.8341	.0035	1.0036	1.0060	.0132	1.0135	1.0114	-.0097
285.9	.6721	.8676	.0042	1.0043	1.0047	.0118	1.0119	1.0138	-.0076
302.9	.7371	.8991	.0011	1.0012	1.0033	.0176	1.0177	1.0171	-.0165
318.9	.7978	.9259	.0036	1.0037	1.0022	,0184	1.0186	1.0210	-.0148
330.7	.8422	.9439	-.0002	.9998	1.0014	.0237	1.0240	1.0244	-.0239
348.3	.9099	.9692	-.0019	.9981	1.0005	.0274	1.0276	1.0310	-.0293

TABLE 13

EXPERIMENTAL VAPOUR-LIQUID EQUILIBRIUM DATA FOR THE SYSTEM CARBON TETRACHLORIDE-TOLUENE AT 65°C

Total Pressure mm. Hg. P	Liquid mole fraction x_1	Vapour mole fraction y_1	Liquid Activity Coefficients						
			$\ln \gamma_1$	γ_1		$\ln \gamma_2$	γ_2		$\ln \gamma_1 / \gamma_2$
				obs.	calc'd		obs.	calc'd	
184.9	.0489	.1386	.0297	1.0301	1.0289	-.0015	.9985	1.0001	.0312
195.4	.0782	.2090	.0258	1.0261	1.0269	-.0009	.9991	1.0002	.0267
220.6	.1483	.3498	.0244	1.0246	1.0226	-.0004	.9996	1.0008	.0248
241.3	.2081	.4475	.0171	1.0173	1.0195	.0036	1.0037	1.0014	.0135
264.0	.2732	.5359	.0191	1.0200	1.0165	.0025	1.0026	1.0023	.0166
296.4	.3646	.6372	.0126	1.0127	1.0129	.0071	1.0072	1.0040	.0055
325.9	.4487	.7122	.0092	1.0093	1.0101	.0061	1.0062	1.0059	.0031
342.3	.4959	.7492	.0103	1.0104	1.0087	.0076	1.0078	1.0072	.0027
360.8	.5491	.7853	.0067	1.0068	1.0072	.0088	1.0089	1.0088	-.0021
391.3	.6362	.8402	.0063	1.0064	1.0050	.0146	1.0148	1.0124	-.0083
405.6	.6761	.8621	.0025	1.0026	1.0041	.0131	1.0133	1.0137	-.0106
423.2	.7242	.8864	.0006	1.0070	1.0031	.0165	1.0170	1.0161	-.0159
448.1	.7947	.9199	.0022	1.0023	1.0019	.0205	1.0208	1.0202	-.0183
461.2	.8306	.9356	-.0008	.9992	1.0013	.0228	1.0231	1.0226	-.0236
475.1	.8753	.9538	-.0004	.9996	1.0007	.0261	1.0264	1.0260	-.0265
485.4	.9054	.9655	-.0014	.9986	1.0004	.0282	1.0283	1.0285	-.0296

TABLE 14

EXPERIMENTAL VAPOUR-LIQUID EQUILIBRIUM DATA FOR THE SYSTEM N-PENTANE-BENZENE AT 35°C

Total Pressure mm. Hg. P	Liquid mole fraction x_1	Vapour mole fraction y_1	Liquid Activity Coefficients						
			$\ln \gamma_1$	γ_1		$\ln \gamma_2$	γ_2		$\ln \gamma_1 / \gamma_2$
				obs.	calc'd		obs.	calc'd	
207.0	.0526	.3252	.5919	1.8074	1.8390	-.0105	.9896	1.0022	.6024
263.7	.1079	.4879	.5175	1.6778	1.6988	.0116	1.0117	1.0092	.5059
310.2	.1609	.5822	.4540	1.5746	1.5858	.0283	1.0287	1.0200	.4257
326.9	.2332	.6672	.3726	1.4516	1.4587	.0439	1.0449	1.0411	.3287
402.0	.2913	.7129	.3162	1.3719	1.3747	.0744	1.0772	1.0632	.2418
454.0	.3848	.7701	.2333	1.2628	1.2661	.1115	1.1180	1.1088	.1218
484.0	.4459	.7992	.1851	1.2033	1.2094	.1426	1.1532	1.1455	.0425
543.1	.5689	.8492	.1136	1.1203	1.1213	.2181	1.2437	1.2382	-.1045
581.1	.6598	.8801	.0663	1.0685	1.0742	.2904	1.3370	1.3258	-.2242
612.1	.7367	.9056	.0345	1.0352	1.0442	.3573	1.4294	1.4156	-.3227
650.1	.8135	.9319	.0218	1.0220	1.0222	.4330	1.5419	1.5233	-.4112
686.6	.8998	.9615	.0045	1.0045	1.0065	.5160	1.7091	1.6713	-.5115

TABLE 15

EXPERIMENTAL VAPOUR-LIQUID EQUILIBRIUM DATA FOR THE SYSTEM N-PENTANE-BENZENE AT 40°C

Total Pressure mm. Hg. P	Liquid mole fraction x_1	Vapour mole fraction y_1	Liquid Activity Coefficients						
			$\ln \gamma_1$	γ_1		$\ln \gamma_2$	γ_2		$\ln \gamma_1/\gamma_2$
				obs.	calc'd		obs.	calc'd	
244.8	.0465	.2872	.5941	1.8113	1.8504	-.0032	.9968	1.0016	.5973
294.1	.0877	.4264	.5352	1.7078	1.7466	.0036	1.0036	1.0058	.5316
349.1	.1386	.5356	.4736	1.6057	1.6329	.0174	1.0176	1.0145	.4562
415.1	.2148	.6369	.3778	1.4590	1.4890	.0235	1.0330	1.0347	.3453
461.9	.2756	.6932	.3172	1.3733	1.3936	.0481	1.0493	1.0572	.2691
505.8	.3368	.7322	.3595	1.2963	1.3123	.0882	1.0922	1.0856	.1713
546.5	.4061	.7701	.1977	1.2187	1.2358	.1205	1.1281	1.1249	.0773
583.3	.4749	.8021	.1465	1.1578	1.1738	.1580	1.1712	1.1713	-.0115
615.9	.5296	.8249	.1163	1.1233	1.1332	.1961	1.2166	1.2137	-.0798
663.0	.6183	.8601	.0740	1.0768	1.0814	.2510	1.2853	1.2925	-.1770
695.1	.6828	.8824	.0457	1.0467	1.0532	.3075	1.3601	1.3537	-.2619
723.9	.7364	.9013	.0301	1.0306	1.0351	.3560	1.4271	1.4163	-.3259
750.0	.7929	.9212	.0119	1.0120	1.0207	.4057	1.5004	1.4826	-.3939
794.1	.8738	.9505	.0002	1.0002	1.0071	.4963	1.6426	1.5841	-.4961

TABLE 16

EXPERIMENTAL VAPOUR-LIQUID EQUILIBRIUM DATA FOR THE SYSTEM N-PENTANE-BENZENE AT 45°C

Total Pressure mm. Hg. P	Liquid mole fraction x_1	Vapour mole fraction y_1	Liquid Activity Coefficients						
			$\ln \gamma_1$	γ_1		$\ln \gamma_2$	γ_2		$\ln \gamma_1/\gamma_2$
				obs.	calc'd		obs.	calc'd	
249.7	.0255	.1819	.5988	1.8200	1.8512	-.0206	.9797	1.0005	.6594
294.0	.0543	.3169	.5588	1.7486	1.7787	-.0106	.9895	1.0021	.5694
412.2	.1467	.5478	.4432	1.5577	1.5763	.0097	1.0098	1.0158	.4335
449.1	.1829	.5996	.3966	1.4868	1.5086	.0147	1.0148	1.0248	.3819
494.1	.2286	.6476	.3434	1.4098	1.4315	.0370	1.0377	1.0386	.3064
533.0	.2706	.6849	.3043	1.3557	1.3683	.0543	1.0558	1.0542	.2499
586.9	.3373	.7322	.2439	1.2762	1.2812	.0804	1.0837	1.0848	.1636
633.0	.4011	.7684	.1919	1.2115	1.2134	.1089	1.1151	1.1202	.0829
676.1	.4636	.7969	.1468	1.1581	1.1582	.1508	1.1628	1.1605	-.0040
700.1	.4991	.8135	.1271	1.1356	1.1317	.1674	1.1822	1.1858	-.0402
740.2	.5678	.8409	.0847	1.0883	1.0889	.2090	1.2325	1.2390	-.1244
783.0	.6328	.8645	.0577	1.0594	1.0580	.2649	1.3032	1.2938	-.2072
836.6	.7171	.8962	.0317	1.0322	1.0295	.3219	1.3797	1.3689	-.2972
881.9	.7899	.9215	.0130	1.0130	1.0139	.3898	1.4767	1.4340	-.3768

TABLE 17

EXPERIMENTAL VAPOUR-LIQUID EQUILIBRIUM DATA FOR THE SYSTEM N-PENTANE-BENZENE AT 50°C

Total Pressure mm. Hg. P	Liquid mole fraction x_1	Vapour mole fraction y_1	Liquid Activity Coefficients						
			$\ln \gamma_1$	γ_1		$\ln \gamma_2$	γ_2		$\ln \gamma_1 / \gamma_2$
				obs.	calc'd		obs.	calc'd	
330.6	.0374	.2282	.5916	1.7712	1.7972	-.0279	.9724	1.0010	.6296
388.2	.0702	.3496	.5268	1.6935	1.7169	-.0066	.9934	1.0036	.5334
467.9	.1239	.4296	.4571	1.5795	1.5982	.0116	1.0116	1.0114	.4455
520.8	.1647	.5469	.4079	1.5037	1.5180	.0245	1.0248	1.0202	.3834
560.6	.2032	.5981	.3587	1.4315	1.4495	.0229	1.0232	1.0309	.3358
610.1	.2472	.6436	.3179	1.3742	1.3795	.0411	1.0419	1.0458	.2768
683.2	.3259	.7042	.2406	1.2720	1.2738	.0737	1.0765	1.0798	.1669
734.9	.3926	.7446	.1802	1.1975	1.2018	.1007	1.1060	1.1156	.0795
770.7	.4352	.7675	.1531	1.1654	1.1633	.1248	1.1330	1.1415	.0283
818.0	.5032	.7986	.1046	1.1102	1.1125	.1661	1.1807	1.1874	-.0616
871.9	.5746	.8296	.0708	1.0733	1.0718	.2146	1.2394	1.2401	-.1438
734.0	.6636	.8652	.0341	1.0347	1.0363	.2799	1.3230	1.3094	-.2458
958.2	.6909	.8765	.0310	1.0315	1.0284	.3011	1.3513	1.3307	-.2700

TABLE 18

VALUES OF THE REDLICH-KISTER EQUATION

1. Carbon Tetrachloride-Toluene System

Temp. °C	B	C	D
35	.0353	.0003	-.0033
40	.0392	.0028	-.0027
45	.0424	.0035	-.0031
55	.0420	.0025	.0089
65	.0413	.0031	.0048

2. Normal Pentane-Benzene System

Temp. °C	B	C	D
35	.6445	-.0277	.0202
40	.6317	-.0595	-.0199
45	.5882	-.0957	-.0319
50	.5567	-.1226	-.0394

TABLE 19

A SUMMARY OF THE RESULTS OF THE AREA TEST

Temperature °C	net area $\left(= \int_{x=0}^{x=1} \ln \gamma_1/\gamma_2 \, dx\right)$	
	Carbon-tetrachloride toluene system	n-pentane-benzene system
35	-0.0005	0.008
40	-0.0004	0.006
45	-0.0004	0.003
50		0.001
55	-0.0001	
65	0.0002	

TABLE 20

VALUES OF a_1, b_1, c_1 FOR EQUATION 29 AT CONSTANT COMPOSITION AND 1 ATM. FOR THE SYSTEM N-PENTANE-BENZENE *

x in mole fraction normal pentane	a_1	b_1	c_1
.05	91.428	-4042.708	13.560
.1	97.949	-4334.260	14.544
.15	101.615	-4498.115	15.102
.2	104.413	-4620.845	15.530
.3	93.142	-4108.522	13.871
.4	93.043	-4085.045	13.883
.5	47.068	-2014.645	7.047
.6	23.832	- 947.145	3.607
.7	- 23.192	1188.360	- 3.381
.8	- 86.373	4078.171	-12.764
.8536	-103.812	4899.841	-15.341
.9	-137.260	6432.069	-20.307

* applicable temperature range: 36.07°C - 80.1°C

TABLE 21

VALUES OF a_2, b_2, c_2 FOR EQUATION 29 AT CONSTANT COMPOSITION AND 1 ATM. FOR THE SYSTEM N-PENTANE-BENZENE*

x in mole fraction normal pentane	a_2	b_2	c_2
.05	- 82.222	3931.536	- 12.122
.1	- 73.365	3524.233	- 10.808
.15	- 71.822	3431.873	- 10.592
.2	- 65.134	3121.305	- 9.603
.3	- 42.034	2050.963	- 6.186
.4	- 10.492	606.033	- 1.509
.5	9.463	- 314.111	1.442
.6	24.553	- 1011.084	3.608
.7	25.620	- 1078.456	3.802
.8	78.707	-3461.540	11.698
.8536	78.082	-3440.376	11.592
.9	134.754	-5966.532	20.037

* applicable temperature range: 36.07°C - 80.1°C

TABLE 22

T, P, x, y, $\ln \gamma_1$, $\ln \gamma_2$ CALCULATED USING EQUATIONS 29, 50 FOR THE SYSTEM N-PENTANE-BENZENE AT ONE ATMOSPHERE PRESSURE

T °C	P mm. Hg.	x mole fraction	y* mole fraction	$\ln \gamma_1$	$\ln \gamma_2$
72.54	760.64	.0500	.2366	.4660	.0012
67.38	761.24	.1000	.2885	.4070	.0098
63.08	760.40	.1500	.4965	.3641	.0135
59.58	760.08	.2000	.5743	.3208	.0246
54.14	760.47	.3000	.6819	.2462	.0587
50.40	760.18	.4000	.7514	.1678	.1020
47.17	760.42	.5000	.8051	.1140	.1620
44.54	760.12	.6000	.8486	.0670	.2327
42.16	760.22	.7000	.8873	.0342	.3186
39.99	760.61	.8000	.9241	.0121	.4148
38.76	760.63	.8536	.9441	.0100	.4714
37.92	760.46	.9000	.9605	.0023	.5396

A plot of $\ln \gamma_i$ vs. composition is shown in fig. 33.

* $y_1 = \left(x_1 \gamma_1 P_1^\circ \operatorname{Exp} \frac{(\beta_{11} - V_1)(P - P_1^\circ)}{RT} \right) / P$

TABLE 23

T, P, x, y, $\ln \gamma_1$, $\ln \gamma_2$ CALCULATED USING EQUATIONS 48, 49 AND 50 FOR THE SYSTEM N-PENTANE-BENZENE AT ONE ATMOSPHERE PRESSURE

T °C	P mm. Hg.	x mole fraction	y^* mole fraction	$\ln \gamma_1$	$\ln \gamma_2$
72.59	759.4	.0500	.2417	.4846	.0028
67.24	761.5	.1000	.3920	.4200	.0091
62.98	761.6	.1500	.4968	.3692	.0179
59.44	761.0	.2000	.5751	.3275	.0288
54.00	760.9	.3000	.6839	.2540	.0582
50.00	760.7	.4000	.7559	.1868	.0995
46.92	760.5	.5000	.8086	.1264	.1537
44.32	759.5	.6000	.8516	.0762	.2194
42.10	759.4	.7000	.8903	.0385	.2925
40.04	760.1	.8000	.9275	.0143	.3665
38.94	759.7	.8536	.9473	.0067	.4030
37.98	759.3	.9000	.9642	.0026	.4314

$$* y = \left(x_1 \gamma_1 P_1^\circ \ \text{Exp} \ \frac{(\beta_{11} - V_1)(P - P_1^\circ)}{RT} \right) / P$$

TABLE 24

COMPARISONS OF CALCULATED VALUES T, P, y FOR THE SYSTEM N-PENTANE-BENZENE AT ONE ATMOSPHERE PRESSURE

	Equations 29, 50			Equations 48, 49, 50			Deviation %		
x_1	T °C	Pmm. Hg.	y_1	T °C	Pmm.Hg.	y_1	ΔT	ΔP	Δy
.05	72.54	760.6	.2366	72.59	759.4	.2417	.07	.2	-2.12
.1	67.38	761.2	.3885	67.24	761.5	.3920	.21	.04	- .9
.15	63.08	760.4	.4965	62.98	761.6	.4968	.16	-.16	- .06
.2	59.58	760.1	.5743	59.44	760.0	.5751	.23	-.12	- .13
.3	54.14	760.5	.6819	54.00	760.9	.6839	.26	-.06	- .29
.4	50.40	760.2	.7514	50.00	760.7	.7559	.79	-.06	- .59
.5	47.17	760.4	.8051	46.92	760.5	.8086	.53	-.01	- .43
.6	44.54	760.1	.8486	44.34	759.5	.8516	.22	.08	- .35
.7	42.16	760.2	.8873	42.10	759.4	.8903	.14	.11	- .34
.8	39.99	760.6	.9241	40.04	760.1	.9275	-.13	.07	- .37
.8536	38.76	760.6	.9441	38.94	759.7	.9473	-.46	.12	- .34
.9	37.92	760.5	.9605	37.98	759.3	.9642	-.16	.2	- .40

The percentage errors are less than 1% except the first point at x = 0.05. Therefore calculated values in Table 22 will be chosen for comparisons with experimental data[8].

