ABSTRACT

The application of fundamental relations and concepts in classical solution thermodynamics to mixed-gas physical adsorption was studied.

Recently proposed methods for predicting the binary equilibria, such as the semi-empirical method (2), the ideal adsorbed solution method (13) and the extended potential theory (12), were extensively discussed. It was proved that the three methods are equivalent to each other at one condition of $(n_1^\circ)_\phi = (n_2^\circ)_\phi$.

The residual term between the semi-empirical method and the ideal adsorbed solution method was derived. It was found that the residue is of no significance for many systems.

Two methods of calculating the adsorbed phase activity coefficients were tested by using a number of literature data. It was found that many systems exhibit non-ideal behavior.

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NOMENCLATURE

A	specific area of adsorbent
a	specific area per mole of adsorbate
a	thermodynamic activity
b	Langmuir parameter, function of temperature only
f	partial fugacity of a component in the gas phase
f_s	saturation fugacity of pure unadsorbed liquid at adsorption temperature
f°	fugacity which a component in a mixture would exert as a pure adsorbate at the same temperature and adsorbate volume as the mixture
G	Gibbs free energy of adsorbed phase
K_i	Henry's law constant for adsorption of pure i
K	equilibrium constant in stoichiometric derivation
$\overline{K}$	defined in Equation (73)
n	moles of component adsorbed from gas mixture per unit mass of adsorbent
n°	moles of pure gas adsorbed per unit mass of adsorbent
n_t	total number of moles of all components adsorbed from gas mixture per unit mass of adsorbent
$P_i^\circ(\phi)$	equilibrium pressure for pure i corresponding to spreading pressure ϕ
P_i	equilibrium partial pressure for component i

R	gas constant
S	entropy of adsorbed phase
T	absolute temperature
U	internal energy of adsorbed phase
V	volume of gas adsorbed per unit mass of adsorbent
V_i	partial volume of component i adsorbed from gas mixture
$\tilde{V}$	molar volume of adsorbed component as a pure unadsorbed liquid at the boiling point corresponding to P°
V_m	volume adsorbed when the surface is covered with a complete unimolecular layer
x_i	mole fraction of component i in adsorbed phase
y_i	mole fraction of component i in gas phase
Z	defined in Equation (78)

Greek Letters

α	relative volatility or separation factor
β	correlating divisor in modified Polanyi theory
ϵ	Polanyi potential
γ	adsorbed phase activity coefficient
π	total pressure
ϕ	spreading pressure
μ_i	chemical potential of component i
ψ	function

Superscripts

°	pure component
a	adsorbed phase
g	gas phase

Subscripts

a	adsorbed phase
g	gas phase
i	component i
1	more volatile component in binary mixture

I INTRODUCTION

In recent years adsorption has become increasingly important as a method of separating small amounts of a heavy gas from a predominantly light gas stream. The petroleum industry in particular has used adsorption columns on natural gas wells to recover heavy components from a methane-rich gas. The design of the adsorbers is complicated by the lack of reliable equilibrium data for the multicomponent gas mixtures involved and by the absence of any reasonably accurate method of predicting such data. A number of useful methods for predicting binary equilibria from the corresponding pure component isotherms can be found in the literature, but the assumptions underlying these methods, such as absence of interactions between the adsorbed molecules, homogeneous adsorbent surface etc., limit their usefulness to specific binary systems or to a particular range of the variables. Therefore, an extensive study of the behavior of adsorbed phase is needed.

The fundamental concepts of classical thermodynamics will be applied in the study of mixed-gas physical adsorption. The notion of an activity coefficient has proved to be useful in correlating and interpreting vapour-liquid equilibrium data, but no extensive calculation of the adsorbed phase activity coefficients is available although Jelinek (17) and Myers et al. (13) introduced the concept of adsorbed phase activity coefficient.

The object of this work was therefore divided into the following parts:

1) the review of the application of classical thermodynamics to the mixed-gas adsorption

2) the critical discussion of the recently developed methods of predicting the binary adsorption equilibria

3) the investigation of the adsorbed phase activity coefficients by means of Myers and Prausnitz's method (13) and the stoichiometric method (17).

II LITERATURE REVIEW

The theoretical treatment of mixed-gas adsorption is somewhat more difficult than that of simple adsorption. Nevertheless, some attempts have been made to attack the problem. A rather complete review of the current status of mixed-gas adsorption is given in the monograph by Young and Crowell (1). Cook and Basmadjian (2) have also given a good brief summary including the principal publications in the literature concerning adsorption of gas mixtures. None of the methods to be mentioned consider adsorbate-adsorbate interactions. In order to avoid redundancy, only those related to this work or published after 1965 are discussed in this chapter.

Much of the early effort was centered on the extension of pure component isotherm equations to include binary mixtures. For instance, Markham and Benton (3) derived equations for the adsorption of binary mixtures based on the same two assumptions underlying the Langmuir equation:

$$V_1 = \frac{V^\circ_{m_1} b^\circ_1 P_1}{1 + b^\circ_1 P_1 + b^\circ_2 P_2} \qquad (1)$$

$$V_2 = \frac{V^\circ_{m_2} b^\circ_2 P_2}{1 + b^\circ_1 P_1 + b^\circ_2 P_2} \qquad (2)$$

A theoretical treatment extending the BET approach to the adsorption of gas mixtures has been suggested by Hill (4), on the basic assumption that molecules in the second and higher layers have evaporation-condensation characteristics of a liquid mixture at the same composition and temperature. The main drawback of this kind of approach lies in the limited range of validity of the conventional isotherm equations (Langmuir, BET) and the number of systems which can be predicted by this method is consequently small.

Szepesy (5) obtained the separation factor α by the division of Equations (1) and (2):

$$\alpha = \frac{x_2}{x_1} \; \frac{P_1}{P_2} = \frac{V^{\circ}_{m_2} \, b^{\circ}_2}{V^{\circ}_{m_1} \, b^{\circ}_1} \tag{3}$$

For the purpose of calculating the full binary isotherms, $V_1 = f_1 (P_1)$ and $V_2 = f_2 (P_2)$, Szepesy proposed that Equation (3) be combined with an empirical relation used by Lewis and co-workers (6)

$$\frac{V_1}{V^{\circ}_1} + \frac{V_2}{V^{\circ}_2} = 1 \tag{4}$$

The novelty in Szepesy's proposition was to consider $V^{\circ}_m \, b^{\circ}$ as a variable parameter determined from the pure component isotherms and applicable to binary systems with variable separation factors.

Because Lewis' equation does not hold for many systems, the Szepesy method consequently requires a priori knowledge regarding the validity of Equation (4).

Several attempts have been made to extend the adsorption potential concept to the binary adsorption equilibria. Tóth (7) has proposed a method to predict binary equilibrium data from individual pure component isotherms. Excellent results were obtained when the method was tested on the data of Szepesy and Illés (8) measured at a total pressure of one atmosphere. The assumptions made, in this method, limit its application to the monolayer adsorption isotherms and a pressure range of about 0.1 - 1.5 atm. The calculation of total and partial volumes requires a somewhat lengthy procedure.

Other methods, based on the potential theory, were used by Lewis, et al. (6), Kapfer, et al. (9) and Bering, et al. (10). Lewis, et al. combined the modified Polanyi equation with their empirical relation (Equation (4)) to determine the separation factors by trial and error. It gave fair results when used at low total pressures. Lewis et al. have stated that uncertainty exists in choosing the proper molar volume for the adsorbed phase as the correlating divisor ("affinity coefficient" of Dubinin (11)).

Kapfer, et al. (9) assume no binary interference, that is, each gas is adsorbed from the mixture as if the other binary component were not present.

Bering, et al. (10) used Dubinin's equation (11) as a starting point, assumed the standard state to be that of a bulk solution whose saturated vapors have the same composition as equilibrium vapors above the adsorbed layer, and by using Lewis' empirical relation (Equation (4)) were able to calculate the full binary isotherms, $V_1 = f_1 (P_1)$ and $V_2 = f_2 (P_2)$. This method was tested only on the system chloroform-diethyl ether on activated charcoal at 50° C. Rather good results were obtained.

Grant and Manes (12) have recently extended the modified Polanyi theory to predict binary hydrocarbon gas adsorption on activated carbon. They used the normal boiling point molar volume as the correlating divisor. The method was claimed to extend over an extremely wide range of separation factors. It was successfully applied to data on mixtures of methane with propane, butane, and hexane at 25° C and total pressure up to 1000 psig. but not so good for higher hydrocarbons.

Thermodynamics has played an important role in the study of mixed-gas adsorption. Lewis, et al. (6), Cook and Basmadjian (2) and Myers and Prausnitz (13) have done much work in this kind of approach.

Lewis, et al. (6) proposed a semi-empirical thermodynamic method which was based on an equation proposed by Broughton (14):

$$\int_0^{V_1^\circ} (\ln P_1\, dV_1)_{P_2 = 0} - \int_0^{V_1^\circ} (\ln P_1\, dV_1)_{P_1 + P_2 = \pi} =$$

$$\int_0^{V_2^\circ} (\ln P_2\, dV_2)_{P_1 = 0} - \int_0^{V_2^\circ} (\ln P_2\, dV_2)_{P_1 + P_2 = \pi} \tag{5}$$

If the separation factor α is assumed constant, Equation (5) may be combined with Equation (4) to give an expression for the prediction of α from the pure component isotherms:

$$\frac{(\alpha - 1)\, V_{1\pi}^\circ}{\alpha\beta - 1} \ln \alpha\beta = (V_{2,\pi}^\circ - V_{1,\pi}^\circ) \ln \pi -$$

$$\int_0^{V_{2,\pi}^\circ} (\ln P_2\, dV_2)_{P_1 = 0} + \int_0^{V_{1,\pi}^\circ} (\ln P_1\, dV_1)_{P_2 = 0} \tag{6}$$

where $\alpha = \frac{y_1}{x_1}\, \frac{x_2}{y_2} = \frac{P_1}{P_2}\, \frac{V_2}{V_1} = \text{constant}$

$$\beta = \frac{V_{1,\pi}^\circ}{V_{2,\pi}^\circ}$$

Complete binary isotherms may be calculated by combining Equations (4) and (6). The experimental results of Lewis and co-workers agree well with the predicted separation factors for a number of hydrocarbon mixtures on activated carbon and silica gel. The lack of agreement for some systems at higher values of α (>15) is undoubtedly due to the deviation from Equation (4) and to the fact that α becomes increasingly concentration dependent.

Basmadjian (15) modified the Lewis-Broughton relation and obtained a simple expression for constant separation factor systems:

$$\log \alpha = \frac{1}{V^{\circ}_{1,\pi}} \int_{0}^{V^{\circ}_{1,\pi}} \log \left(\frac{P_1^{\circ}}{P_2^{\circ}}\right)_V dV^{\circ} \qquad (7)$$

where $\alpha < 4$ and $V^{\circ}_{2,\pi}/V^{\circ}_{1,\pi} < 1.5$.