TABLE 25

COMPARISONS OF LITERATURE VALUES (MYERS' DATA)[8] WITH VALUES CALCULATED IN TABLE 22 FOR THE SYSTEM N-PENTANE-BENZENE

	Literature (Myers')			Calculated (Table 22)			Deviation		
x_1	T °C	P mm.Hg.	y_1	T °C	P mm.Hg.	y_1	ΔT	ΔP	Δy
.05	72.6	760	.2382	72.54	760.6	.2366	.06	-.06	.0016
.1	67.4	760	.3886	67.38	761.2	.3885	.02	-1.2	.0001
.15	63.0	760	.4966	63.08	760.4	.4965	-.08	-.4	.0001
.2	59.7	760	.5755	59.58	760.1	.5743	.12	-.1	.0012
.3	54.3	760	.6832	54.14	760.5	.6819	.16	-.5	.0013
.4	50.4	760	.7511	50.40	760.2	.7514	0	-.2	-.0003
.5	47.2	760	.8099	47.17	760.4	.8051	.03	-.4	.0048
.6	44.6	760	.8536	44.54	760.1	.8486	.06	-.1	.0050
.7	42.2	760	.8946	42.16	760.2	.8873	.04	-.2	.0068
.8	40.0	760	.9255	39.99	760.6	.9241	.01	-.06	.0014
.8536	38.8	760	.9444	38.76	760.6	.9441	.04	-.6	.0003
.9	37.9	760	.9666	37.92	760.5	.9605	-.02	-.5	.0061

Values of T, P, y of Myers' are read off from figure 34 at the liquid composition indicated at first column of the table.

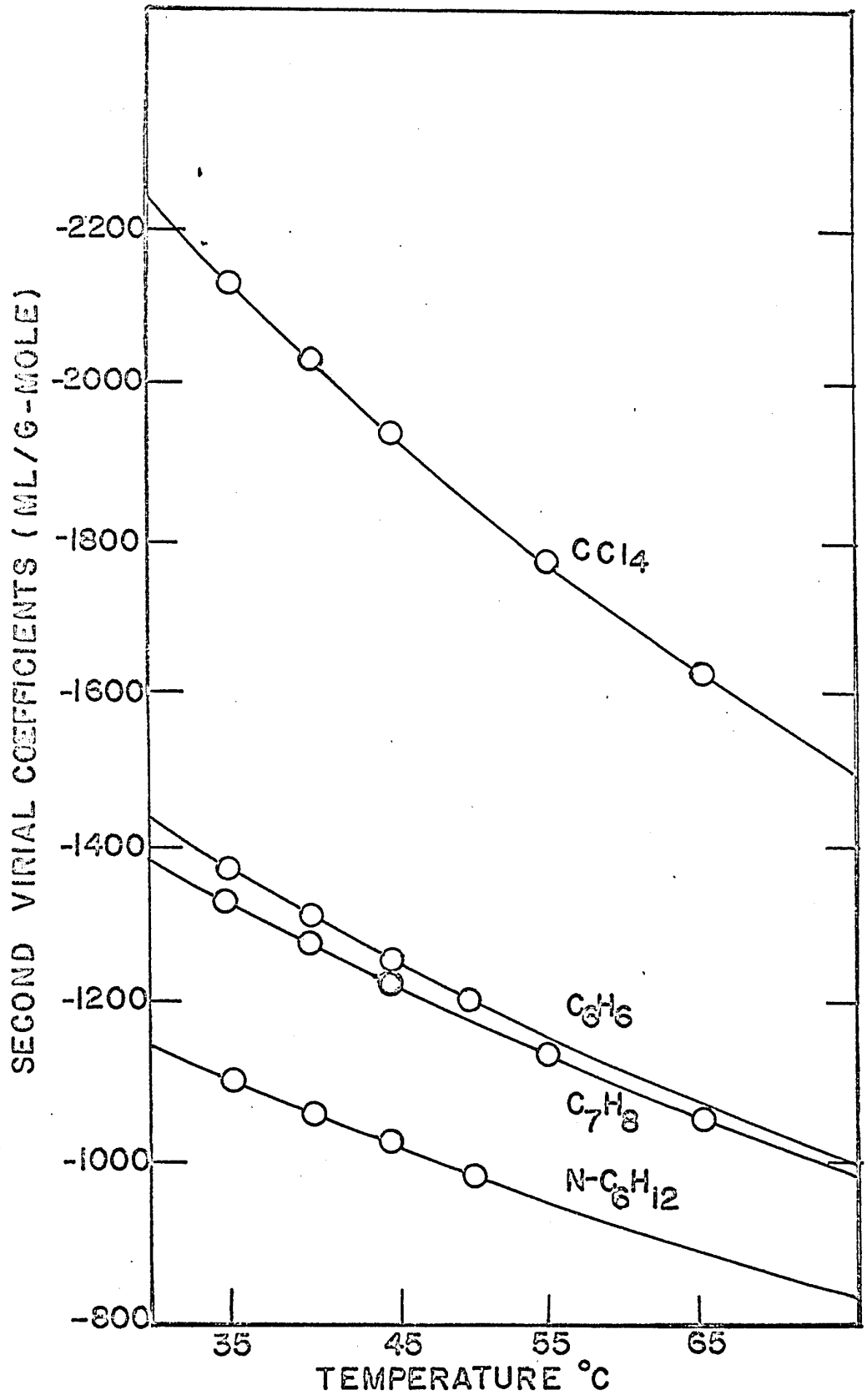

Fig. 5 Second Virial Coefficients vs. Temperature

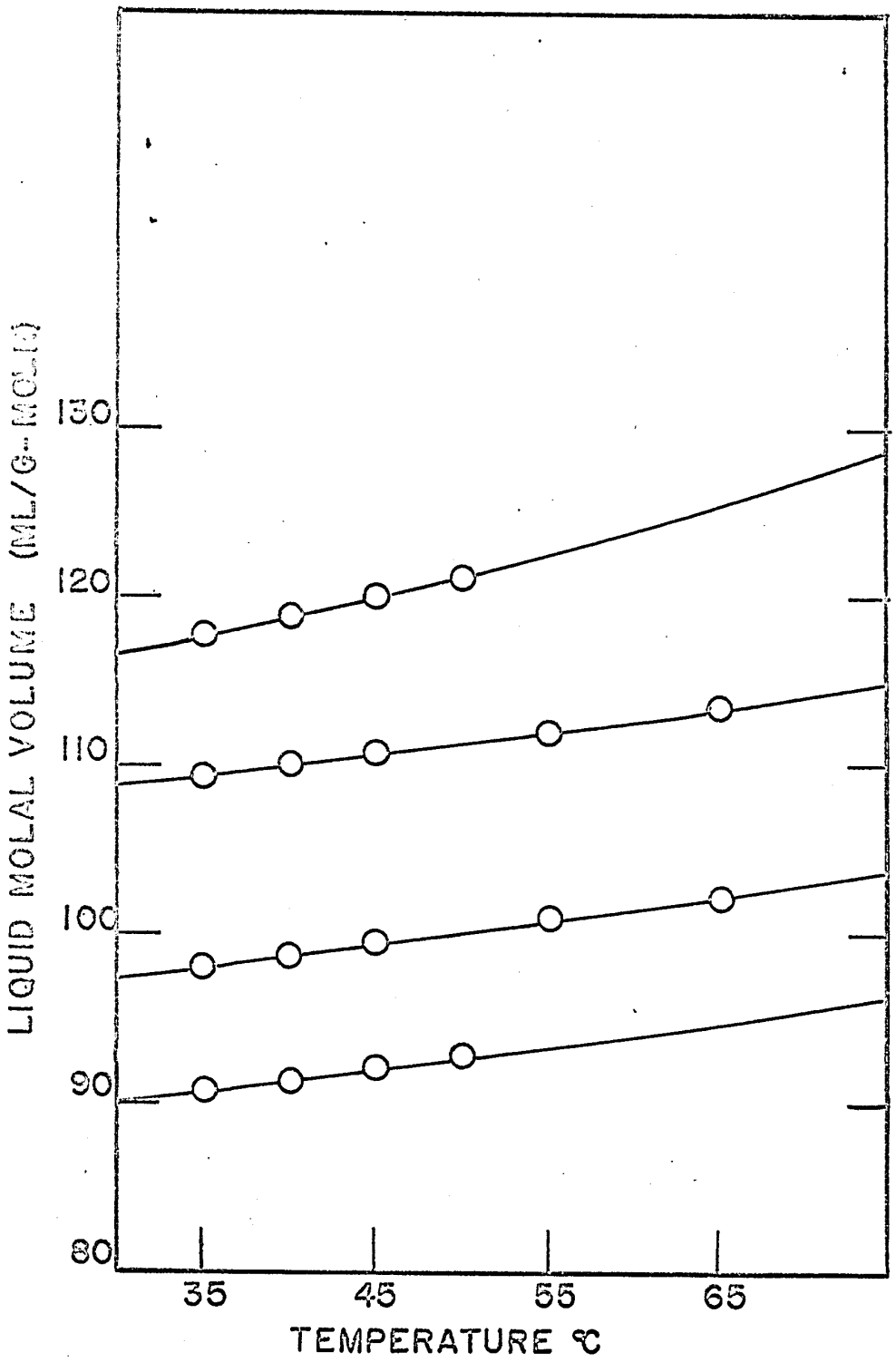

Fig. 6 Liquid Molal Volumes vs. Temperature

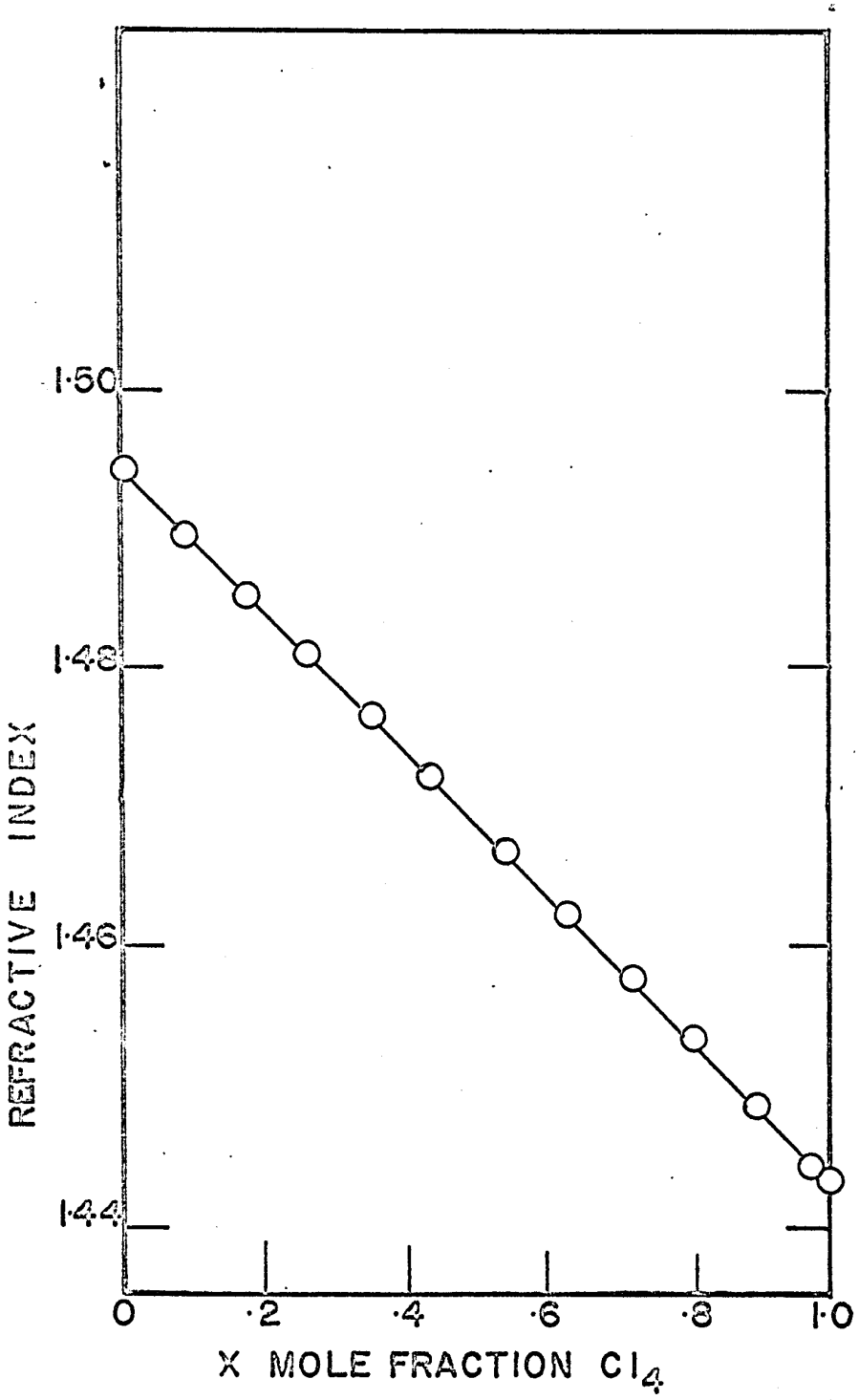

Fig. 7 Calibration Curve of Refractive Index vs. Compositions for the System Carbon Tetrachloride-Toluene at 25°C

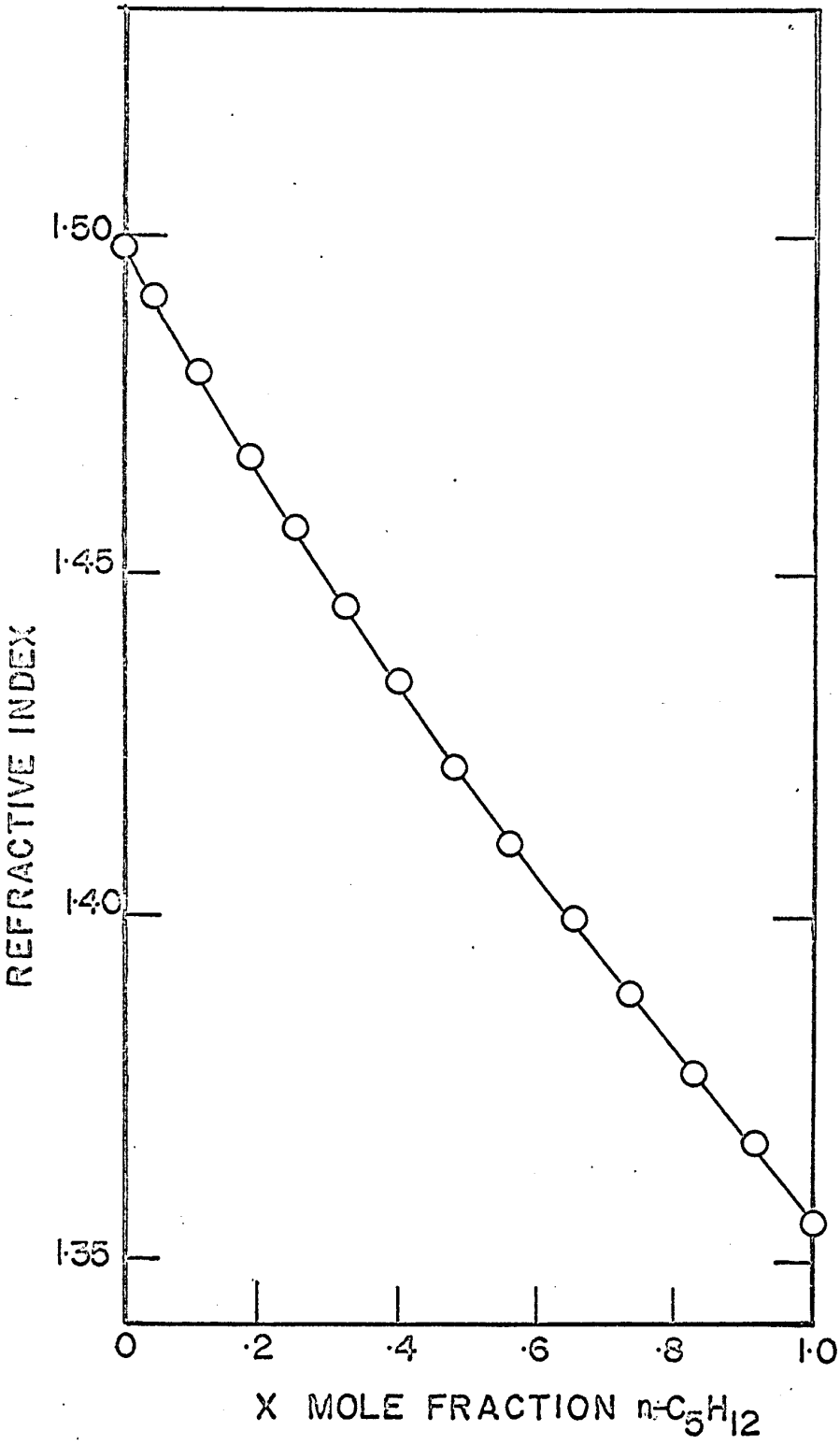

Fig. 8 Calibration Curve of Refractive Index vs. Compositions for the System N-Pentane-Benzene at 25°C

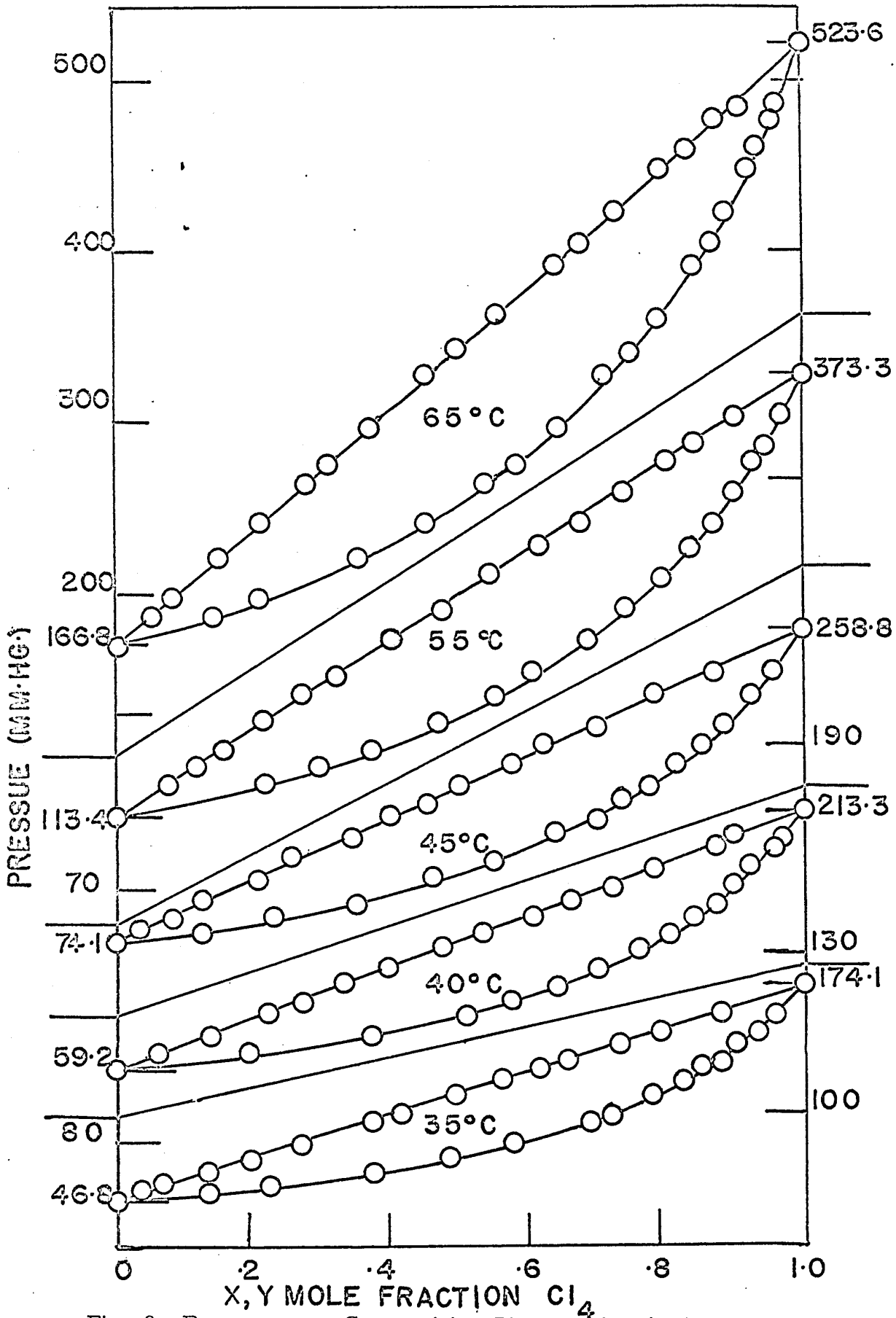

Fig. 9 Pressure vs. Composition Diagram for the System Carbon Tetrachloride-Toluene at Isothermal Conditions

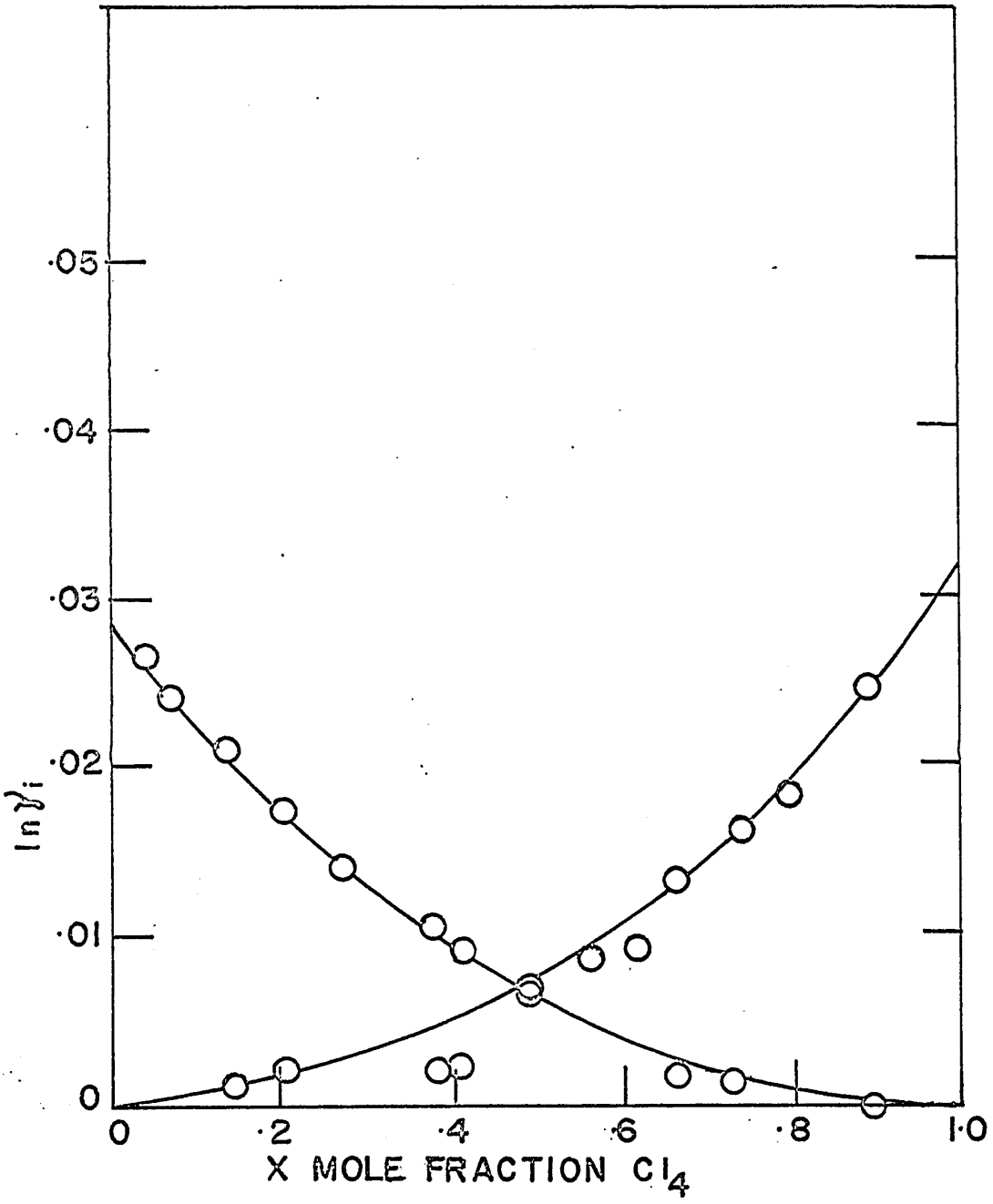

Fig. 10 Natural Logarithm of Activity Coefficients vs. Compositions for the System Carbon Tetrachloride-Toluene at 35°C

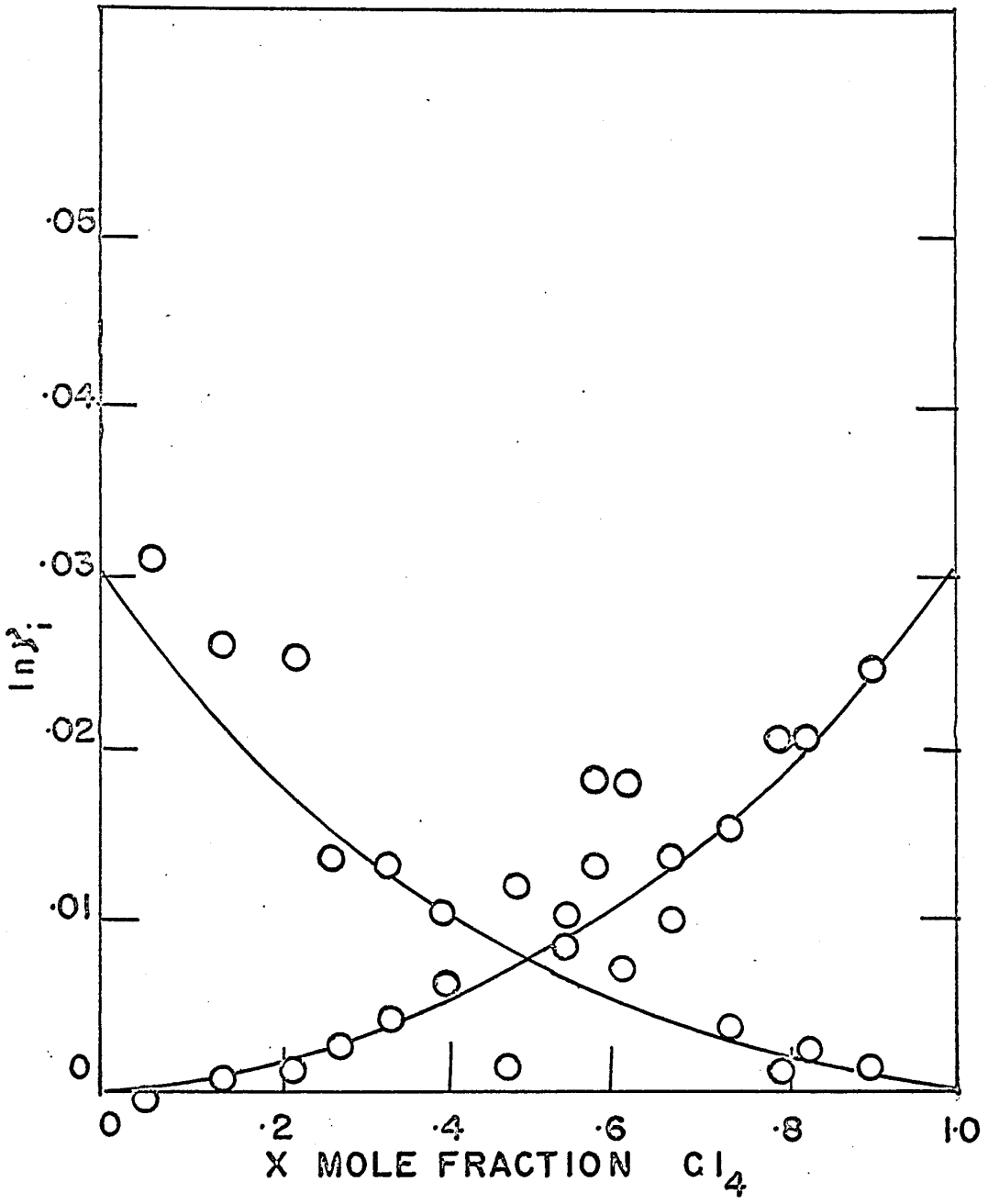

Fig. 11 Natural Logarithm of Activity Coefficients vs. Compositions for the System Carbon Tetrachloride-Toluene at 40°C

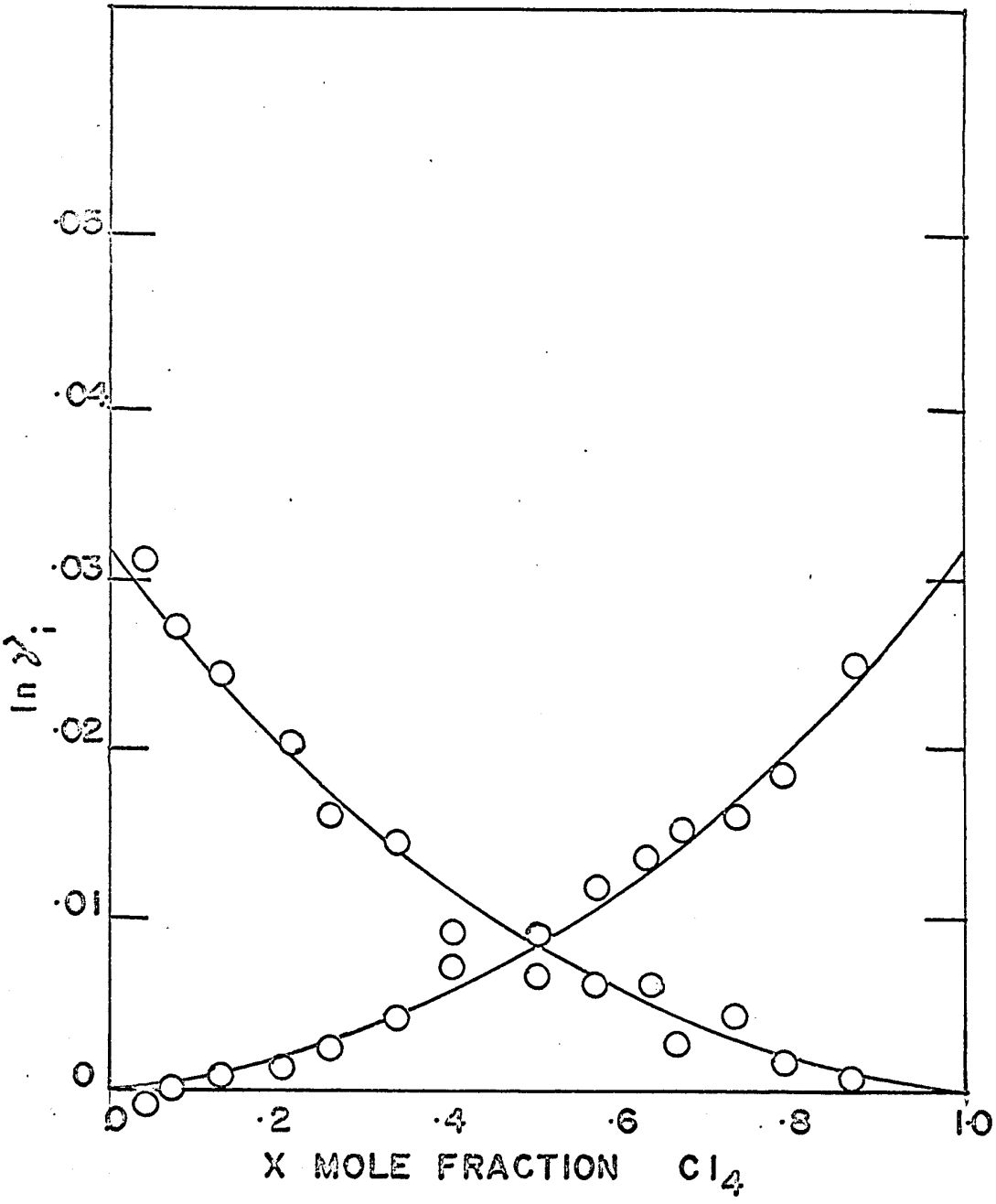

Fig. 12 Natural Logarithm of Activity Ceofficients vs. Compositions for the System Carbon Tetrachloride-Toluene at 45°C