If $\left(\frac{P^{\circ}_1}{P^{\circ}_2}\right)_V$ is constant, this expression can be reduced to

$$\alpha = \left(\frac{P^{\circ}_1}{P^{\circ}_2}\right)_{V^{\circ}_{1,\pi}}$$

which is analogous to Raoult's law for vapor-liquid equilibria.

A simple semi-empirical method was developed by Cook and Basmadjian (2) for the prediction of adsorption equilibria of binary gas mixtures from corresponding pure component isotherms. The approach used Equation (7) as its starting point. It is applicable to systems with variable separation factors, valid at low and high concentrations and pressures, and is not contingent on the validity of Equation (4). The only failure of this method is that it cannot provide a quantitative prediction of binary equilibria in the region of multi-layer adsorption and for systems exhibiting azeotropes. It also does not take the adsorbate-adsorbate interactions into account.

Recently, Myers and Prausnitz (13) made a thermodynamic study of mixed-gas adsorption equilibria. A simple technique for calculating the adsorption equilibria for components in a gaseous mixture was proposed, using only pure component adsorption equilibrium data at the same temperature and on the same adsorbent. The essential idea of the calculation lies in the recognition that in an ideal solution the partial pressure of an adsorbed component is given by the product of its mole fraction in the adsorbed phase and the pressure which it would exert as a pure adsorbed component at the same temperature and spreading pressure as those of the mixture.

III THERMODYNAMIC CONSIDERATIONS

The application of solution thermodynamics to mixed-gas adsorption has been studied by Myers and Prausnitz (13). It was shown that the traditional method of treating the problem using classical thermodynamics would be useful in: (1) obtaining an ideal adsorbed solution concept analogous to Raoult's law in vapour-liquid equilibria, (2) calculating the activity coefficients in the adsorbed phase from pure isotherms and binary equilibrium data, and (3) deriving a method for predicting the binary equilibria. For this purpose, it is worthwhile to make a general review of adsorption thermodynamics.

A. Adsorption Equilibria

Hill (16, 22) pointed out that the validity of the usual thermodynamic equations for the adsorbed phase rests upon three assumptions:

(1) the adsorbent is assumed to be thermodynamically inert

(2) the adsorbent has a temperature - invariant area which is the same for all adsorbates

(3) the Gibbs' definition of adsorption applies.

Based on these assumptions, Myers and Prausnitz (13) derived the phase rule for adsorption:

$$\binom{\text{degrees of}}{\text{freedom}} + \binom{\text{number of}}{\text{phase}} = \binom{\text{number of}}{\text{component}} + 3 \tag{8}$$

Now, the basic thermodynamic equations for the adsorbed phase can be written in a form almost analogous to the familiar thermodynamic equations. For instance, the equations for internal energy U and Gibbs free energy G would be:

$$dU = TdS - \phi dA + \sum \mu_i \, dn_i \tag{9}$$

$$dG = -SdT + Ad\phi + \sum \mu_i \, dn_i \tag{10}$$

where S is the entropy of the adsorbed phase; A is the specific area of adsorbent; ϕ is the spreading pressure or the surface pressure which is defined by (16, 22, 25)

$$\phi(P_i^\circ) = \frac{RT}{A} \int_{P_i^\circ = 0}^{P_i^\circ = P_i^\circ} n_i^\circ (P_i^\circ) \, d\ln P_i^\circ \quad (\text{constant } T) \tag{11}$$

$n_i^\circ(P_i^\circ)$ is the adsorption isotherm for pure component i, and the integration may be performed graphically by plotting n_i°/P_i° vs. P_i° and determining the area under the curve. μ_i is the chemical potential of component i, and is defined as follows:

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,\, A,\, n_j} = \left(\frac{\partial G}{\partial n_i}\right)_{T,\, \phi,\, n_j} \tag{12}$$

Thus, the intensive variables for the Gibbs free energy are temperature, spreading pressure and composition. From Euler's theorem, the total Gibbs free energy may be written as

$$G = \sum n_i \mu_i \quad \text{(constant } \phi \text{ and } T) \tag{13}$$

An activity coefficient of component i in the mixed adsorbed phase may be defined as

$$\left.\begin{aligned} \mu_i &= \mu_i^* + RT \ln \gamma_i x_i, \\ \gamma_i &\rightarrow 1 \text{ as } x_i \rightarrow 1 \end{aligned}\right\} \tag{14}$$

where μ_i^* is a function of temperature and spreading pressure only. It is identical to the molar Gibbs free energy of pure component i, when i is adsorbed in the absence of the other components, at the temperature T and the spreading pressure ϕ.

According to Equation (8), there are only two degrees of freedom for the adsorption of a pure component. The pressure P_i° in the gas phase is therefore uniquely determined by specification of T and ϕ, and

$$\mu_i^*(T, \phi) = \mu_i^\circ(T) + RT \ln P_i^\circ(\phi) \tag{15}$$

where μ_i° is the chemical potential of pure i at the perfect gas state and at unit pressure.

Equations (14) and (15) may be combined to give the chemical potential of component i in the adsorbed phase

$$\mu_i^a\ (T, \emptyset, x_1 \ldots\ldots) = \mu_i^\circ\ (T) + RT \ln \gamma_i x_i P_i^\circ\ (\emptyset) \qquad (16)$$

Assuming the gas phase obeys the perfect gas law, the chemical potential of component i in the gas phase would be

$$\mu_i^g\ (T, \pi, y_i) = \mu_i^\circ\ (T) + RT \ln \pi y_i \qquad (17)$$

At equilibrium, the chemical potential in the adsorbed phase should be equal to the chemical potential in the gas phase, i.e.,

$$\mu_i^a\ (T, \emptyset, x_1 \ldots\ldots) = \mu_i^g\ (T, \pi, y_i) \qquad (18)$$

therefore, the equation of equilibrium for mixed-gas adsorption is

$$\pi y_i = \gamma_i x_i P_i^\circ\ (\emptyset) \qquad (19)$$

B. Adsorbed Phase Behavior

The adsorbed phase may be classified into two categories: ideal adsorbed phase and non-ideal adsorbed phase. These may be defined in the same manner as used in solution thermodynamics (26).

a. Ideal Adsorbed Phase: An adsorbed phase may be considered to be ideal if the chemical potential of every component is a linear function of the logarithm of its mole fraction according to the relation

$$\mu_i^a = \mu_i^* + RT \ln x_i \tag{20}$$

where μ_i^* is a function only of temperature and spreading pressure. The significance of μ_i^* will be seen when x_i is equal to unity. Thus, if we consider Component 1, μ_1^* is simply the chemical potential of pure 1, at the same temperature and spreading pressure as the adsorbed solution under discussion.

Comparing Equation (20) with Equation (14), γ_i should be equal unity for all values of temperature, spreading pressure and composition. Thus Equation (19) can be simplified to

$$\pi y_i = P_i^\circ (\phi) x_i \tag{21}$$

This is analogous to Raoult's law for vapour-liquid equilibria.

b. Non-ideal Adsorbed Phase: The method usually adopted in dealing with real adsorbed solutions, is to find the magnitude of the pure number (or the factor) which, when multiplied by the mole fraction of the particular species, makes applicable a relation of the form like Equation (20). That is to say, one defines an activity coefficient γ_i such that the equation

$$\mu_i^a = \mu_i^* + RT \ln \gamma_i x_i \tag{14}$$

is correct, however large the deviation from ideality. In this identity μ_i^* is to be taken as a function of temperature and spreading pressure only, but γ_i may be a function of these variables together with the mole fractions of all substances in the adsorbed solution.

C. The Gibbs-Duhem Equation

In classical solution thermodynamics, the Gibbs-Duhem equation is primarily useful in checking the consistency of experimental phase-composition data and in reducing the quantity of experimental work required to determine completely the composition of vapor and liquid phase in equilibrium. The same argument may be applied to the case of mixed-gas adsorption.

If the adsorbed phase is enlarged in size, its temperature spreading pressure, and the relative proportions of its components remain unchanged. Under such conditions the μ_i's which are intensive variables like T and ϕ, must also remain unchanged. Thus the direct integration of Equation (9) gives

$$\Delta U = T\Delta S - \phi\Delta A + \sum \mu_i \Delta n_i \tag{22}$$

Let the original values of the internal energy, entropy, etc., of the system be U, S, A, n_i. If the system enlarged to k times its original size then the final values of the internal energy, etc., are kU, kS, kA and kn_i. This is because the extensive properties are proportional to the size of the system. Thus

$$\Delta U = kU - U = (k-1)\,U \tag{23}$$

etc. Substituting in the previous equation one obtains

$$(k-1)\,U = T\,(k-1)\,S - \phi\,(k-1)\,A + \sum \mu_i\,(k-1)\,n_i \tag{24}$$

and therefore

$$U = TS - \phi A + \sum \mu_i n_i \tag{25}$$

Taking the complete differential of Equation (25) one gets

$$\begin{aligned} dU = {} & TdS - \phi dA + \sum \mu_i dn_i \\ & + SdT - Ad\phi + \sum n_i d\mu_i \end{aligned} \tag{26}$$

Comparing with Equation (9) gives

$$SdT - Ad\phi + \sum n_i d\mu_i = 0 \tag{27}$$

At constant T, dT = 0, so that

$$-Ad\phi + \sum n_i d\mu_i = 0 \tag{28}$$

this is the Gibbs adsorption isotherm. When the spreading pressure is constant, Equation (28) becomes

$$\sum n_i \, d\mu_i = 0 \quad \text{(constant T and } \phi\text{)} \qquad (29)$$

Substituting Equation (16) into Equation (29), one gets

$$\sum x_i \, d \ln \gamma_i = 0 \qquad (30)$$

This is the Gibbs-Duhem equation for an adsorbed phase at constant T and ϕ.

D. Separation Factor - Relative Volatility

The composition of the adsorbed phase will usually be different from that of the gas phase, and in considering a binary mixture three types of equilibrium relations may be visualized. Figure 1 is a sketch of the typical equilibrium curves that may be expected if the composition of the two phases are plotted in the manner commonly used to express vapour-liquid equilibria. Curve A represents a situation in which Component 1 is leaner in the adsorbed phase than the gas phase and Curve B represents the case where the adsorbed phase is always richer in Component 1 than the gas phase. It is conceivable that volatility reversals may occur in some binary gas systems, and such a case is represented by Curve C. This situation is analogous to the existence of an azeotrope in vapour-liquid equilibria. Molecular interactions in the adsorbed phase are apparently responsible for effects of this kind (1, 27).

The concept of relative volatility in vapour-liquid equilibria can also be used conveniently in the interpretation of binary gas mixture

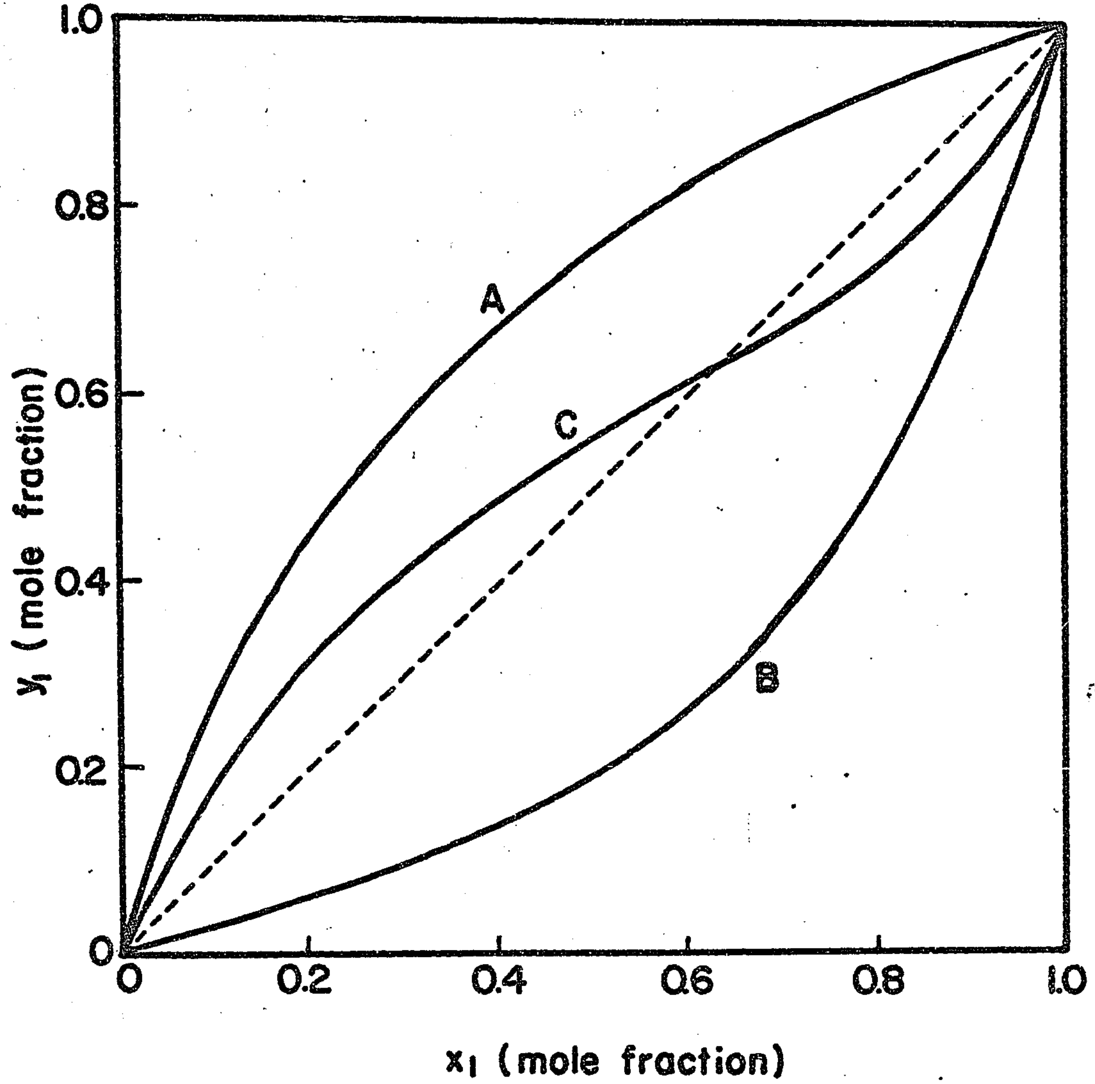


Figure I. TYPES OF EQUILIBRIUM CURVES

adsorption data. Separation factor or adsorption relative volatility of Component 1 with respect to Component 2 is defined as

$$\alpha_{12} = \frac{x_2}{x_1}\frac{y_1}{y_2} = \frac{x_2}{x_1}\frac{P_1}{P_2} \tag{31}$$

The prediction of adsorption relative volatilities from single gas isotherms is of considerable interest in chemical engineering. Several methods (2, 5, 6) have been proposed. It is evident that prediction of adsorption relative volatilities from the isotherms of the individual gases will be difficult. Clearly, it cannot be assumed that relative volatility does not vary with composition. In fact, the variation in α is so large in many systems, that the assumption of any sort of an "average" value would lead to incorrect equilibrium representation.

It would appear that any attempt to predict adsorption equilibria in mixtures of gases from pure gas isotherms is bound to be unsuccessful unless some way is also available of predicting the likelihood of interactions between the adsorbed molecules.

IV. COMPARISON OF RECENTLY DEVELOPED METHODS FOR PREDICTION OF BINARY EQUILIBRIA

Although Myers and Prausnitz's is a more rigorous method, other methods seem to give equally good prediction. Below, we give a discussion of these and show that for a certain condition, the three methods are completely equivalent.

A. Presentation of the Various Methods

a. Semi-empirical method of Cook and Basmadjian (2): The method is based on Equation (7) derived by Basmadjian (15) on the assumption of small and constant relative volatility. From Equation (31), it is seen that α_{12} has an indeterminate value for $x_1 = 1$ or $x_2 = 1$. Equation (7) is employed for evaluating these limiting relative volatilities at total pressure π. Thus

$$\log (\alpha)_{x_1 = 1} = \frac{1}{V^\circ_{1,\pi}} \int_0^{V^\circ_{1,\pi}} \log \left(\frac{P^\circ_1}{P^\circ_2}\right)_{V^\circ} dV^\circ \qquad (32)$$

and

$$\log (\alpha)_{x_2 = 1} = \frac{1}{V^\circ_{2,\pi}} \int_0^{V^\circ_{2,\pi}} \log \left(\frac{P^\circ_1}{P^\circ_2}\right)_{V^\circ} dV^\circ \qquad (33)$$

Using these limiting α's, end-point $(\frac{P}{x})$ values for the binary $(\frac{P}{x})$ versus V_T curve may be obtained as follows:

$$\left(\frac{P_1}{x_1}\right)_{x_2 = 1} = \left(\frac{P_2}{x_2}\right)_{x_2 = 1} (\alpha)_{x_2 = 1} = \pi (\alpha)_{x_2 = 1} \qquad (34)$$

and

$$\left(\frac{P_2}{x_2}\right)_{x_1 = 1} = \left(\frac{P_1}{x_1}\right)_{x_1 = 1} \frac{1}{\alpha} = \frac{\pi}{(\alpha)_{x_1 = 1}} \qquad (35)$$

The values are located at the points C and D in Figure 2, which also shows plots of the pure component isotherms 1 and 2. The binary curves AC and BD are next constructed based on the assumption that they can be represented by the same form of equation as the pure component isotherms over the binary concentration range.

Using the binary curves, the fraction x_2 may be calculated and hence also the partial isotherms $V_1 = f_1 (P_1)$ and $V_2 = f_2 (P_2)$ for a given total pressure. The appropriate equation for x_2 is given by

$$x_2 = \frac{\left(\frac{P_1}{x_1}\right)_{V_T} - \pi}{\left(\frac{P_1}{x_1}\right)_{V_T} - \left(\frac{P_2}{x_2}\right)_{V_T}} \qquad (36)$$

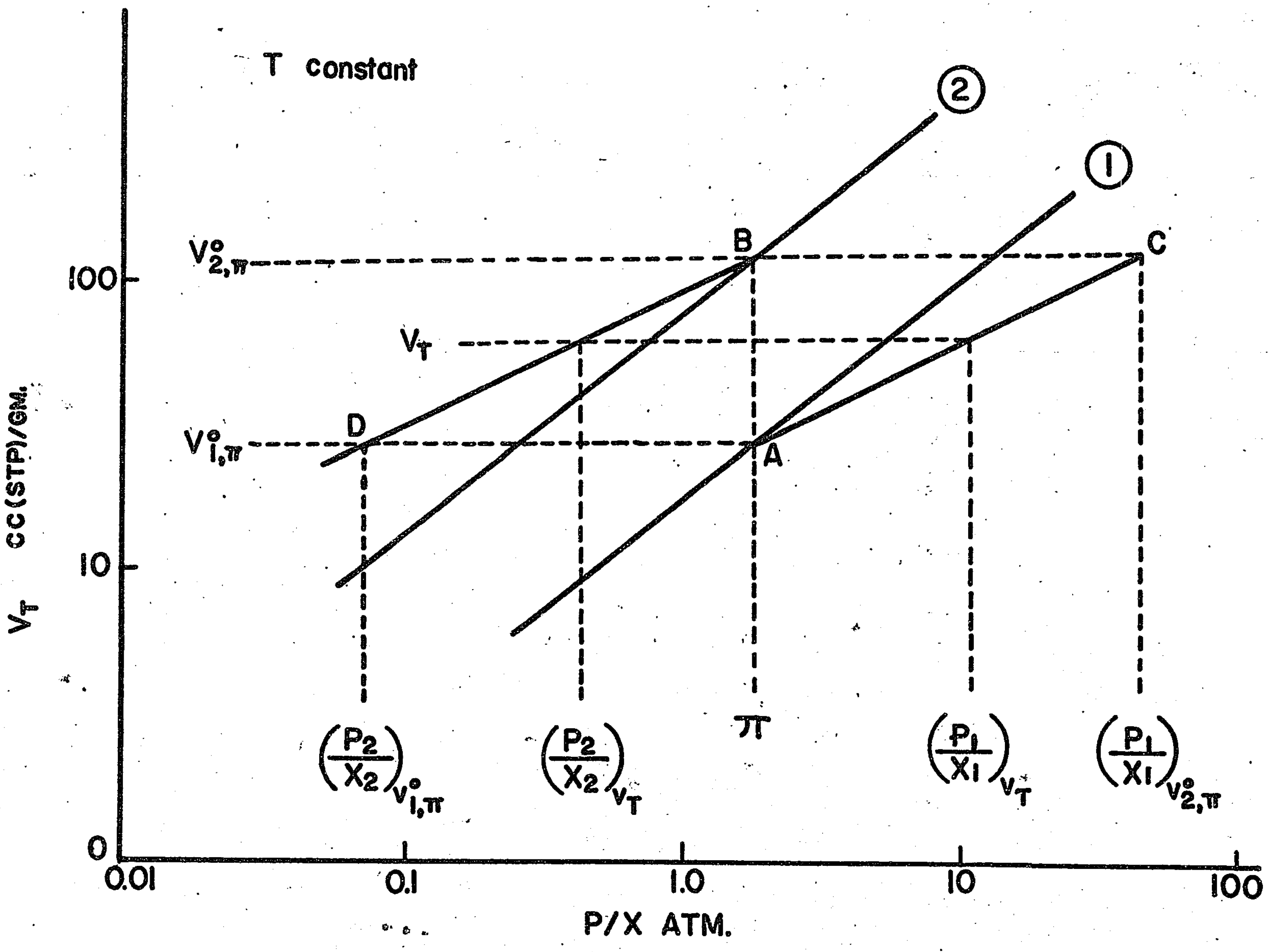


Figure 2 CONSTRUCTION DIAGRAM FOR BINARY PREDICTION

b. Ideal Adsorbed Solution-Method of Myers and Prausnitz (13): The calculation of the isothermal binary adsorption equilibria proceeds as follows:

(1) Equation (11) is applied to the experimental data for pure component adsorption $n_i^\circ = F_i\,(P_i^\circ)$, yielding two relationships:

$$\phi_1^\circ = \psi_1\,(P_1^\circ) \tag{37}$$

$$\phi_2^\circ = \psi_2\,(P_2^\circ) \tag{38}$$

(2) Equation (21) is written for both components:

$$\pi\, y_1 = P_1^\circ\, x_1 \tag{39}$$

$$\pi\, y_2 = P_2^\circ\, x_2 \tag{40}$$

(3) Since the mixing process is carried out at constant spreading pressure as indicated by Equation (30)

$$\phi_1^\circ = \phi_2^\circ \tag{41}$$

(4) Also

$$x_1 + x_2 = 1 \tag{42}$$

$$y_1 + y_2 = 1 \tag{43}$$

(5) There are nine unknowns: ϕ_1°, ϕ_2°, P_1°, P_2°, π, x_1, x_2, y_1 and y_2. Equations (37) through Equation (43) yield seven independent equations. By specifying two independent quantities, such as π and y_1, it is possible to calculate all of the other variables.