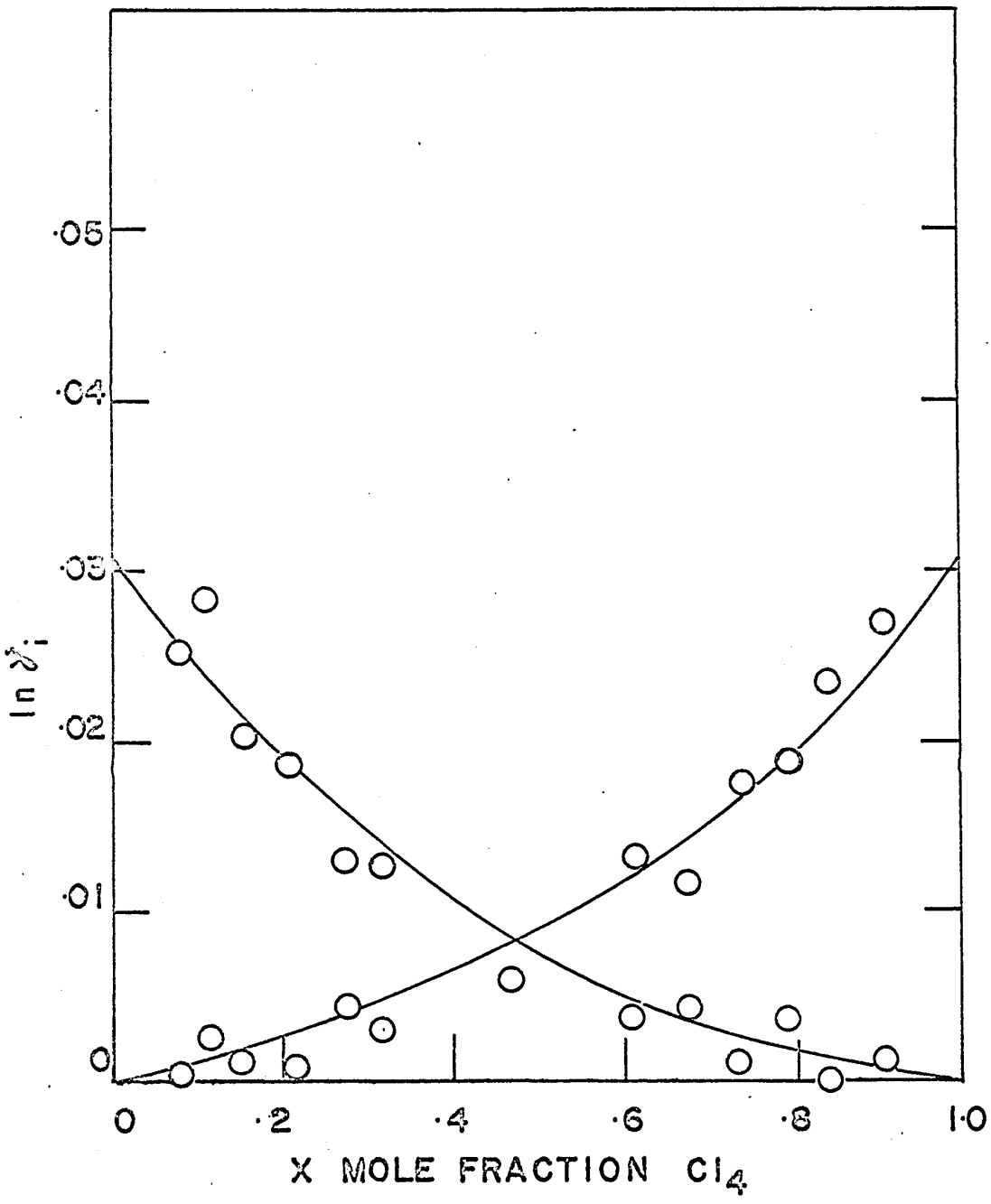

Fig. 13 Natural Logarithm of Activity Coefficients vs. Compositions for the System Carbon Tetrachloride-Toluene at 55°C.

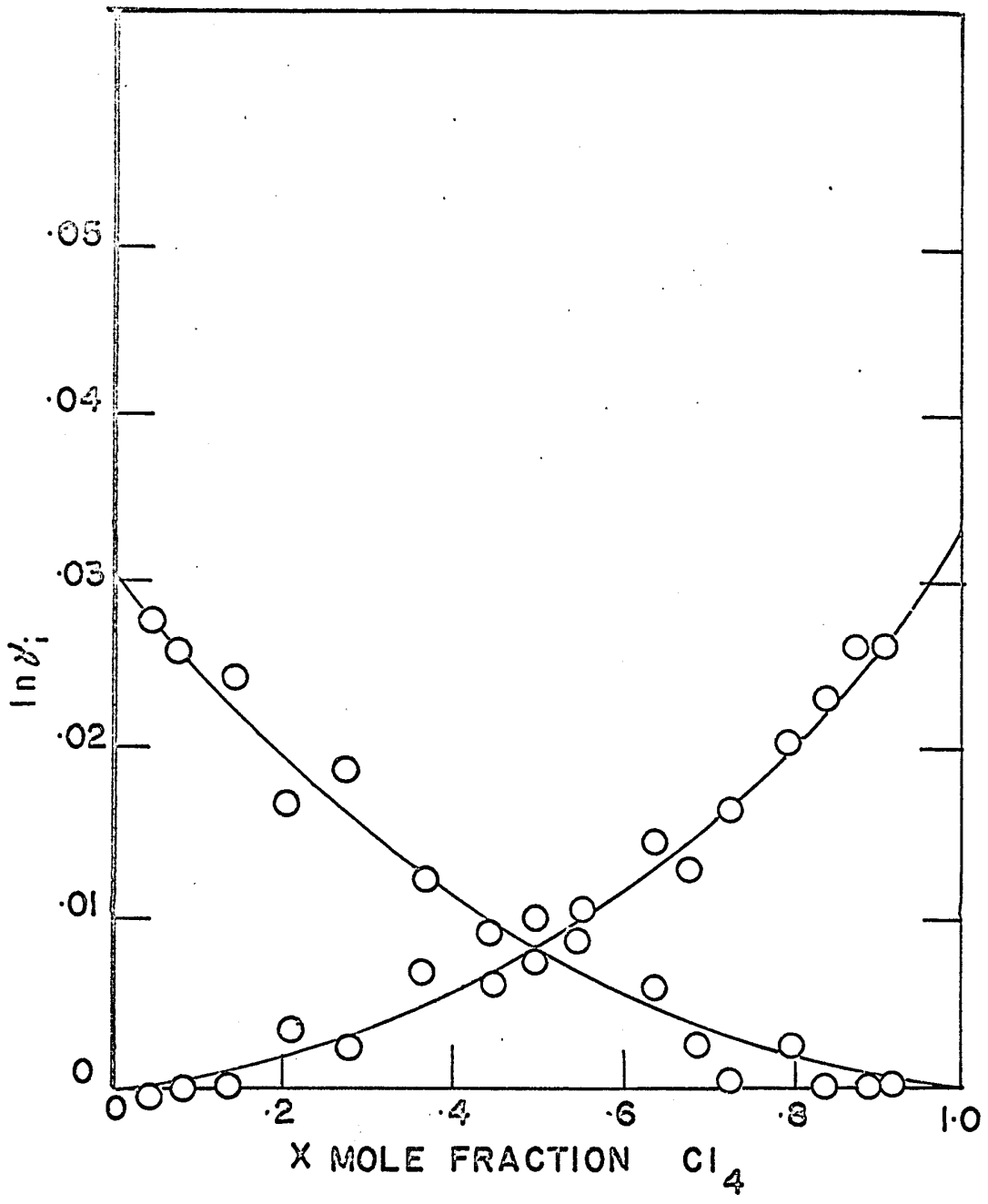

Fig. 14 Natural Logarithm of Activity Coefficients vs. Compositions for the System Carbon Tetrachloride-Toluene at 65°C.

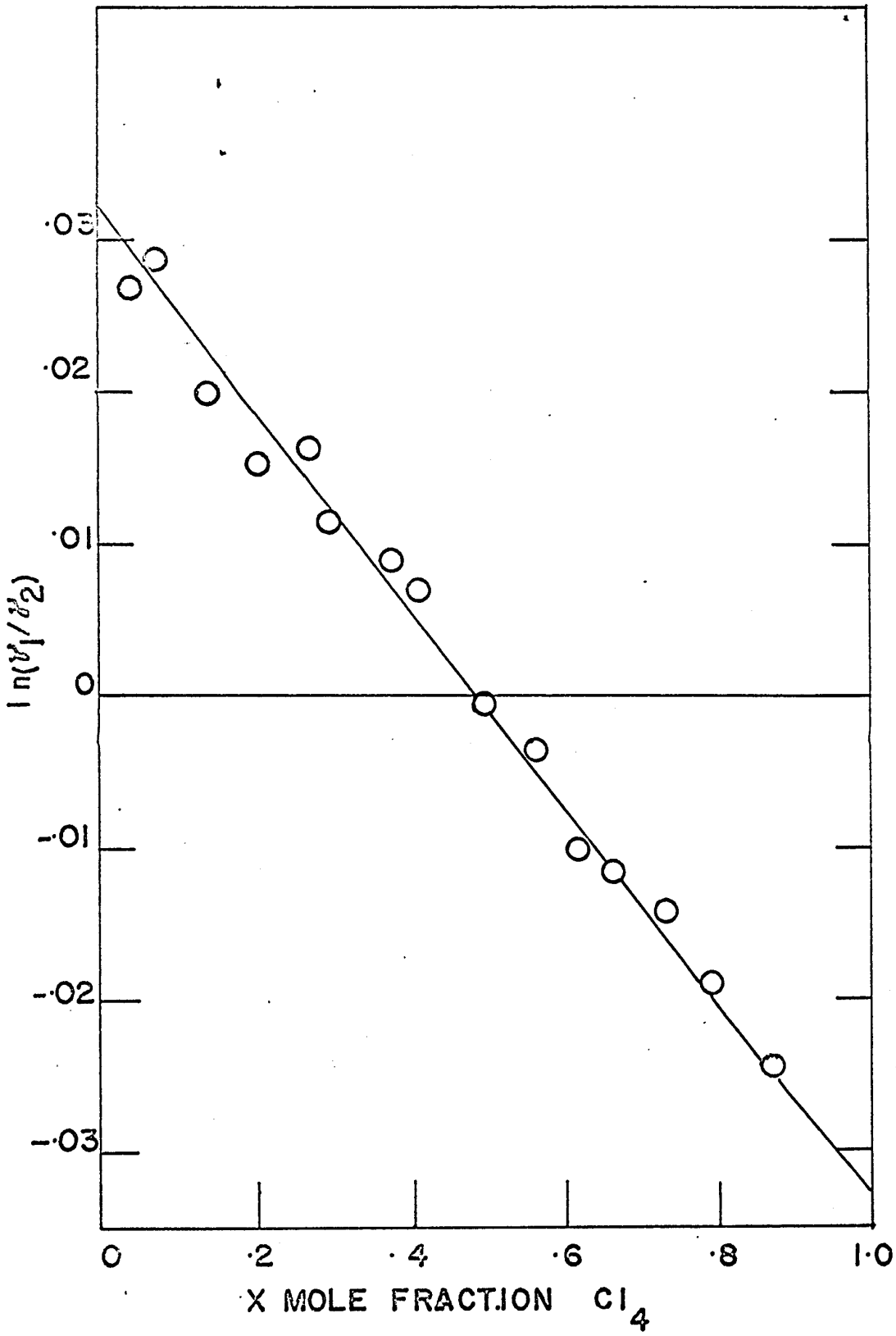

Fig. 15 Ratio of Natural Logarithm of Activity Coefficients vs. Compositions for the System Carbon Tetrachloride-Toluene

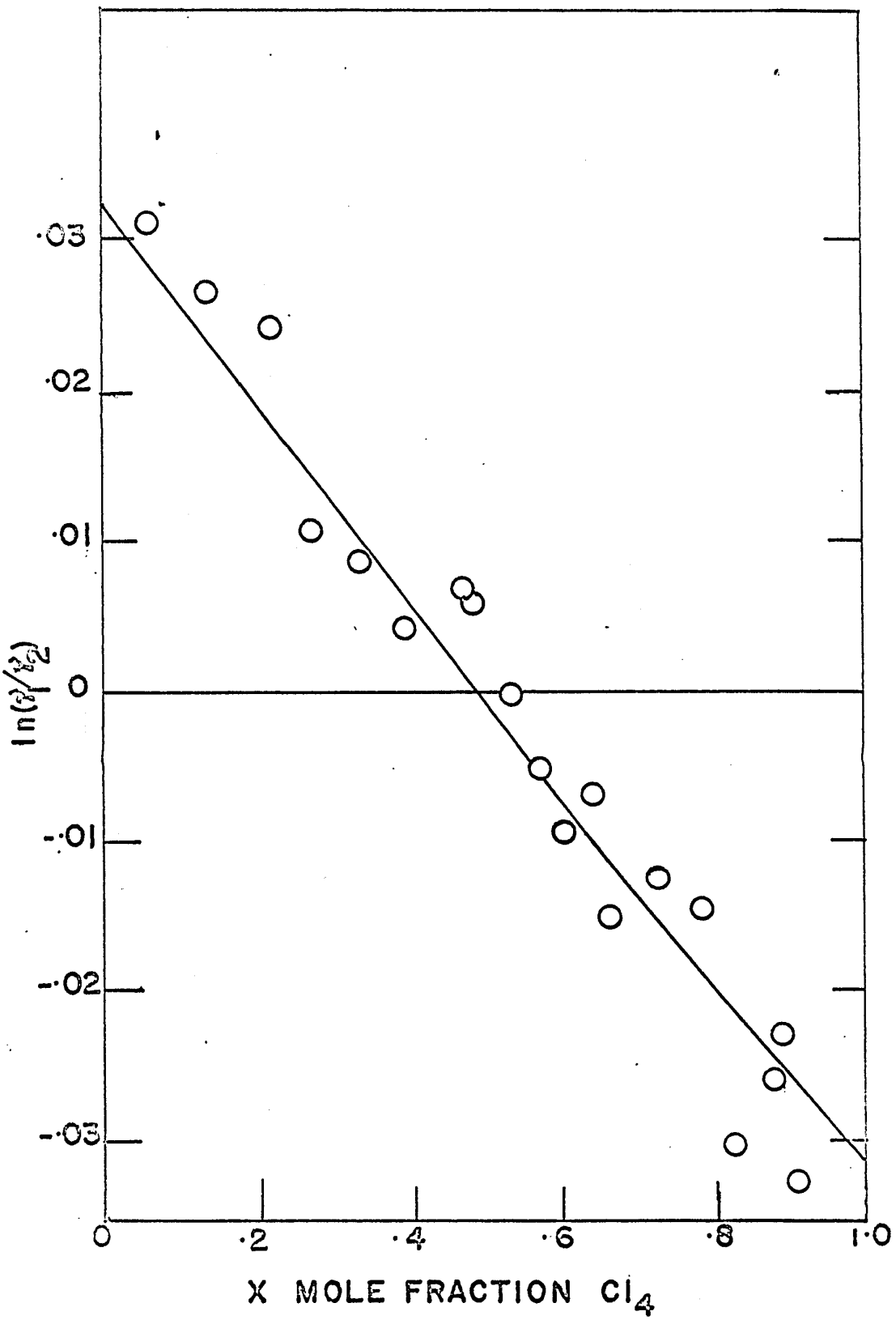

Fig. 16 Ratio of Natural Logarithm of Activity Coefficients vs. Compositions for the System Carbon Tetrachloride-Toluene at 40°C.

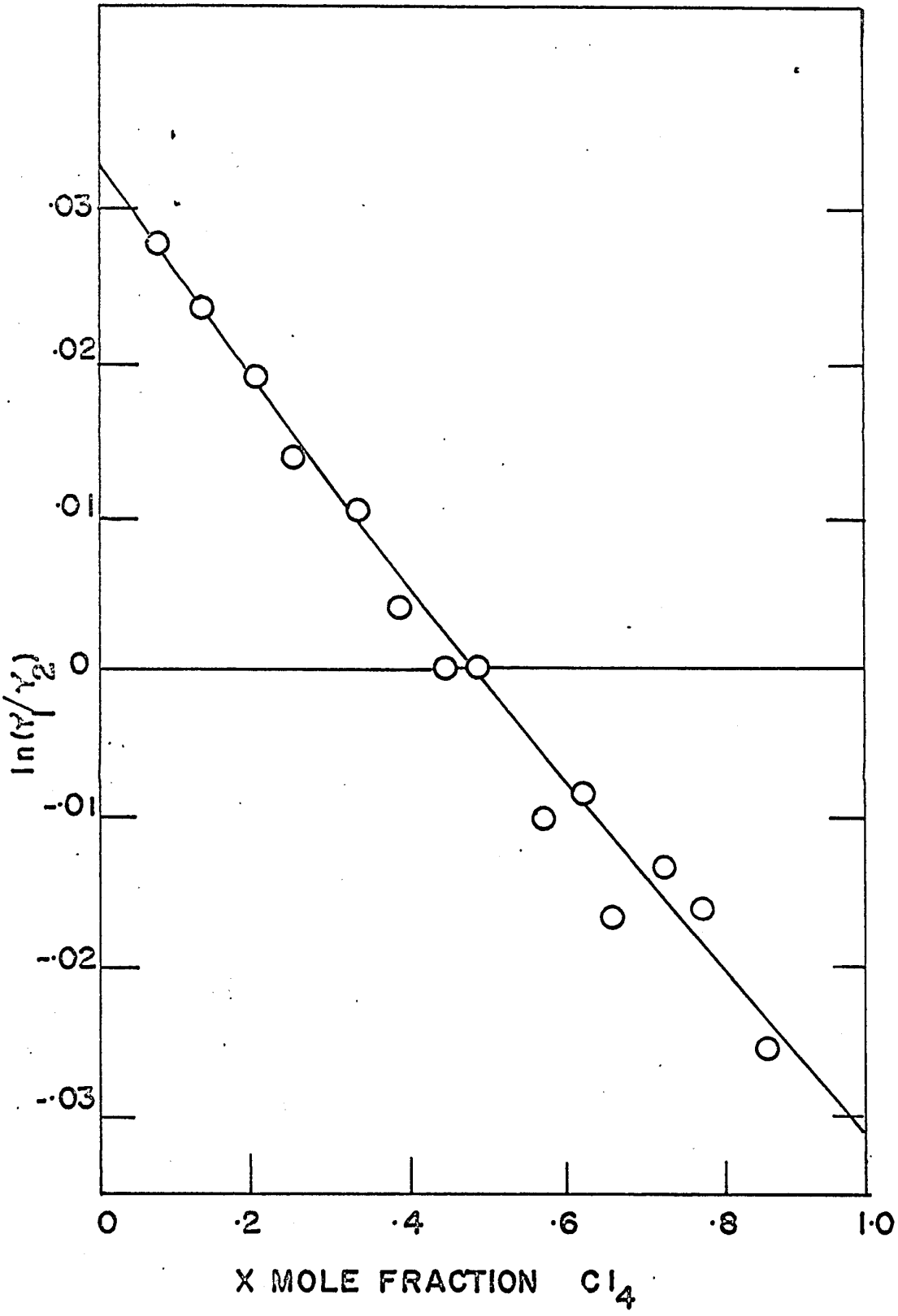

Fig. 17 Ratio of Natural Logarithm of Activity Coefficients vs. Compositions for the System Carbon Tetrachloride-Toluene at 45°C.