(6) The total amount of adsorption n_t can be calculated by means of Equation (4).

c. Extended Potential Theory of Grant and Manes (12): The calculation is made as follows:

(1) Assuming Raoult's law for gas mixture fugacities can be applied for each component,

$$f_i = x_i f_i^* \tag{44}$$

where f_i is the fugacity of the i'th component in the gas phase and f_i^* is the fugacity which the component would exert as a pure adsorbate at the adsorbate volume of the mixture.

(2) The adsorption potential, ϵ_i, of each component, can be written as

$$\epsilon_i = RT \ln \left(\frac{f_s}{f^*}\right)_i \tag{45}$$

combining Equations (44) and (45) gives

$$\epsilon_i = RT \ln x_i \left(\frac{f_s}{f}\right)_i \tag{46}$$

where $(f_s)_i$ is the saturation fugacity of pure unadsorbed liquid at adsorption temperature.

Since according to the Polanyi theory all characteristic curves on a given adsorbent are superimposable on a single curve by means of a correlating divisor applied to the abscissa, i.e., since at equal adsorbate volumes we can write

$$\frac{\epsilon_1}{\beta_1} = \frac{\epsilon_2}{\beta_2} \tag{47}$$

where β_1 and β_2 are the correlating divisors, it follows that at constant temperature

$$\frac{1}{\beta_1} \ln x_1 \left(\frac{f_s}{f}\right)_1 = \frac{1}{\beta_2} \ln x_2 \left(\frac{f_s}{f}\right)_2 \tag{48}$$

The normal boiling point molar volume has been used as the correlating divisor in this case.

(3) Equation (48), together with the condition

$$x_1 + x_2 = 1 \tag{49}$$

suffice to determine the x_i from the given values of f_i, $(f_s)_i$ and β_i.

B. Comparison and Residue Study

(1) The comparison of two adsorbates at the same spreading pressure is equivalent to comparing P_i° at equal adsorbed (liquid) volumes (as in Polanyi theory), provided that the curves of the individual pure components can be collapsed to a single curve by using the molar volume as correlating divisor. This equivalence may be seen by writing the expression for spreading pressure as

$$\phi = \frac{RT}{A} \int_0^{P_i^\circ} n_i^\circ \, (P_i^\circ) \, d \ln P_i^\circ = \frac{1}{A} \int_0^{P_i^\circ} n_i^\circ \, \tilde{V}_i \, d \left(\frac{\epsilon_i}{\tilde{V}_i} \right) \quad (50)$$

the second equality following from the substitution of $d\epsilon_i$ for $RT d \ln P_i^\circ$ and multiplying and dividing the integrand by $\tilde{V}_i$. The geometric equivalence of the latter integral is seen from Figure 3. It is simply the area beneath the generalized correlation curve of Lewis et al. (6) and to the right of a perpendicular dropped from the ordinate $n_i^\circ \tilde{V}_i (P_i^\circ)$. It thus appears that the method of Myers and Prausnitz is practically equivalent to the extended Polanyi theory. The method of Myers and Prausnitz has the disadvantage of requiring an integration of the adsorption pressure from zero coverage which is extremely difficult for components of low volatility.

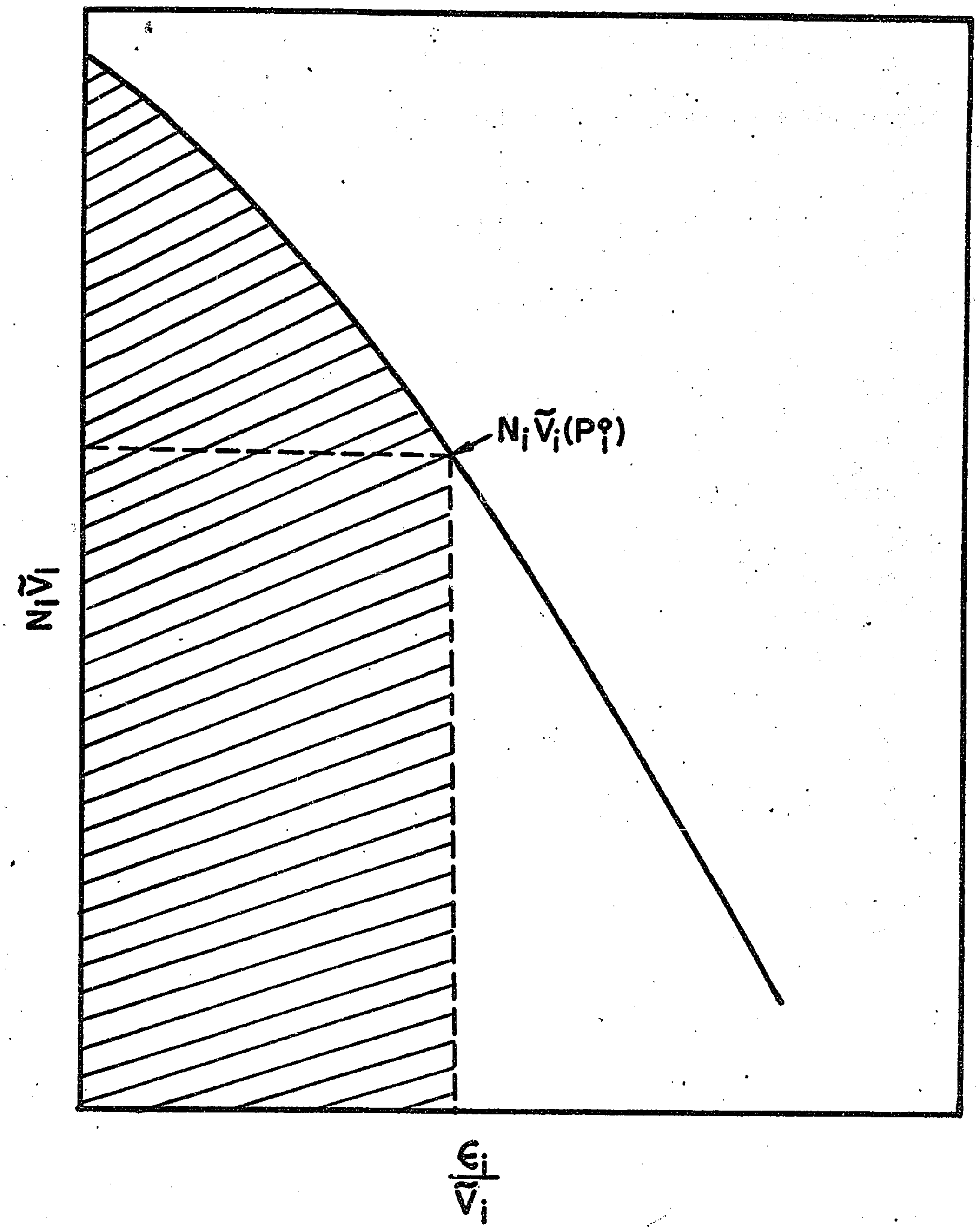


Figure 3 GEOMETRICAL EQUIVALENCE OF THE LATTER INTEGRAL OF EQUATION (50)

(2) The method of Myers and Prausnitz may be transformed to the semi-empirical method of Cook and Basmadjian if $(n_1^\circ)_\phi = (n_2^\circ)_\phi$ at the same spreading pressure. This can be proved as follows:

For binary adsorption, Myers and Prausnitz's method requires

$$\int_0^{(P_1^\circ)_\phi} n_1^\circ \, d\ln P_1^\circ = \int_0^{(P_2^\circ)_\phi} n_2^\circ \, d\ln P_2^\circ \tag{51}$$

Integrating each side by parts gives

$$n_1^\circ \ln P_1^\circ \Big|_0^{(P_1^\circ)_\phi} - n_2^\circ \ln P_2^\circ \Big|_0^{(P_2^\circ)_\phi} = \int_0^{(n_1^\circ)_\phi} \ln P_1^\circ \, dn_1^\circ - \int_0^{(n_2^\circ)_\phi} \ln P_2^\circ \, dn_2^\circ \tag{52}$$

As P_1° — 0, we have

$$P_1^\circ \longrightarrow P_2^\circ \longrightarrow P^\circ$$

$$n_1^\circ \longrightarrow n_2^\circ \longrightarrow n^\circ$$

Hence

$$n_1^\circ \ln P_1^\circ \Big|_0 - n_2^\circ \ln P_2^\circ \Big|_0 = n^\circ \ln P^\circ - n^\circ \ln P^\circ = 0 \tag{53}$$

Thus the left hand side of Equation (52) becomes

$$\begin{aligned} \text{LHS} &= (n_1^\circ)_\phi \ln (P_1^\circ)_\phi - (n_2^\circ)_\phi \ln (P_2^\circ)_\phi \\ &= (n_2^\circ)_\phi \ln \left(\frac{P_1^\circ}{P_2^\circ}\right)_\phi + \left[(n_1^\circ)_\phi - (n_2^\circ)_\phi\right] \ln (P_1^\circ)_\phi \end{aligned} \tag{54}$$

But according to the derivation of Myers and Prausnitz for an ideal adsorbed solution, one obtains

$$\ln \alpha = \ln \left(\frac{P_1^\circ}{P_2^\circ}\right)_\phi \qquad (55)$$

Hence

$$\mathrm{LHS} = (n_2^\circ)_\phi \ln \alpha + \left[(n_1^\circ)_\phi - (n_2^\circ)_\phi \right] \ln (P_1^\circ)_\phi \qquad (56)$$

The right hand side of Equation (52) can be rearranged to give

$$\begin{aligned} \mathrm{RHS} &= \int_0^{(n_1^\circ)_\phi} \ln P_1^\circ \, d n_1^\circ - \int_0^{(n_2^\circ)_\phi} \ln P_2^\circ \, d n_2^\circ \\ &= \int_0^{(n_2^\circ)_\phi} \ln P_1^\circ \, d n_1^\circ - \int_0^{(n_2^\circ)_\phi} \ln P_2^\circ \, d n_2^\circ + \int_{(n_2^\circ)_\phi}^{(n_1^\circ)_\phi} \ln P_1^\circ \, d n_1^\circ \end{aligned} \qquad (57)$$

The first two integrals can be combined as follows

$$\int_0^{(n_2^\circ)_\phi} \ln P_1^\circ \, d n_1^\circ - \int_0^{(n_2^\circ)_\phi} \ln P_2^\circ \, d n_2^\circ = \int_0^{(n_2^\circ)_\phi} \ln \left(\frac{P_1^\circ}{P_2^\circ}\right) d n^\circ \qquad (58)$$

The validity of this is seen from the geometrical equivalence of the integrals (Figure 4).

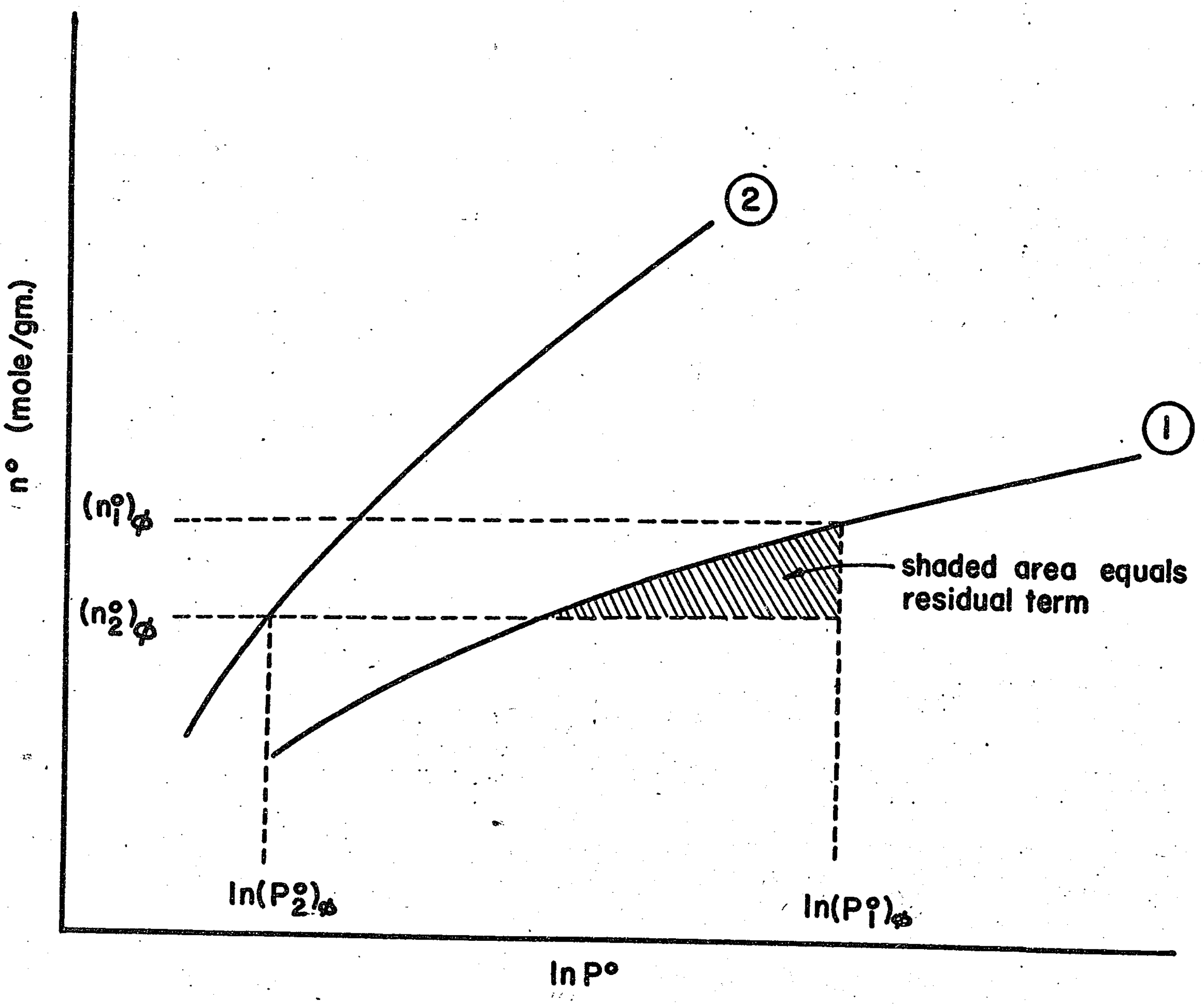


Figure 4 GEOMETRIC INTERPRETATION OF THE RESIDUAL TERM

Thus

$$\text{RHS} = \int_{0}^{(n_2^\circ)_\phi} \ln\left(\frac{P_1^\circ}{P_2^\circ}\right)_{n^\circ} dn^\circ + \int_{(n_2^\circ)_\phi}^{(n_1^\circ)_\phi} \ln P_1^\circ \, d n_1^\circ \qquad (59)$$

Equating Equations (56) and (59) gives

$$(n_2^\circ)_\phi \ln \alpha + \left[(n_1^\circ)_\phi - (n_2^\circ)_\phi\right] \ln (P_1^\circ)_\phi = \int_{0}^{(n_2^\circ)_\phi} \ln\left(\frac{P_1^\circ}{P_2^\circ}\right)_{n^\circ} dn^\circ + \int_{(n_2^\circ)_\phi}^{(n_1^\circ)_\phi} \ln P_1^\circ \, dn_1^\circ \qquad (60)$$

or

$$\ln \alpha = \frac{1}{(n_2^\circ)_\phi} \int_{0}^{(n_2^\circ)_\phi} \ln\left(\frac{P_1^\circ}{P_2^\circ}\right)_{n^\circ} dn^\circ + \frac{1}{(n_2^\circ)_\phi}\left[\int_{(n_2^\circ)_\phi}^{(n_1^\circ)_\phi} \ln P_1^\circ \, dn_1^\circ - (n_1^\circ - n_2^\circ)_\phi \ln (P_1^\circ)_\phi\right] \qquad (61)$$

Comparing Equation (61) with Equation (33), Equation (61) is identical to the Cook-Basmadjian expression for limiting α at $x_2 = 1$ if the resident term, $\frac{1}{n_2^\circ}\left[\int_{n_2^\circ}^{n_1^\circ} \ln P_1^\circ \, dn_1^\circ - (n_1^\circ - n_2^\circ) \ln P_1^\circ\right]$, is zero. The geometric interpretation of the residue is shown in Figure 4.

This residue will be zero if

(1) Isotherm 1 is horizontal over the range in question

(2) Isotherm 1 is vertical over the range in question

(3) $(n_1^\circ)_\phi = (n_2^\circ)_\phi$

Actually, the cases (1) and (2) seldom occur within the range of pressures which we are interested in. As for the last case, there are two possibilities to have $(n_1^\circ)_\phi = (n_2^\circ)_\phi$: (1) very low surface coverage and (2) equal a_i° at the same spreading pressure (where a_i° is defined as the specific area per mole of pure adsorbate i). The specific molar area ratios of the adsorbates for some systems at various spreading pressures have been investigated and listed in Table 3 (Appendix A). Some systems reveal almost equal adsorbed specific molar area, and for these cases the Myers-Prausnitz and Cook-Basmadjian methods yield identical results.

At very low surface coverage we have

$$n_i^\circ = K_i P_i^\circ \tag{62}$$

where K_i is Henry's law constant, a function only of temperature. Substituting Equation (62) into Equation (11) gives

$$\frac{\phi A}{RT} = K_i P_i^\circ = n_1^\circ = n_2^\circ \tag{63}$$

Several systems have been tested, and the results are presented in Table 4 (Appendix B). Many systems have zero residue, but some systems, such as the system H_2 - N_2 on charcoal (23), have a rather big residual value. However, it turns out to be of little significance in view of the high value of α.

Ideal behavior of the adsorbate was assumed for all three methods, but non-ideality may actually exist because of the adsorbate-adsorbate interactions. An extensive investigation of the behavior of adsorbed phase is therefore needed.

V INVESTIGATION OF BINARY ADSORBED PHASE ACTIVITY COEFFICIENTS

Myers and Prausnitz (13) claimed that their method was tested on the equilibrium data for the systems CH_4 - C_2H_6 (8) and C_2H_4 - CO_2 (18) on activated carbon and for CO - O_2 (3) and C_3H_8 - C_3H_6 (19) on silica gel, and that they found the calculated activity coefficients to be equal to unity within the experimental error. However, they did not show the calculation results. Jelinek (17) calculated γ's for only one system using his "stoichiometric method". In order to obtain a better understanding as to whether the method is useful and valid for any binary system, it was decided to extend the investigation to other systems.

A. Calculation

a. Myers and Prausnitz's method: Equation (19) can be used to calculate an activity coefficient if we know the total pressure of gas-phase mixture, the composition x_i of the adsorbed phase, the composition y_i of the gas phase, the spreading pressure ϕ for the adsorbed mixture, as well as the pure component adsorption isotherms for each adsorbate.

The problem encountered is the evaluation of the spreading pressure ϕ for the adsorbed mixture. The spreading pressure ϕ for the corresponding individual components at the same temperature T and total pressure π can be calculated by means of Equation (11). For the case of adsorption of a binary mixture, Equations (16), (19) and (28) may be combined to give

$$\frac{A}{RT} d\phi = n_1 d \ln \pi y_1 + n_2 d \ln \pi y_2 \text{ (constant T)} \qquad (64)$$

With the total pressure π of the mixture held constant, Equation (64) becomes

$$\frac{A}{RT} d\phi = n_1 d \ln y_1 + n_2 d \ln y_2 \text{ (constant T and } \pi \text{)} \qquad (65)$$

Integration of Equation (65) gives

$$\frac{A}{RT} \int_{\phi_2^\circ}^{\phi} d\phi = \int_0^{y_1} n_1 d \ln y_1 + \int_1^{y_2} n_2 d \ln y_2 \qquad (66)$$

or

$$\frac{A}{RT} \int_{\phi_1^\circ}^{\phi} d\phi = \int_1^{y_1} n_1 d \ln y_1 + \int_0^{y_2} n_2 d \ln y_2 \qquad (67)$$

Thus, the spreading pressure ϕ for the adsorbed mixture, can be calculated, provided that the experimental adsorption data, at constant temperature and pressure for the entire range of vapour compositions, are available. Once the spreading pressure for the adsorbed mixture is obtained, the corresponding individual equilibrium pressure P_1° and

P_2° at the same spreading pressure can be found from the results of Equation (11). Substituting P_1°, P_2°, π, x_1, x_2, y_1 and y_2 in Equation (19), γ_1 and γ_2 can then be calculated.