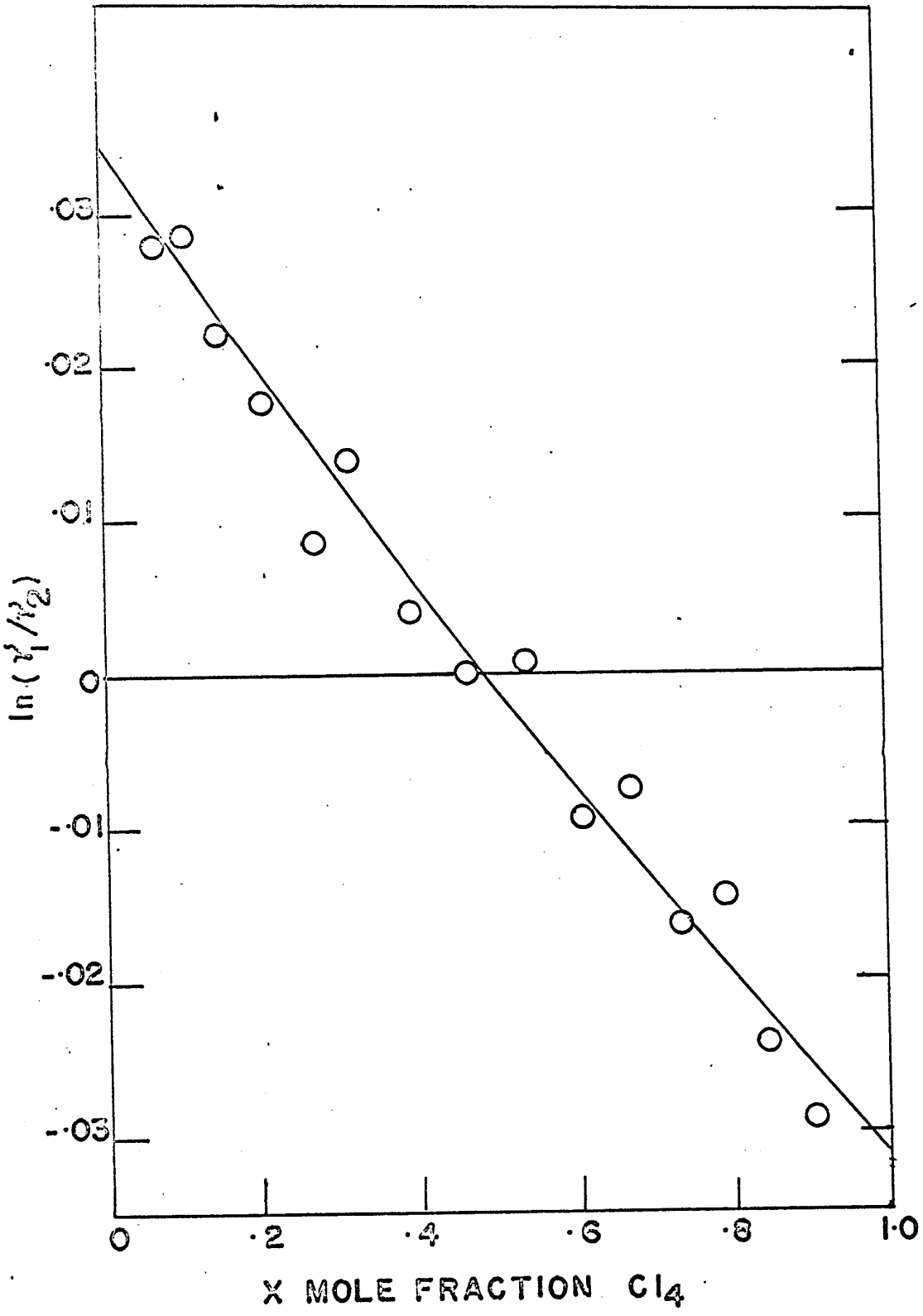

Fig. 18 Ratio of Natural Logarithm of Activity Coefficients vs. Compositions for the System Carbon Tetrachloride-Tolueen at 55°C.

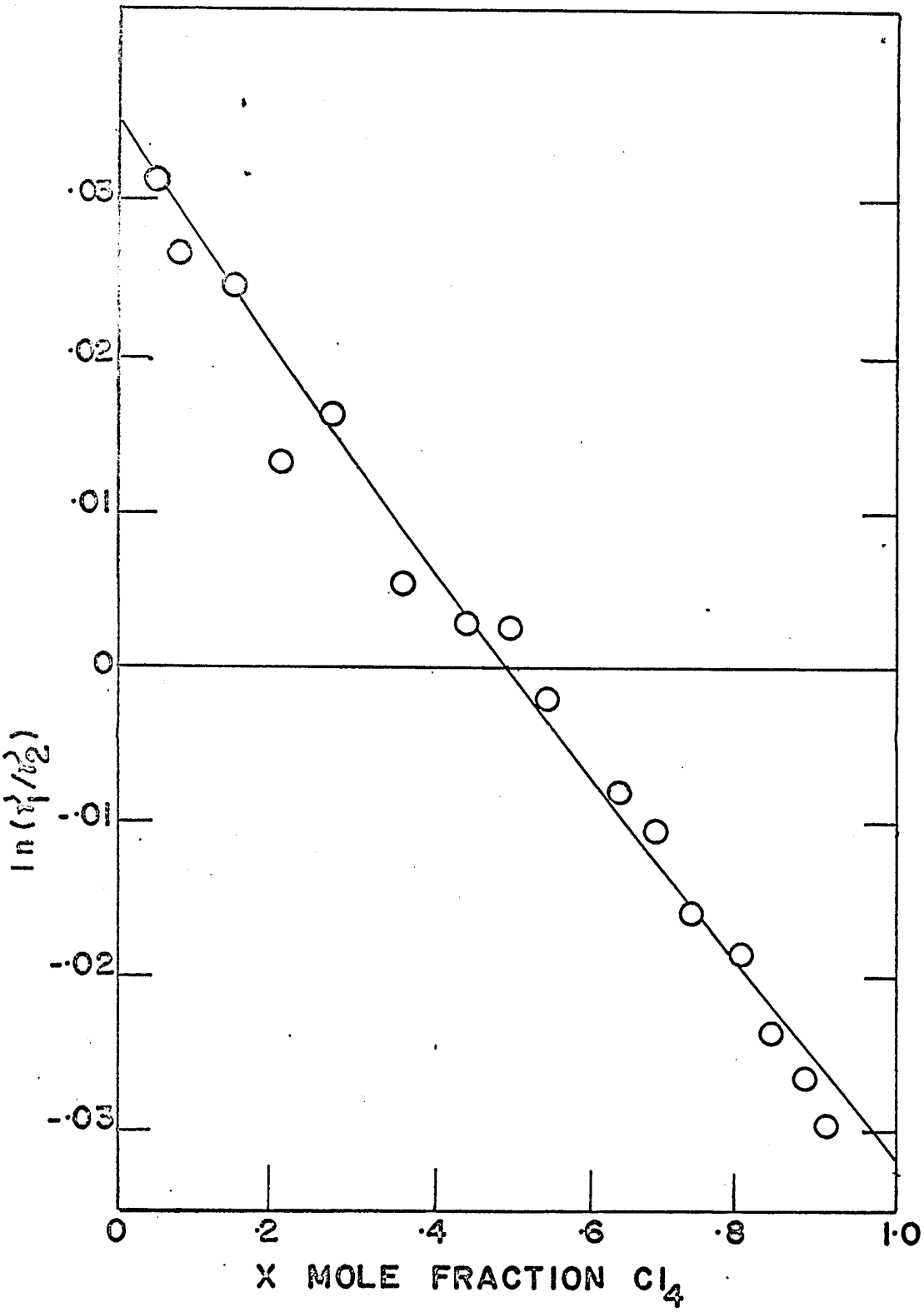

Fig. 19 Ratio of Natural Logarithm of Activity Coefficients vs. Compositions for the System Carbon Tetrachloride-Toluene at 65°C.

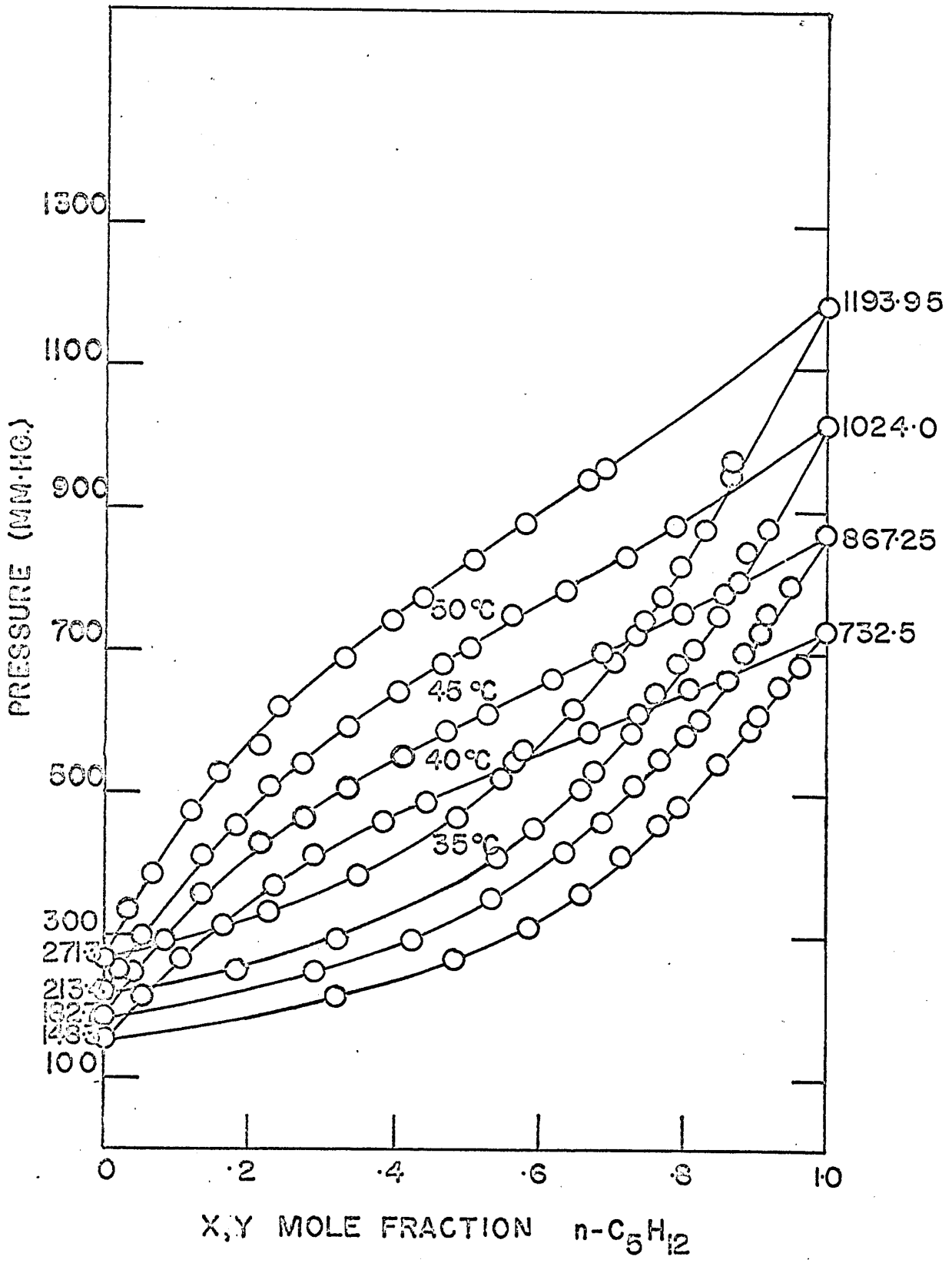

Fig. 20 Pressure vs. Composition Diagram for the System N-Pentane-Benzene at Isothermal Conditions.

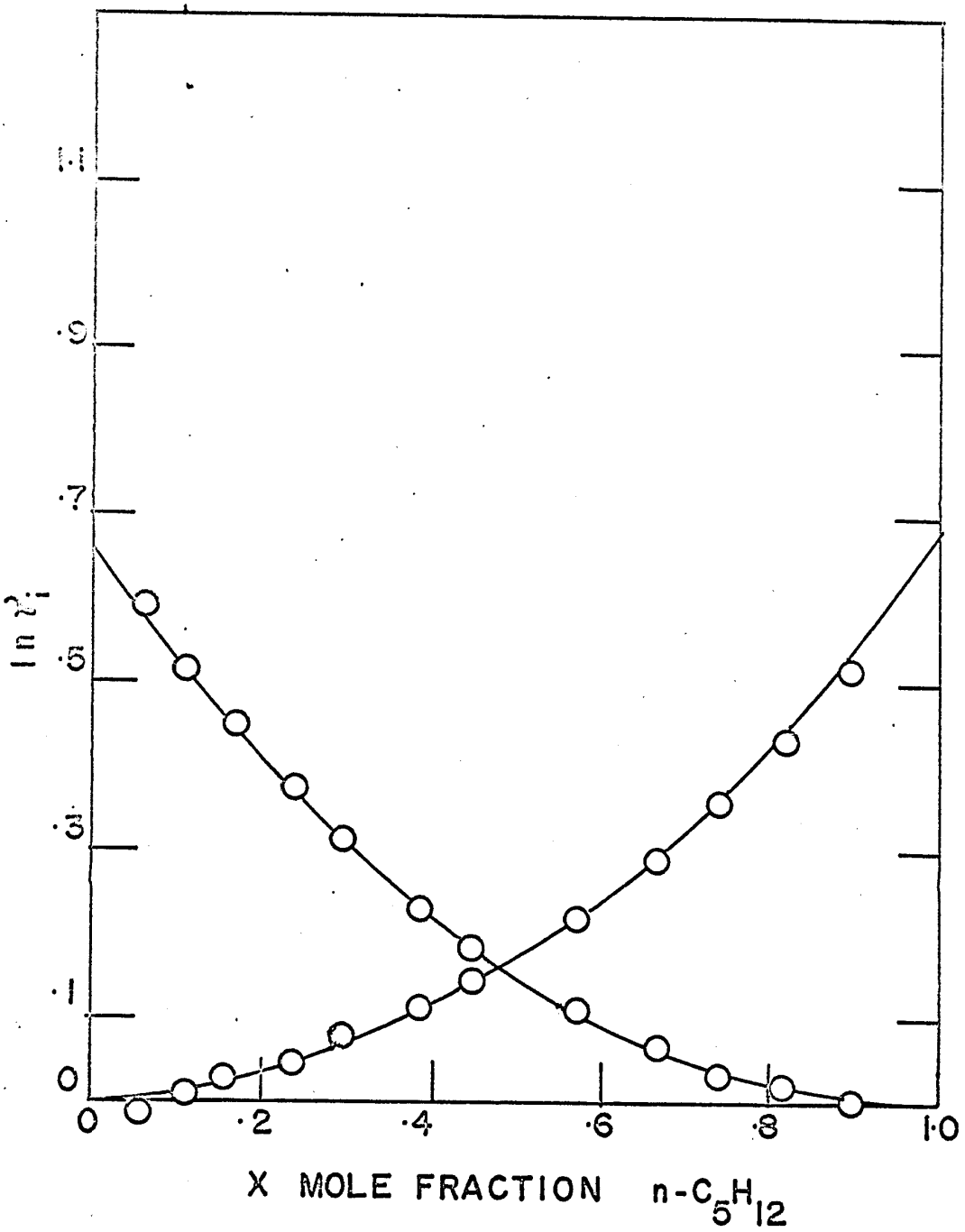

Fig. 21 Natural Logarithm of Activity Coefficients vs. Compositions for the System N-Pentane-Benzene at 35°C.