This method is applied to the equilibrium data for the following systems:

Systems						
No.	Comp't. 1	Comp't. 2	Adsorbent	Temp.	Pressure	Ref.
A-1	O_2	CO	Silica Gel	0° C	1 atm.	(3)
A-2	CH_4	C_2H_6	Activated Carbon	20° C	750 mm Hg	(8)
A-3	C_3H_8	C_4H_{10}	Activated Carbon	20° C	750 mm Hg	(8)
A-4	N_2	Ar	Silica Gel	89.5° K	250 mm Hg	(20)
A-5	N_2	Ar	Silica Gel	111° K	250 mm Hg	(20)
A-6	C_2H_4	CO_2	Col. "G" Carbon	0° C	1 atm.	(17)
A-7	C_2H_6	CO_2	Col. "G" Carbon	30° C	1 atm.	(17)
A-8	C_3H_6	CO_2	Col. "G" Carbon	0° C	1 atm.	(17)
A-9	C_3H_8	CO_2	Col. "G" Carbon	0° C	1 atm.	(17)
A-10	C_2H_6	CO_2	Silica Gel	0° C	1 atm.	(17)
A-11	C_3H_8	CO_2	Silica Gel	30° C	1 atm.	(17)

The results are presented in Tables 5-15 (Appendix C) and Figures 5 - 14. The summary is shown in Table 1.

Table 1

Summary of Calculation of Adsorbed Phase Activity Coefficients by the Method of Myers and Prausnitz (13)

System	Adsorbed Phase Activity Coefficients	Reference
A-1	All γ's are near unity.	(3)
A-2	Only half the range of adsorbed phase concentration is covered. The smallest γ_1 is about 0.74 at $x_1 = 0.025$ and the largest γ_1 is about 0.82 at $x_1 = 0.395$, γ_1 increases with increasing x_1. The largest γ_2 is about unity and the smallest γ_2 is about 0.905 at $x_1 = 0.395$, γ_2 decreases with increasing x_1.	(8)
A-3	γ_1 changes with x_1 in the range of 1.22 - 0.82 (x_1 from 0.262 to 0.868), γ_1 decreases with increasing x_1. γ_2 varies with x_1 in the range of 0.67 - 0.33, γ_2 also decreases with increasing x_1.	(8)
A-4	The smallest γ_1 is about 0.45 at $x_1 = 0.062$, and the smallest γ_2 is about 0.66 at $x_1 = 0.925$. γ_1 increases with increasing x_1 and γ_2 decreases with increasing x_1. $\gamma_1 \rightarrow 1$ as $x_1 \rightarrow 1$ and $\gamma_2 \rightarrow 1$ as $x_1 \rightarrow 0$.	(20)

Table 1 (Continued)

System	Adsorbed Phase Activity Coefficients	Reference
A-5	The smallest γ_1 is about 0.756 at $x_1 = 0.19$, the smallest γ_2 is about 0.82 at $x_1 = 0.923$. γ_1 increases with increasing x_1 and γ_2 decreases with increasing x_1. $\gamma_1 \rightarrow 1$ as $x_1 \rightarrow 1$ and $\gamma_2 \rightarrow 1$ as $x_1 \rightarrow 0$.	(20)
A-6	The largest γ_1 is about 8.4 at $x_1 = 0.072$, the smallest γ_1 is about 2.58 at $x_1 = 0.875$; $\gamma_2 = 1.03$ at $x_1 = 0.072$, $\gamma_2 = 1.041$ at 0.875 and the maximum value of γ_2 is about 1.15 at $x_1 = 0.415$.	(17)
A-7	The largest γ_1 is about 5.26 at $x_1 = 0.36$, the smallest γ_1 is about 3.25 at $x_1 = 0.95$, γ_1 decreases with increasing x_1. The largest γ_2 is about 1.52 at $x_1 = 0.95$ and the smallest γ_2 is about 1.105 at $x_1 = 0.36$. γ_2 increases with increasing x_1.	(17)
A-8	The largest γ_1 is about 7.4 at $x_1 = 0.415$, the smallest γ_1 is about 2.44 at $x_1 = 0.979$, γ_1 decreases with increasing x_1. The smallest γ_2 is about 1.294 at $x_1 = 0.415$ and the largest γ_2 is about 5.95 at $x_1 = 0.979$, γ_2 increases with increasing x_1.	(17)

Table 1 (Continued)

System	Adsorbed Phase Activity Coefficients	Reference
A-9	Only half the range of x is covered. The largest γ_1 is about 12.1 at $x_1 = 0.094$ and the smallest γ_1 is about 6.19 at $x_1 = 0.541$. γ_1 decreases with increasing x_1. The smallest γ_2 is about 1.041 at $x_1 = 0.094$ and the largest γ_2 is about 1.24 at $x_1 = 0.541$. γ_2 increases with increasing x_1.	(17)
A-10	γ_1 and γ_2 are nearly constant, $\gamma_1 \approx 0.74$ and $\gamma_2 \approx 1.083$.	(17)
A-11	γ_1 and γ_2 are nearly constant, $\gamma_1 \approx 1.35$ and $\gamma_2 \approx 1$.	(17)

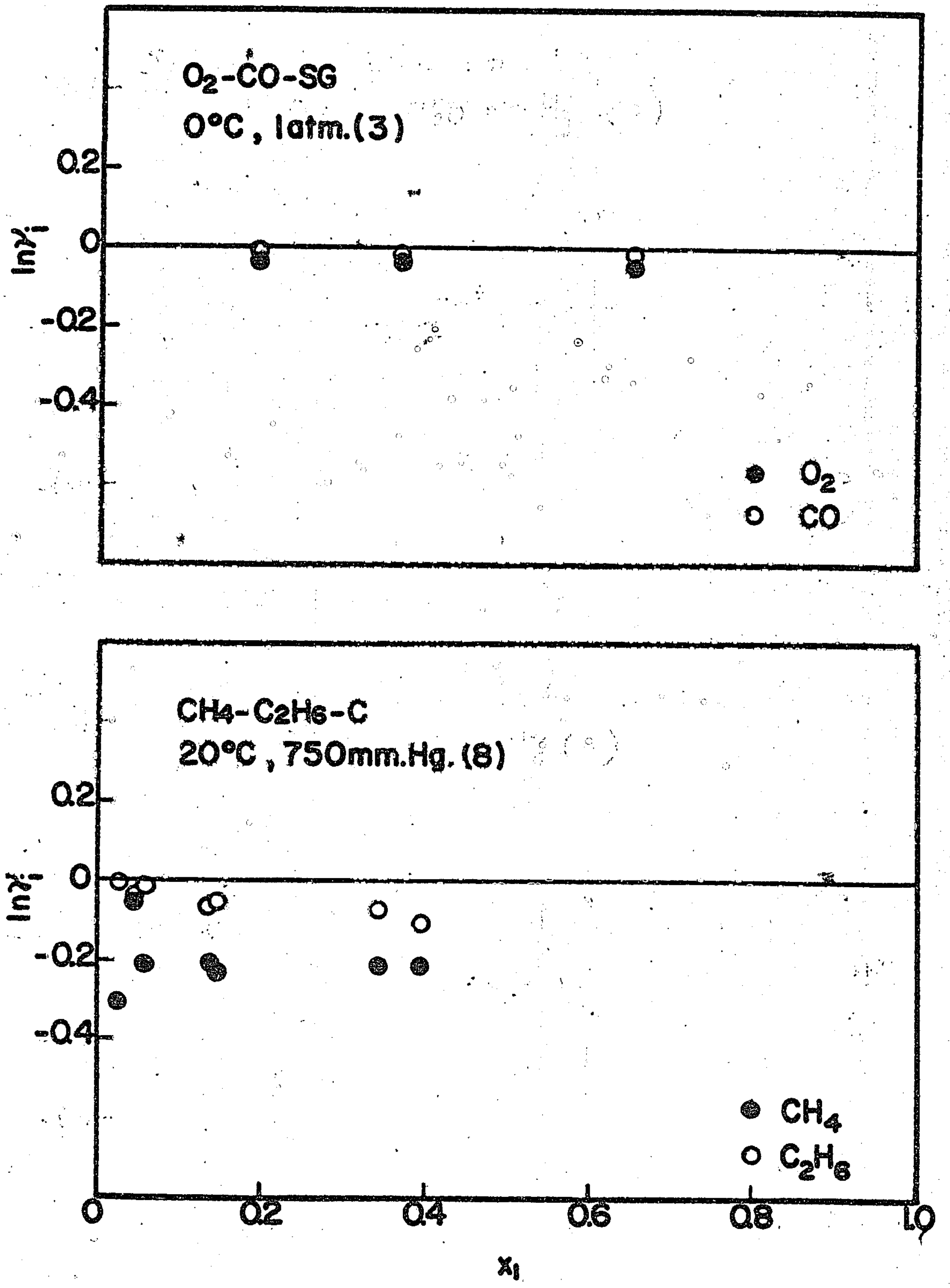


Figure 5 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (METHOD OF MYERS et al. (13))

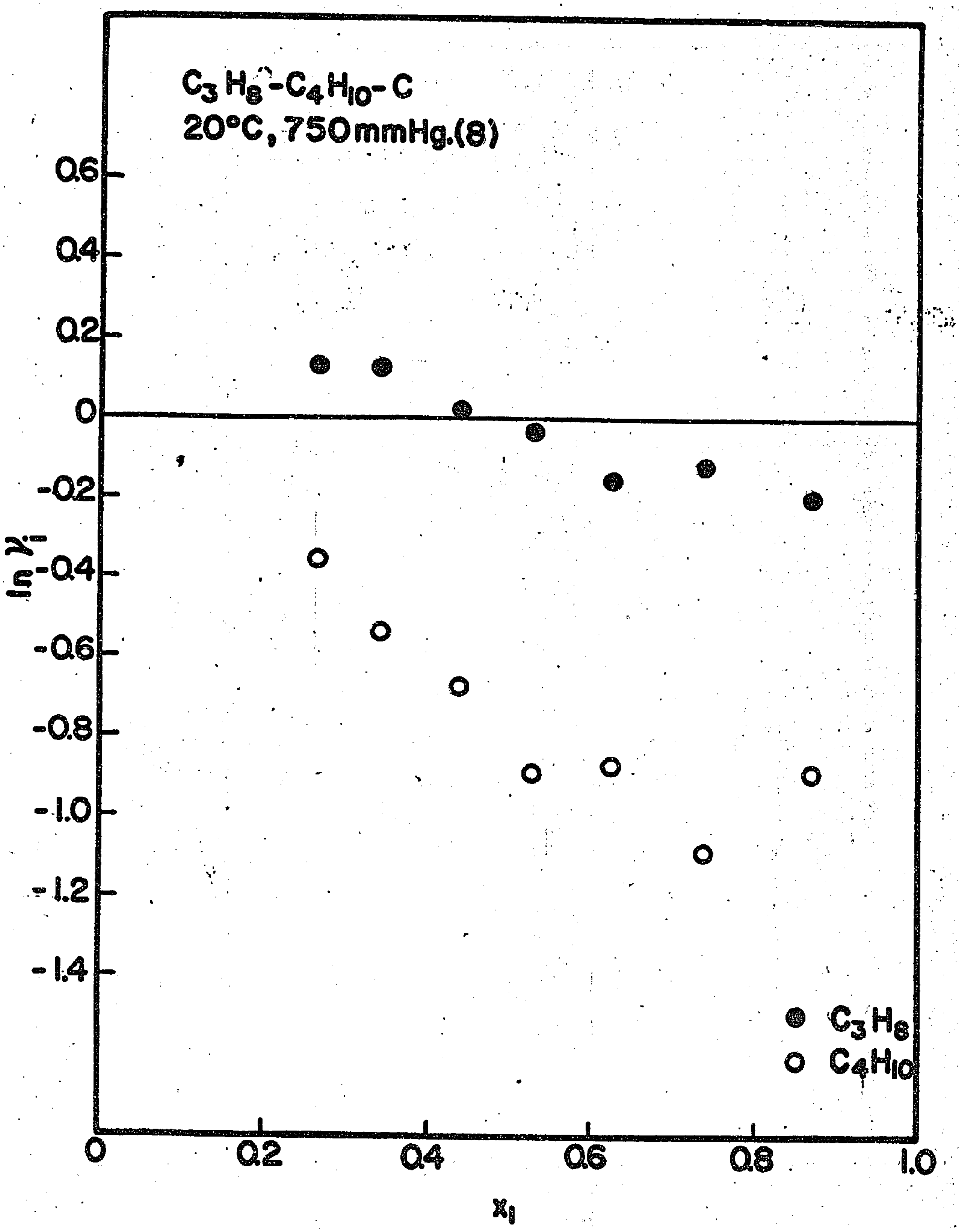


Figure 6 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (METHOD OF MYERS et al.(13))

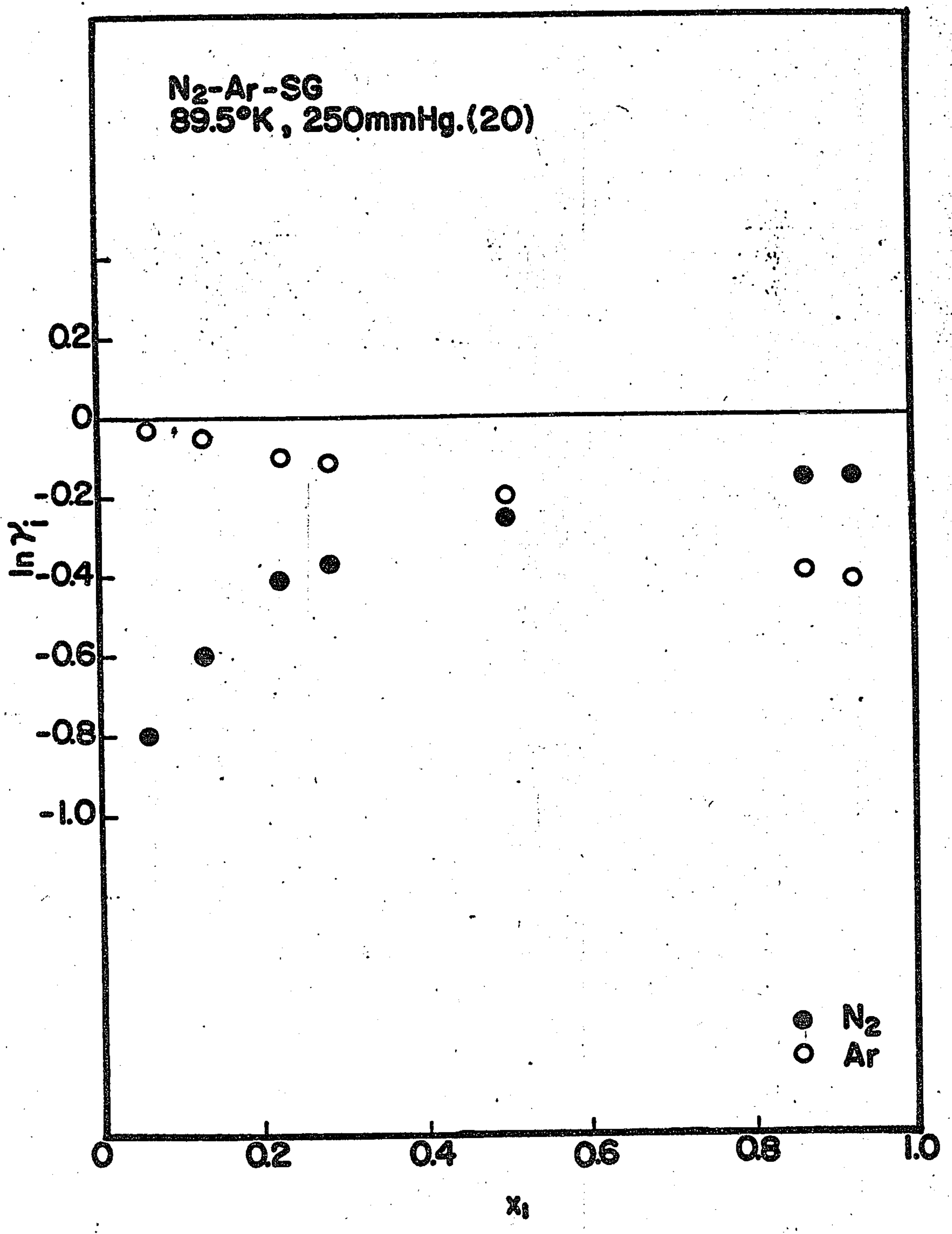


Figure 7 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (METHOD OF MYERS et al.(13))

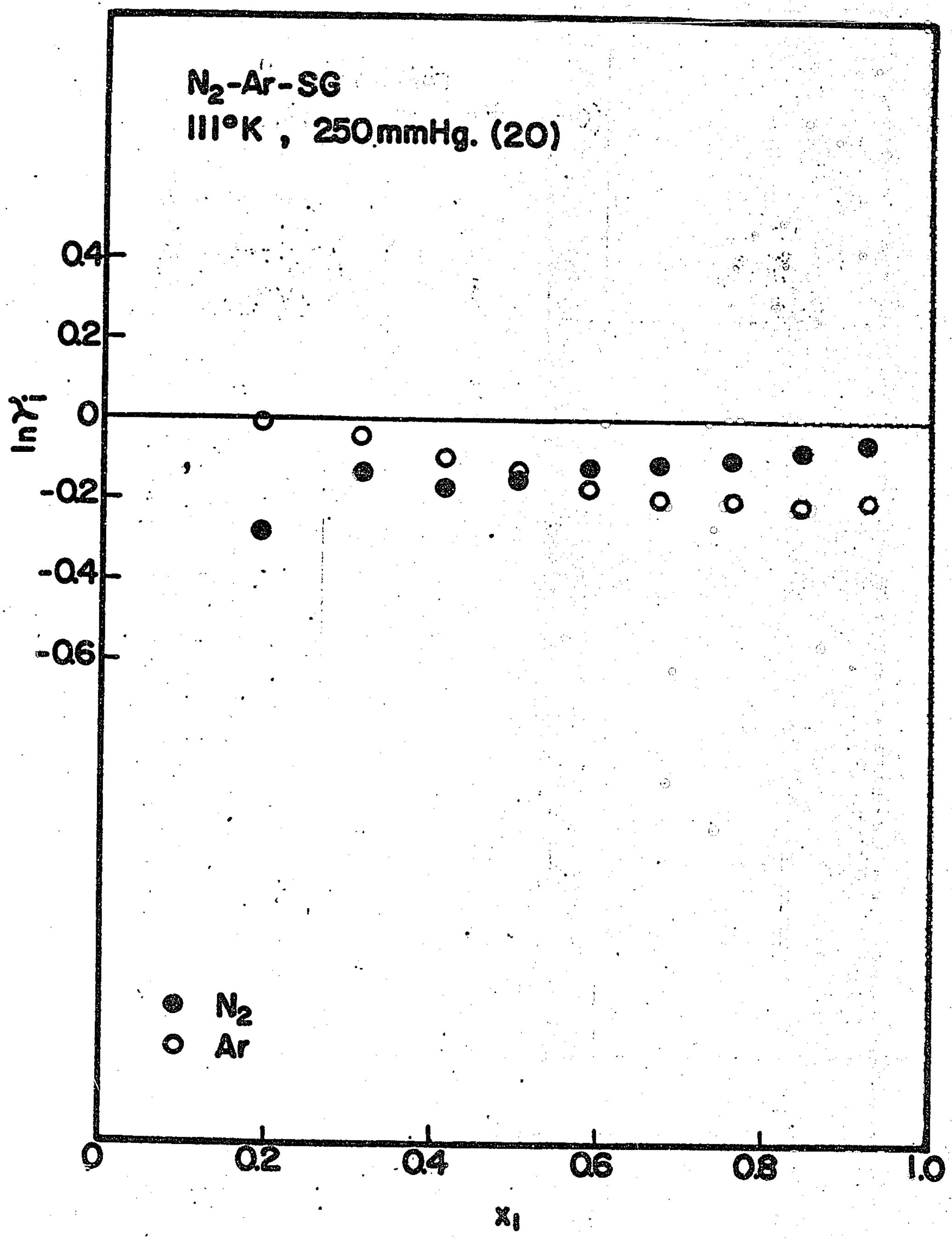


Figure 8 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (METHOD OF MYERS et al.(13))