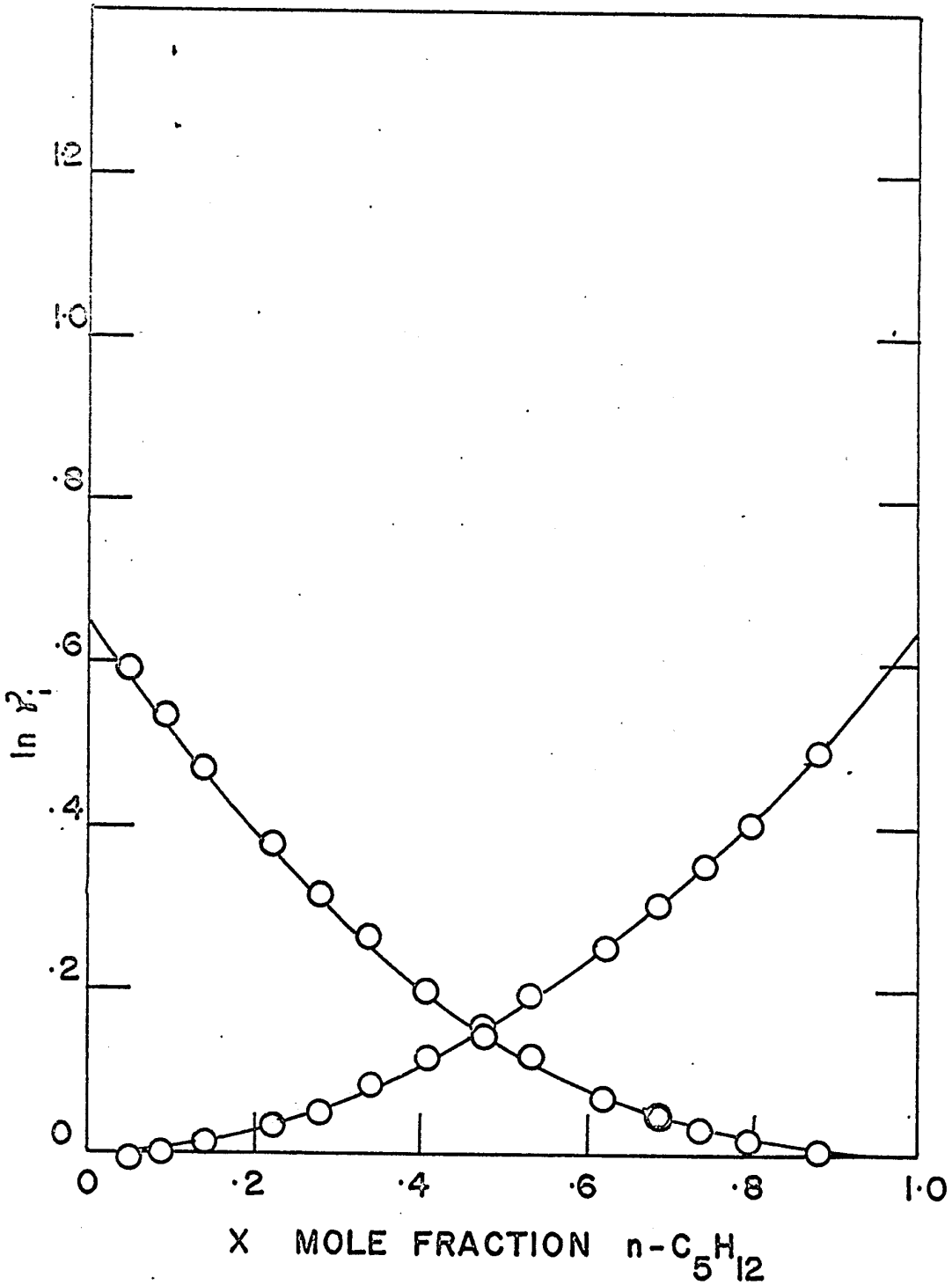

Fig. 22 Natural Logarithm of Activity Coefficients vs. Compositions for the System N-Pentane-Benzene at 40°C.

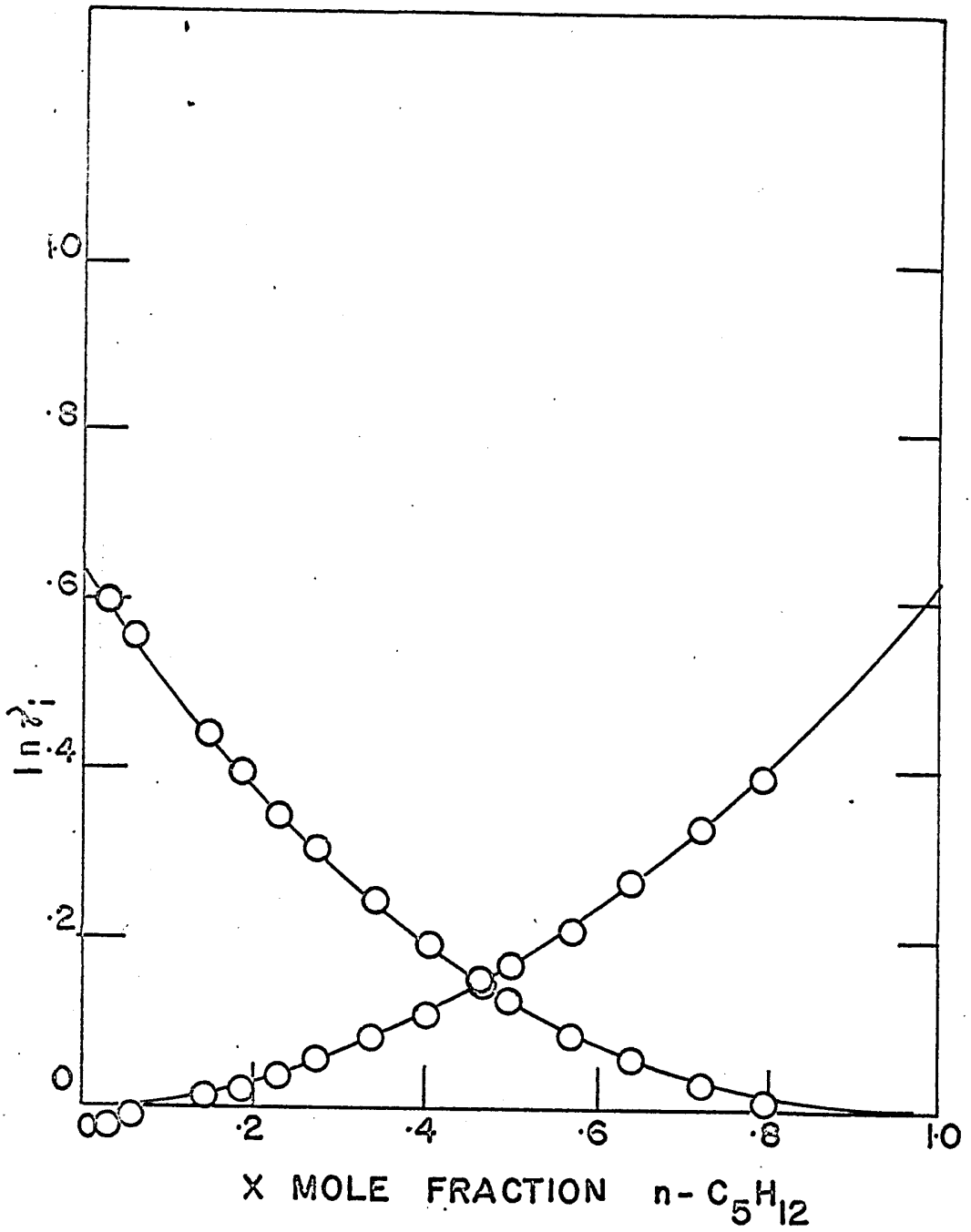

Fig. 23 Natural Logarithm of Activity Coefficients vs. Compositions for the System N-Pentane-Benzene at 45°C.

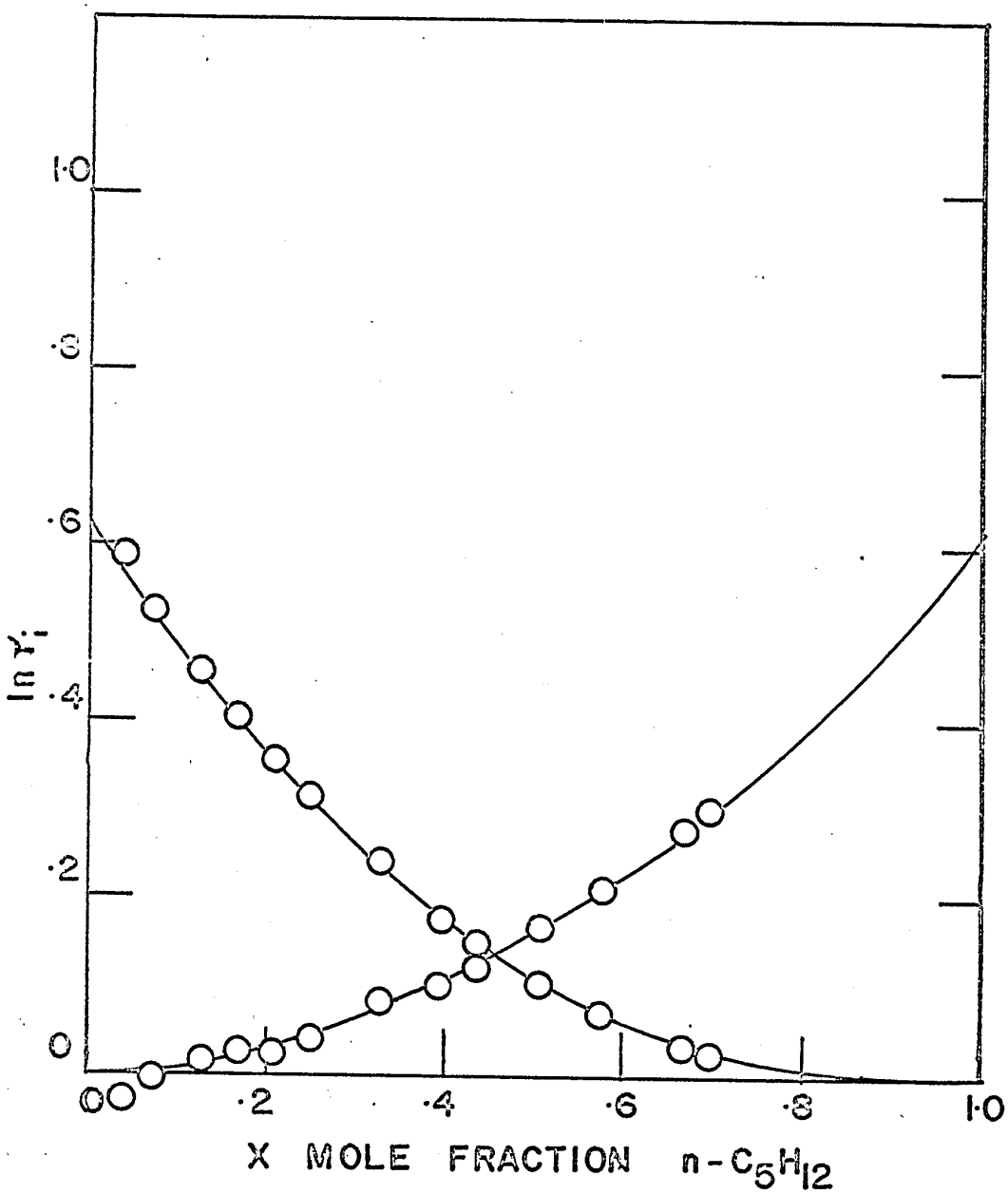

Fig. 24 Natural Logarithm of Activity Coefficients vs. Compositions for the System N-Pentane-Benzene at 50°C.

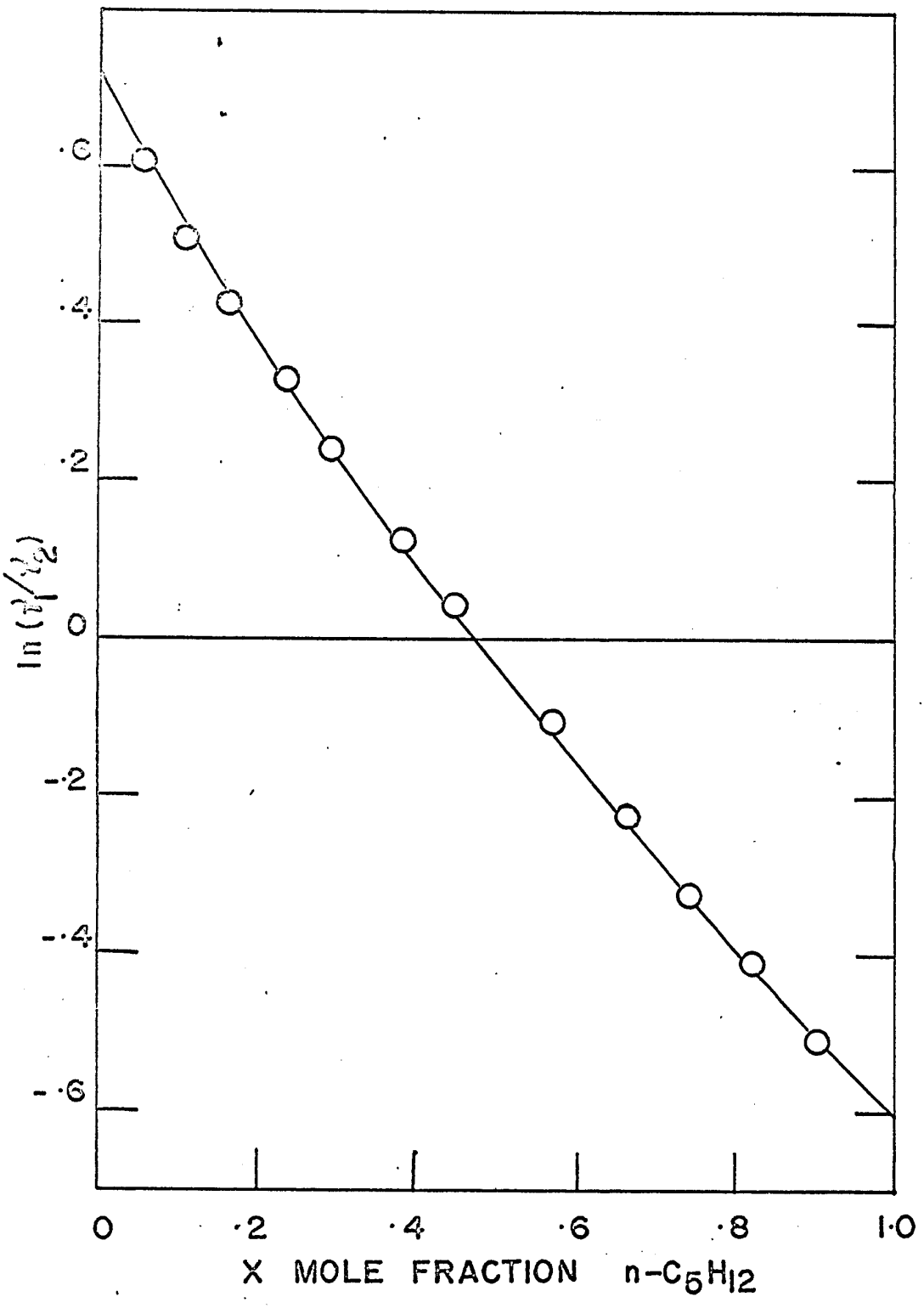

Fig. 25 Ratio of Natural Logarithm of Activity Coefficients vs. Compositions for the System N-Pentane-Benzene at 35°C.

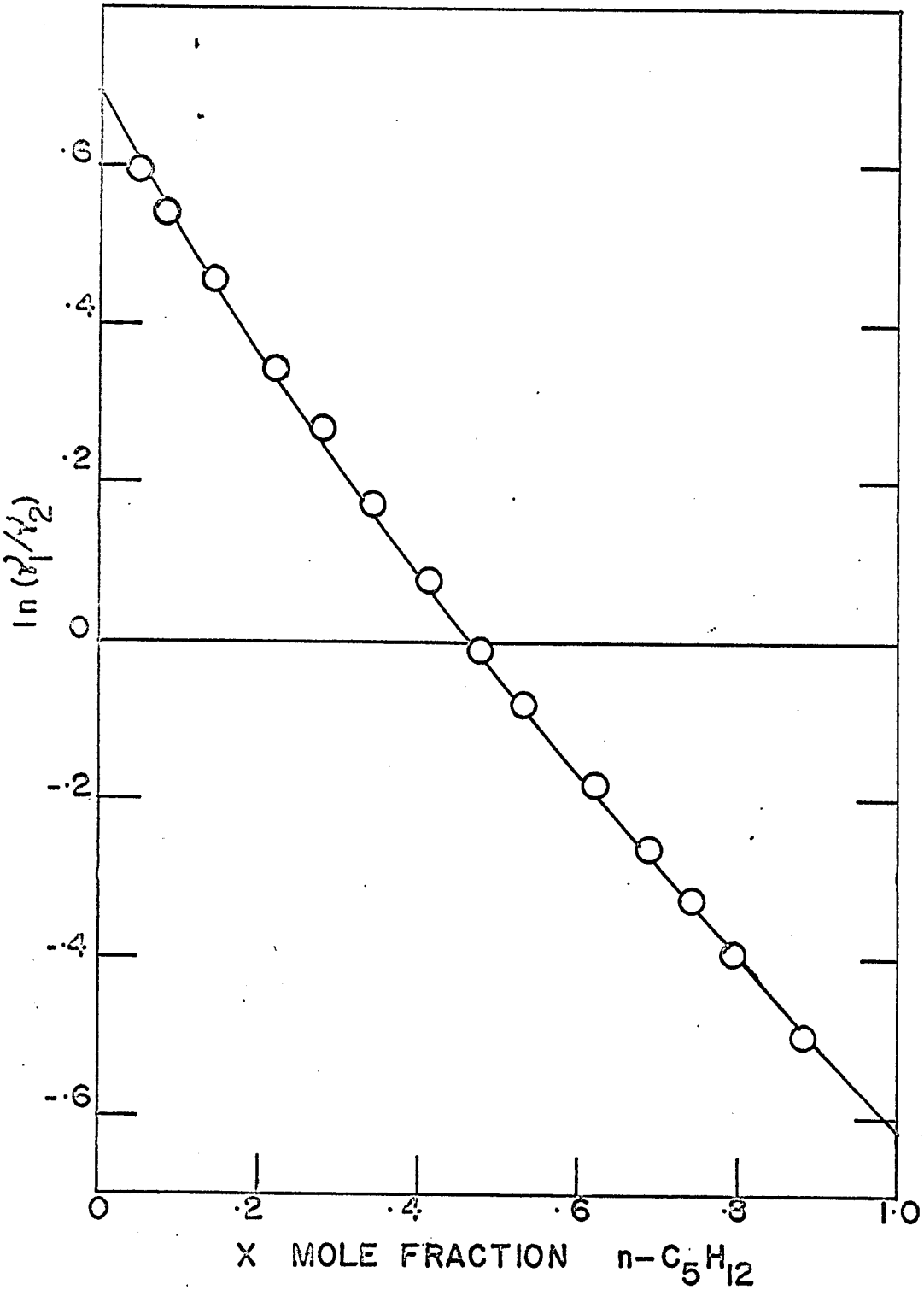

Fig. 26 Ratio of Natural Logarithm of Activity Coefficients vs. Compositions for the System N-Pentane-Benzene at 40°C.

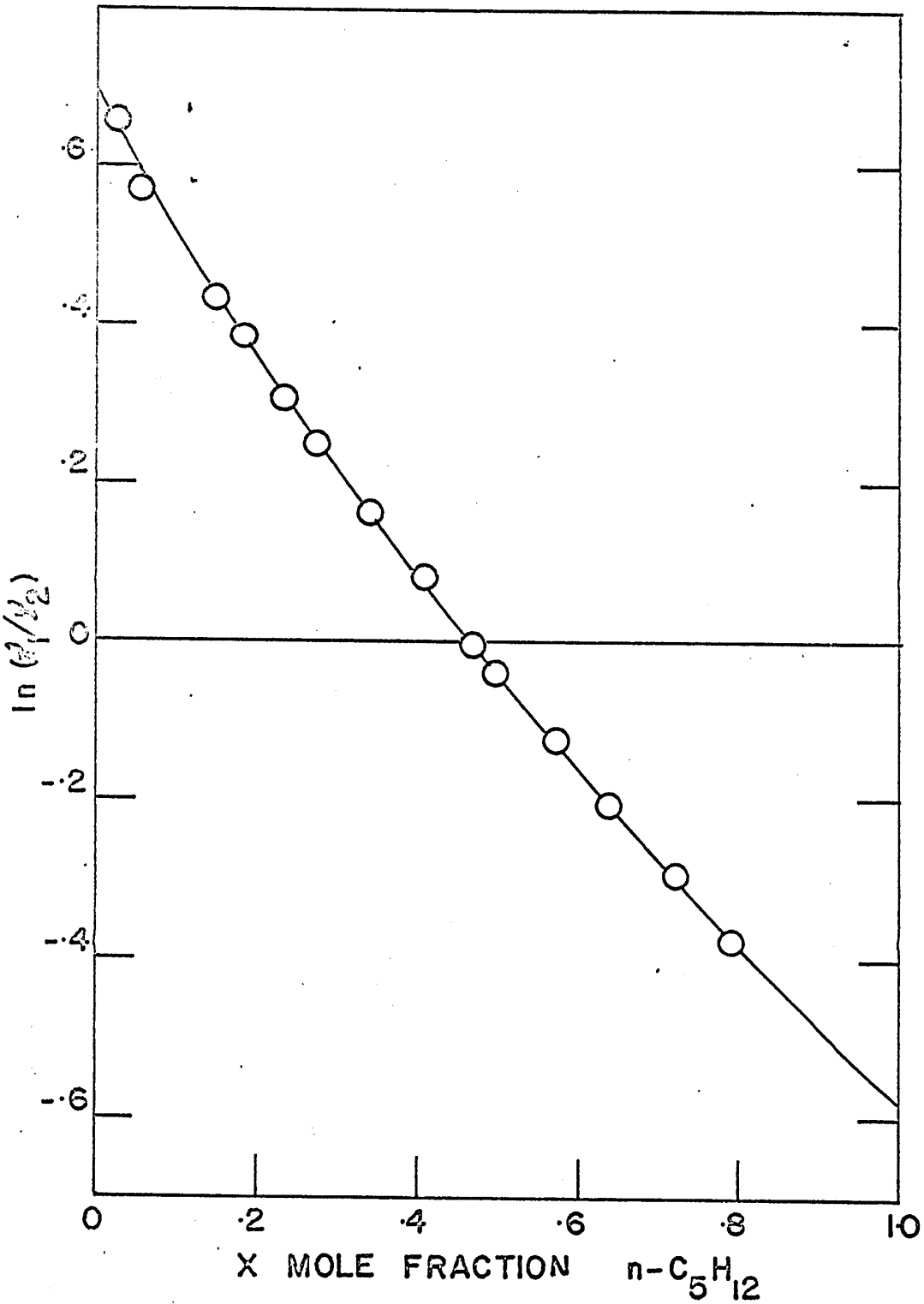

Fig. 27 Ratio of Natural Logarithm of Activity Coefficients vs. Compositions for the System N-Pentane-Benzene at 45°C.

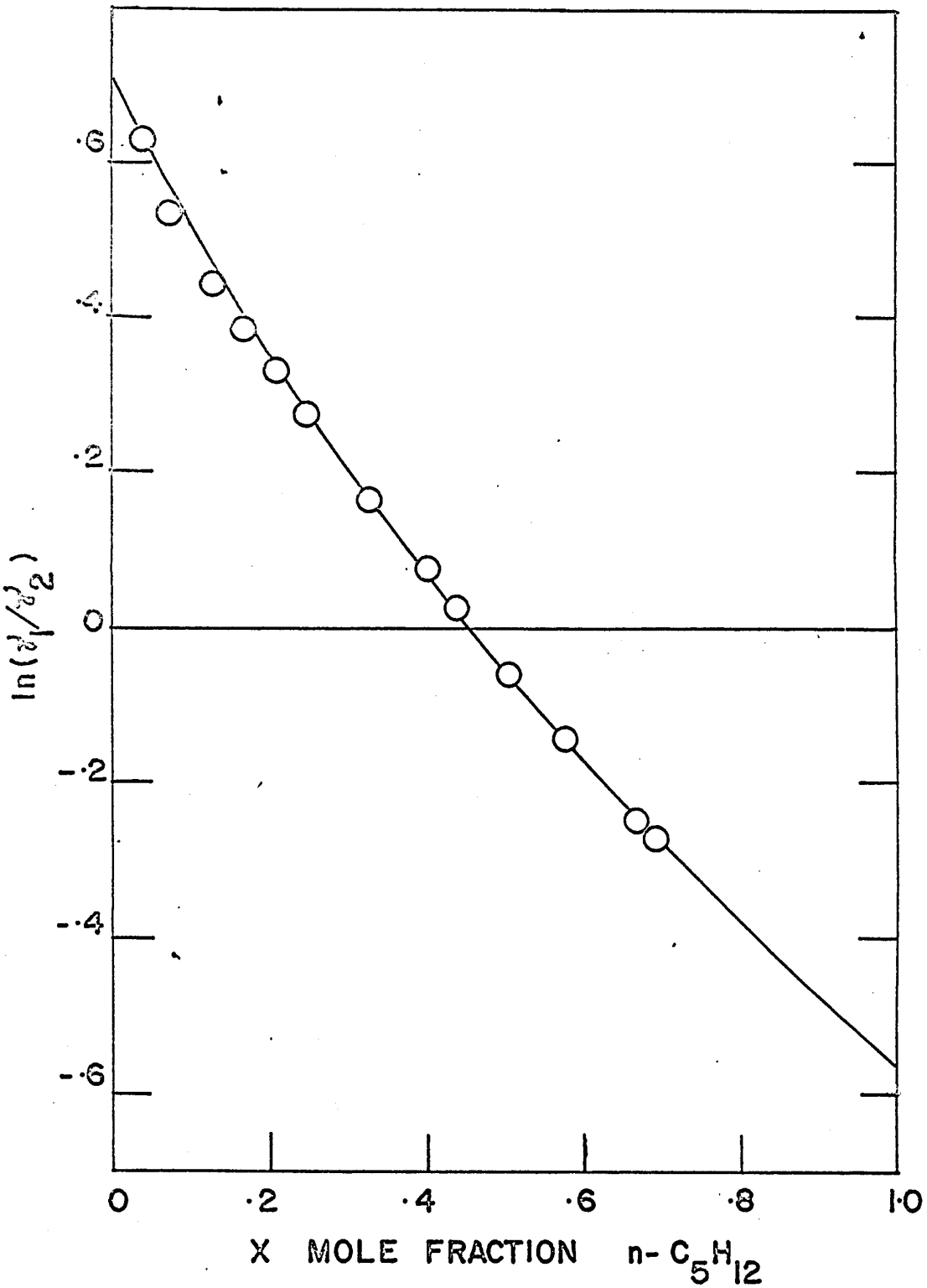

Fig. 28 Ratio of Natural Logarithm ofActivity Coefficients vs. Compositions for the System N-Pentane-Benzene at 50°C.

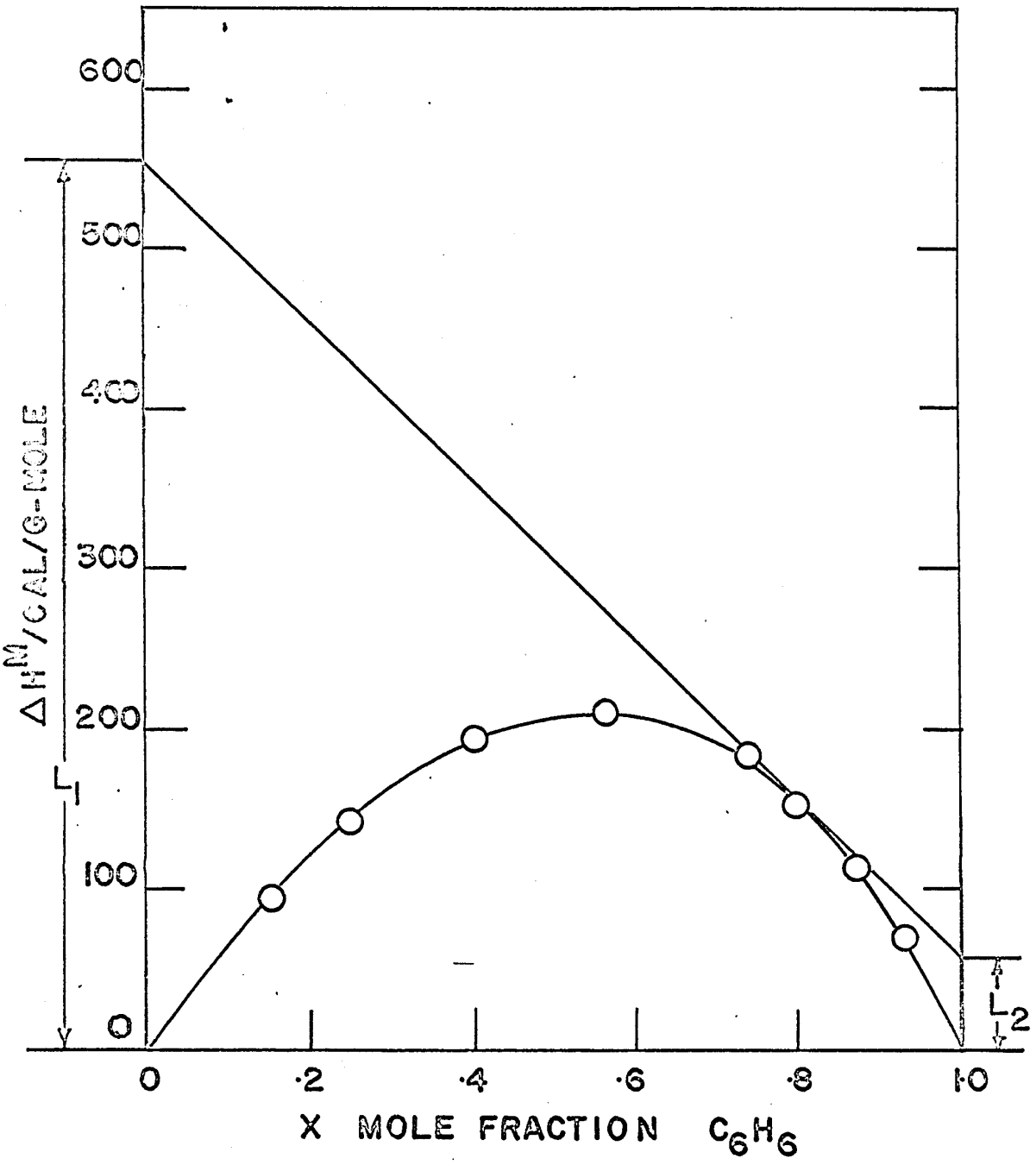

Fig. 29 Heat of Mixing vs. Compositions for the System N-Pentane-Benzene at 25°C, 1 Atm.

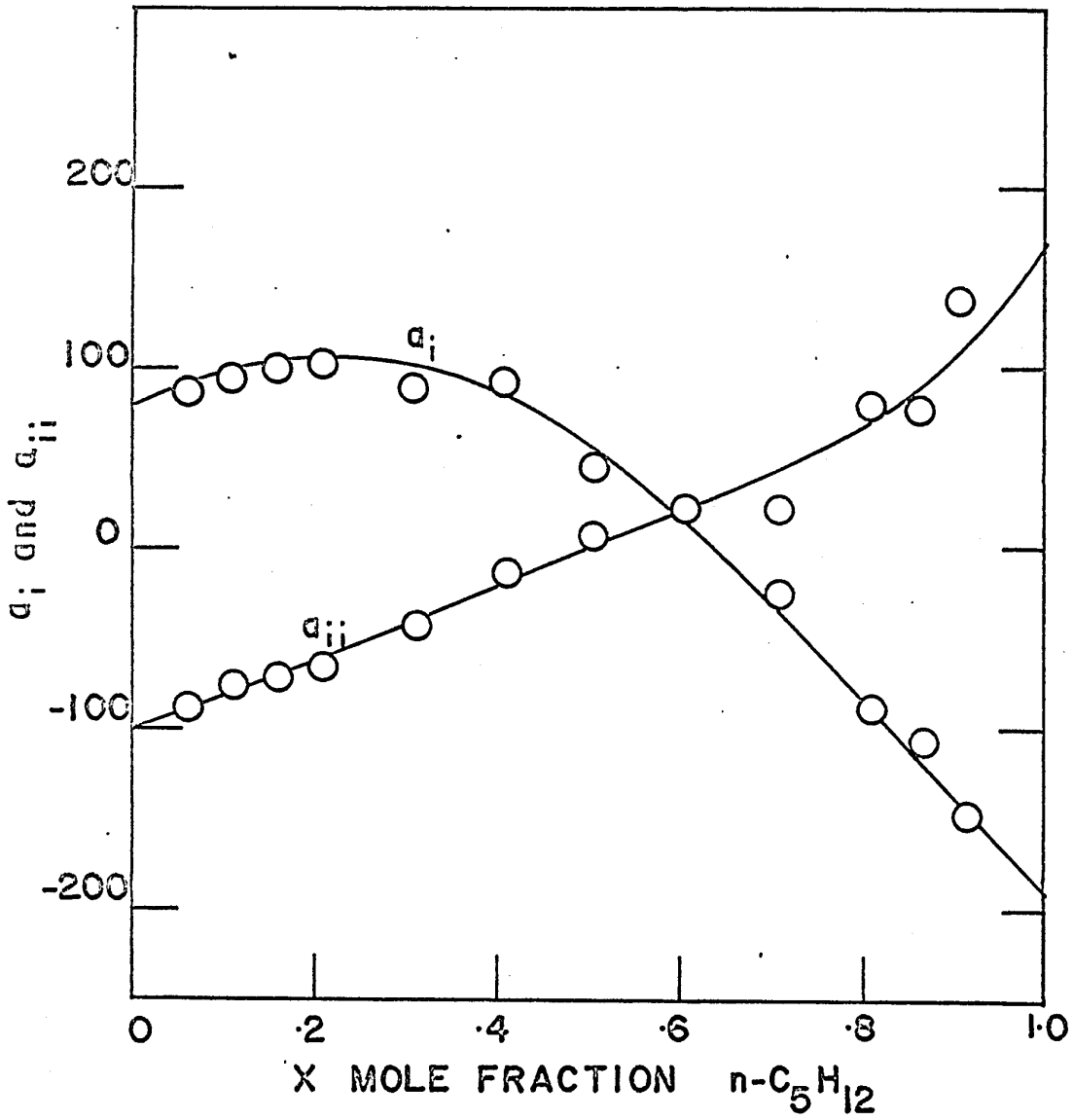

Fig. 30 Constants a_i and a_{ii} of Equation 29 vs. Compositions for the System N-Pentane-Benzene

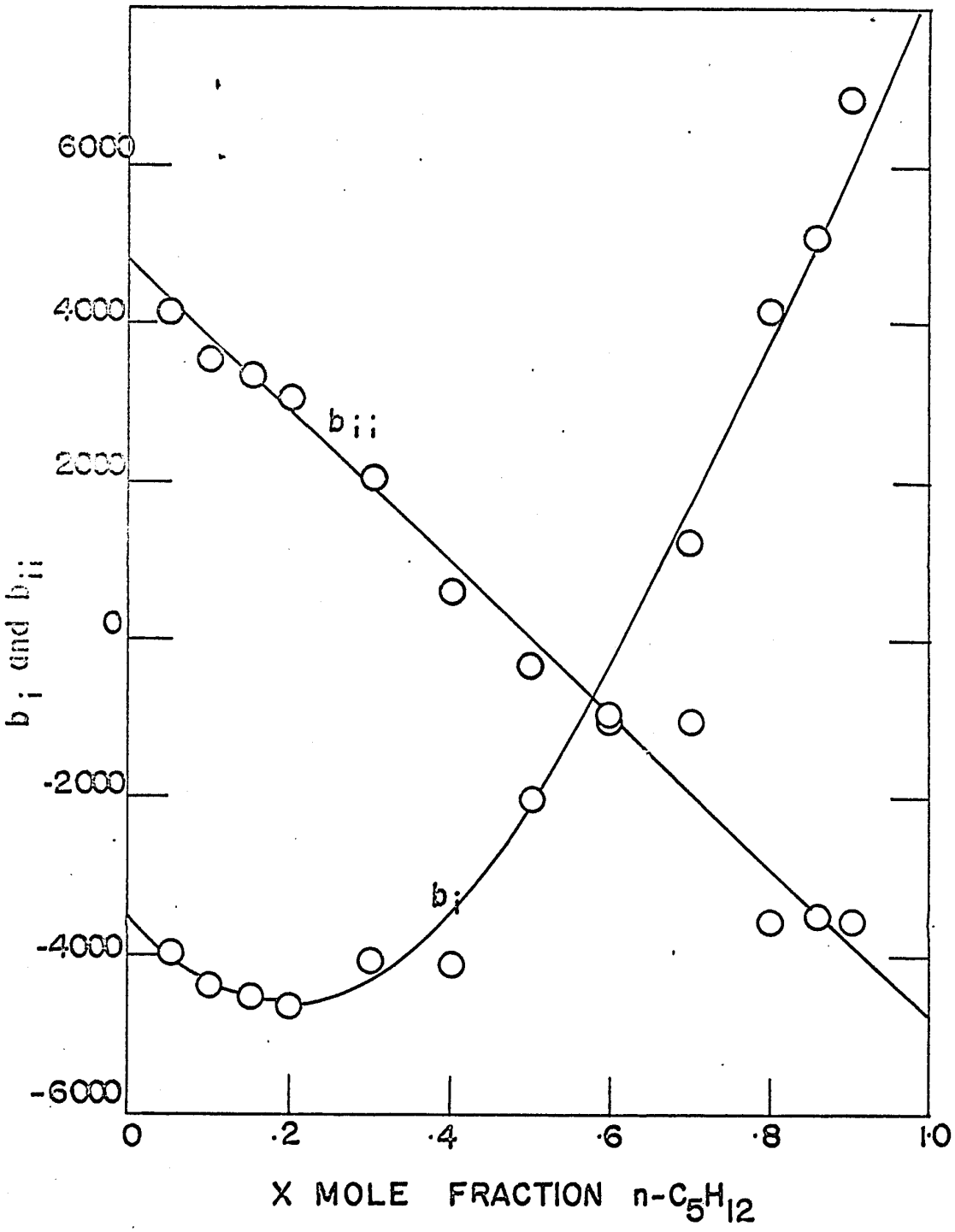

Fig. 31 Constants b_i and b_{ii} of Equation 29 vs. Compositions for the System N-Pentane-Benzene

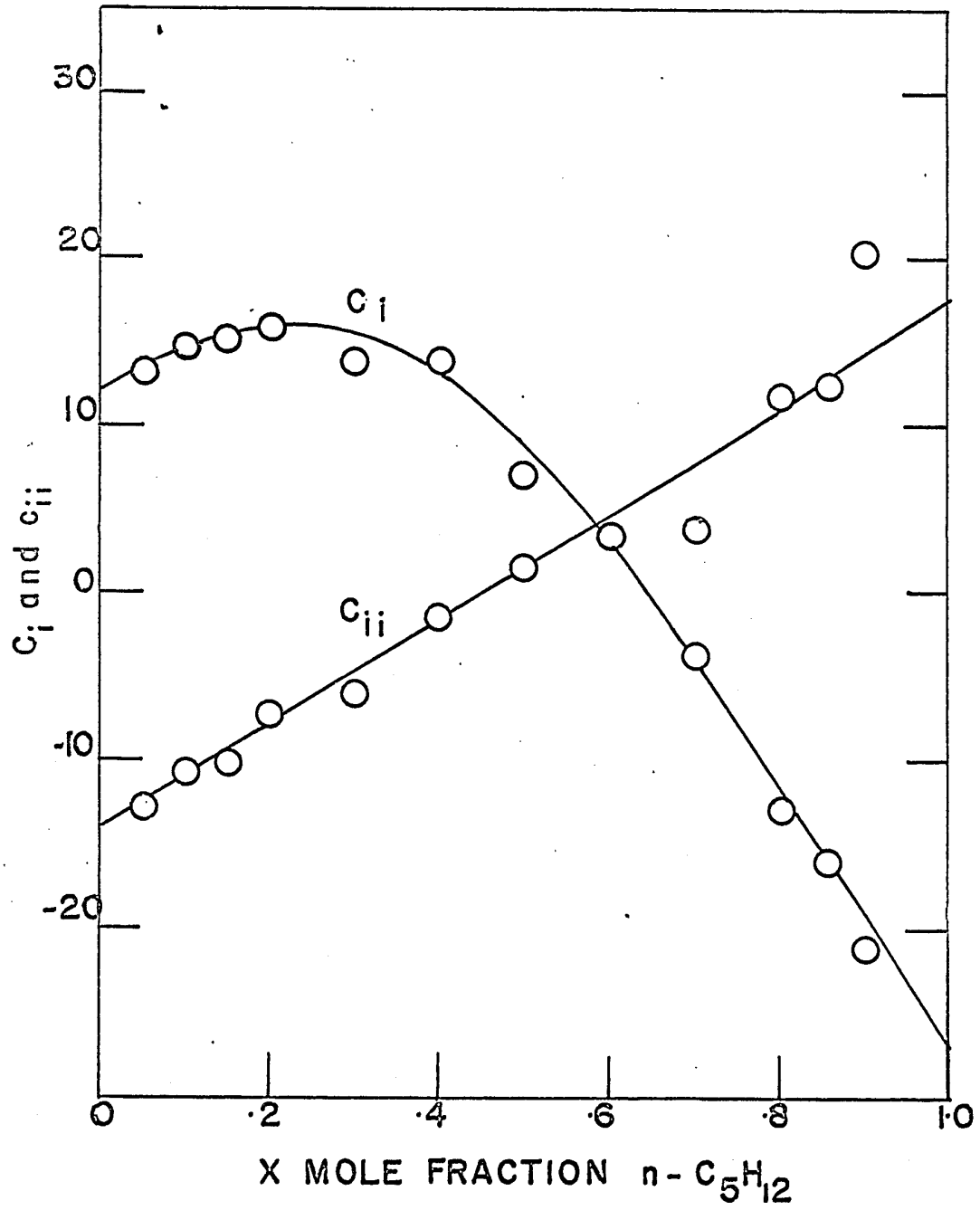

Fig. 32 Constants c_i and c_{ii} of Equation 29 vs. Compositions for the System N-Pentane-Benzene.

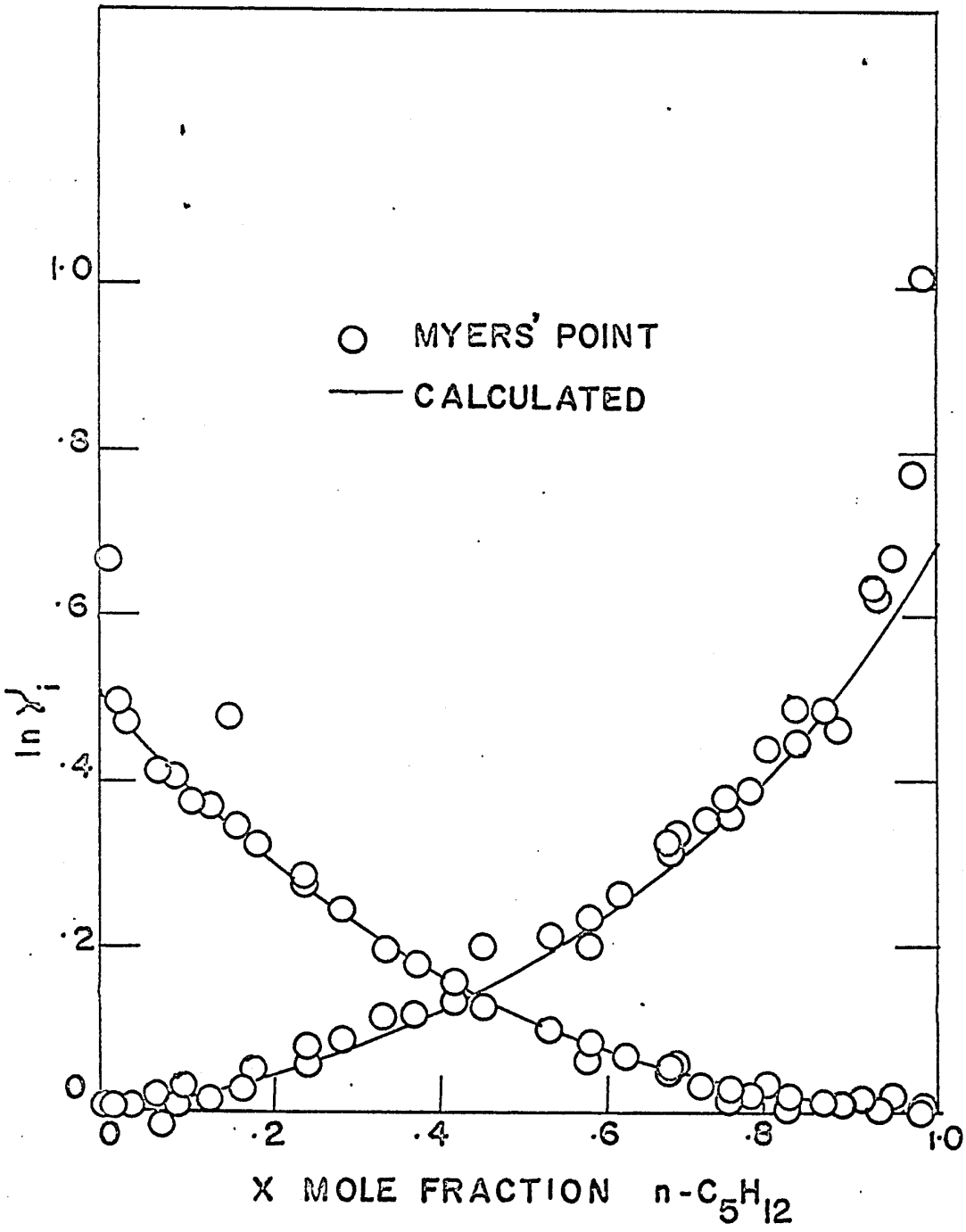

Fig. 33 Natural Logarithm of Activity Coefficients vs. Compositions for the System N-Pentane-Benzene at 1 Atm.

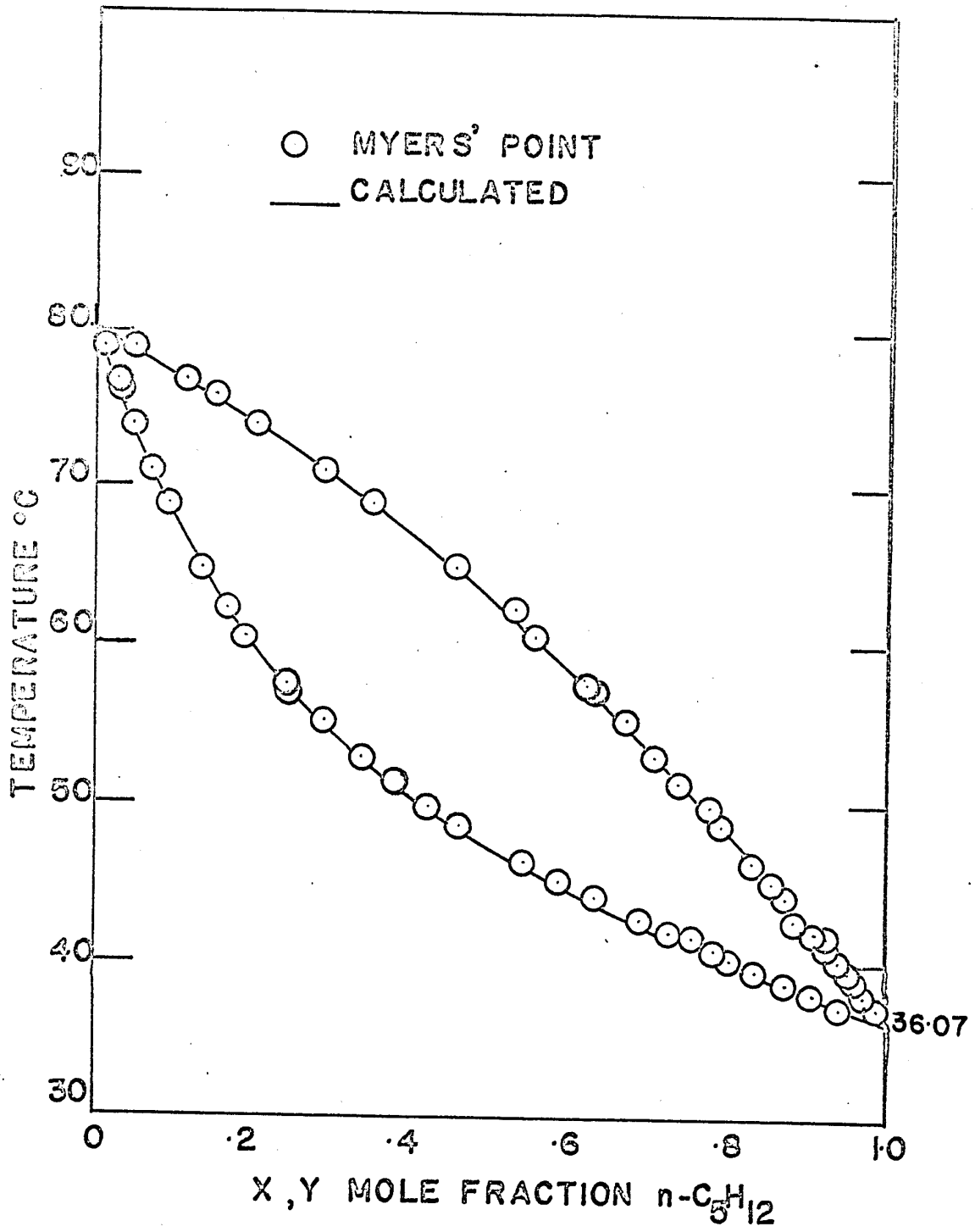

Fig. 34 Temperature vs. Compositions for the System N-Pentane-Benzene at 1 Atm.