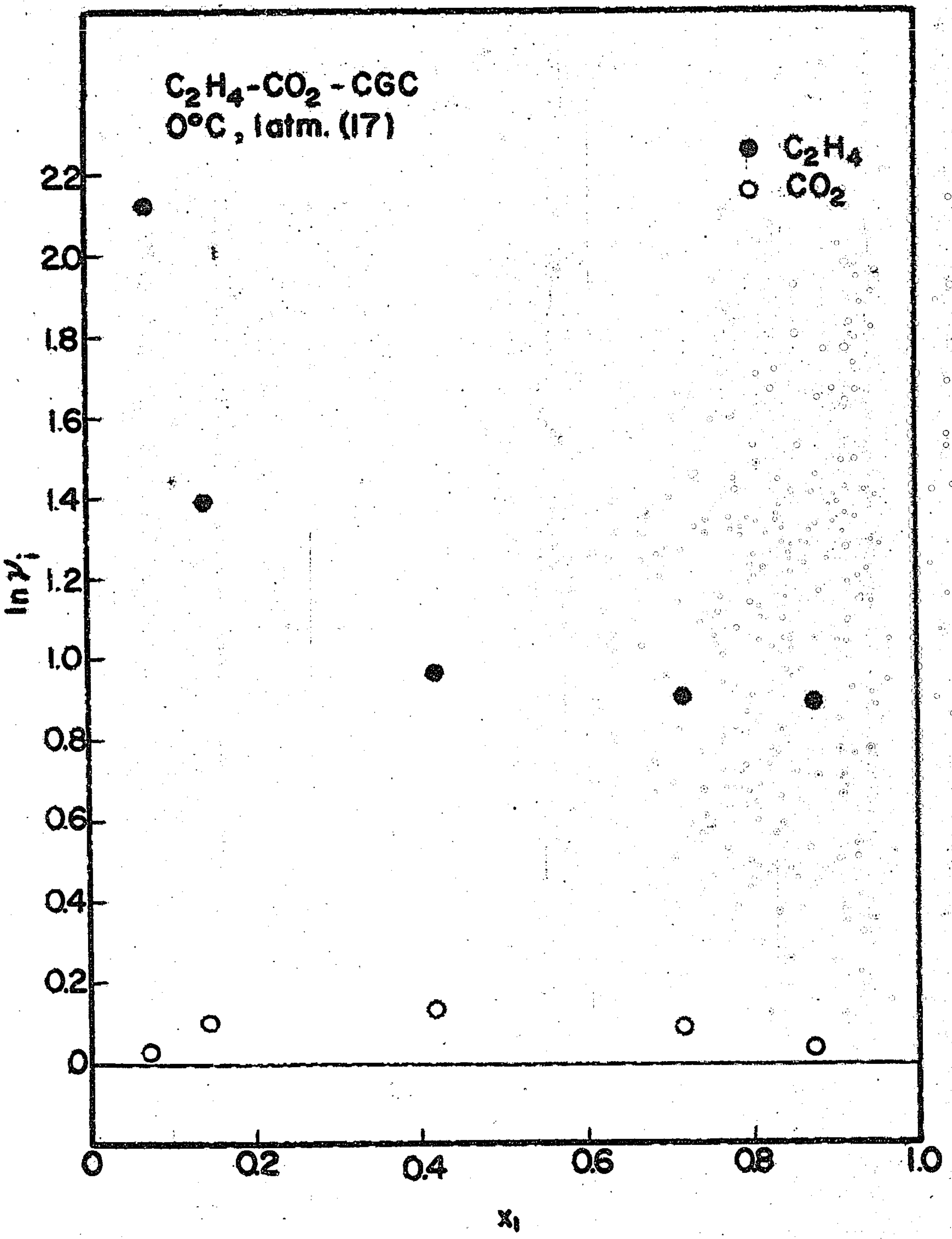


Figure 9 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (METHOD OF MYERS et al.(13))

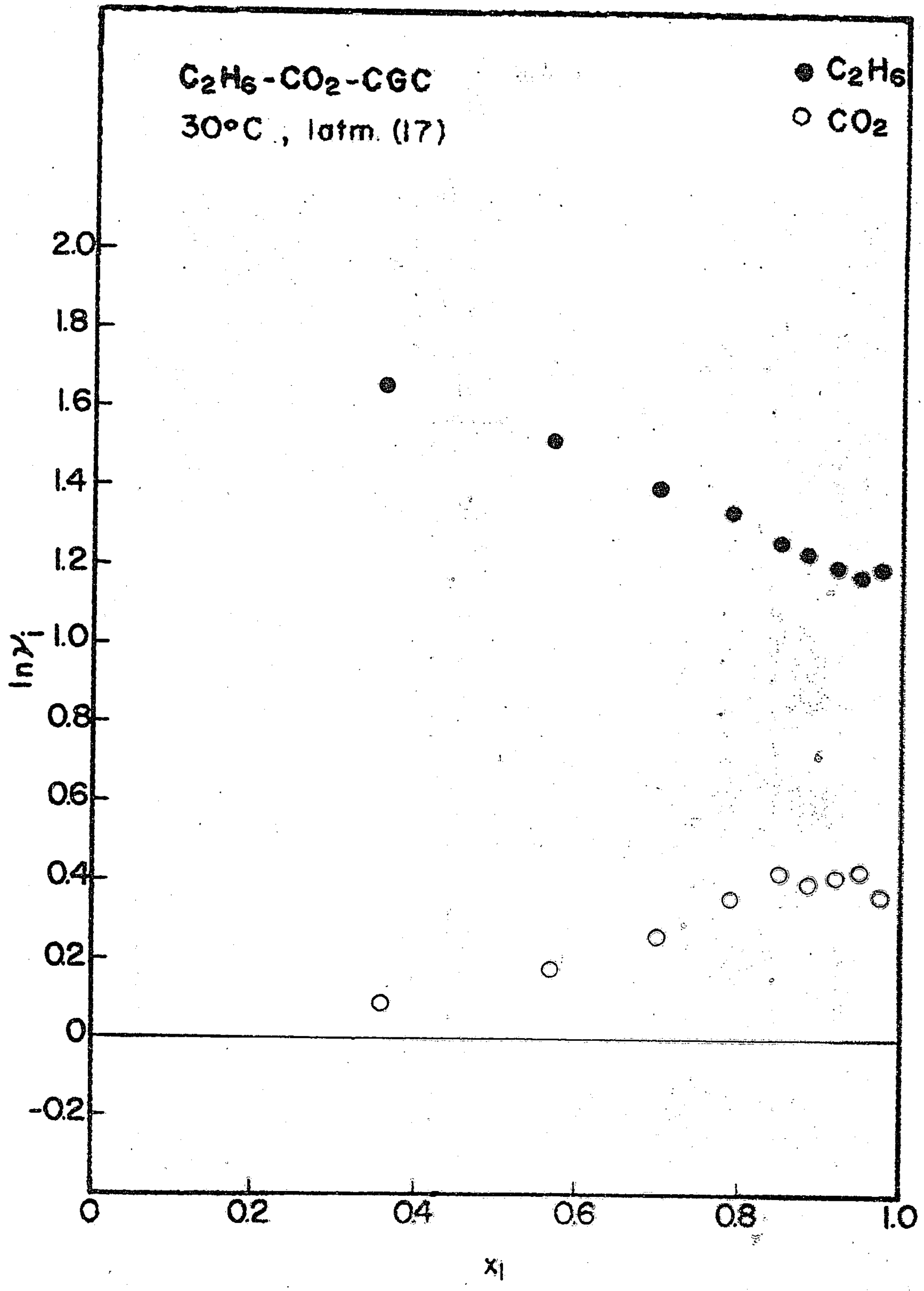


Figure 10 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (METHOD OF MYERS et al.(13))

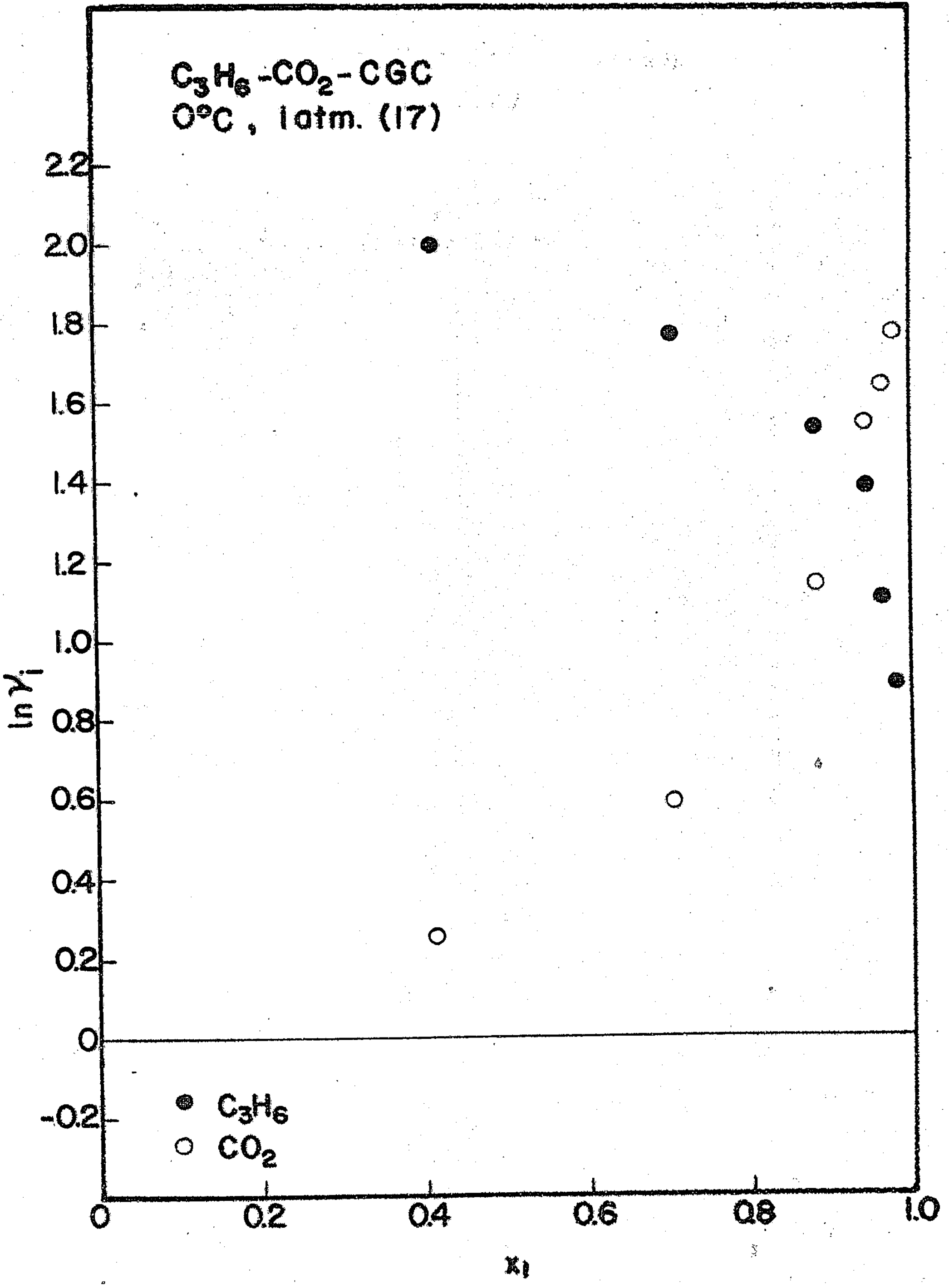


Figure 1.1 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (METHOD OF MYERS et al. (13))

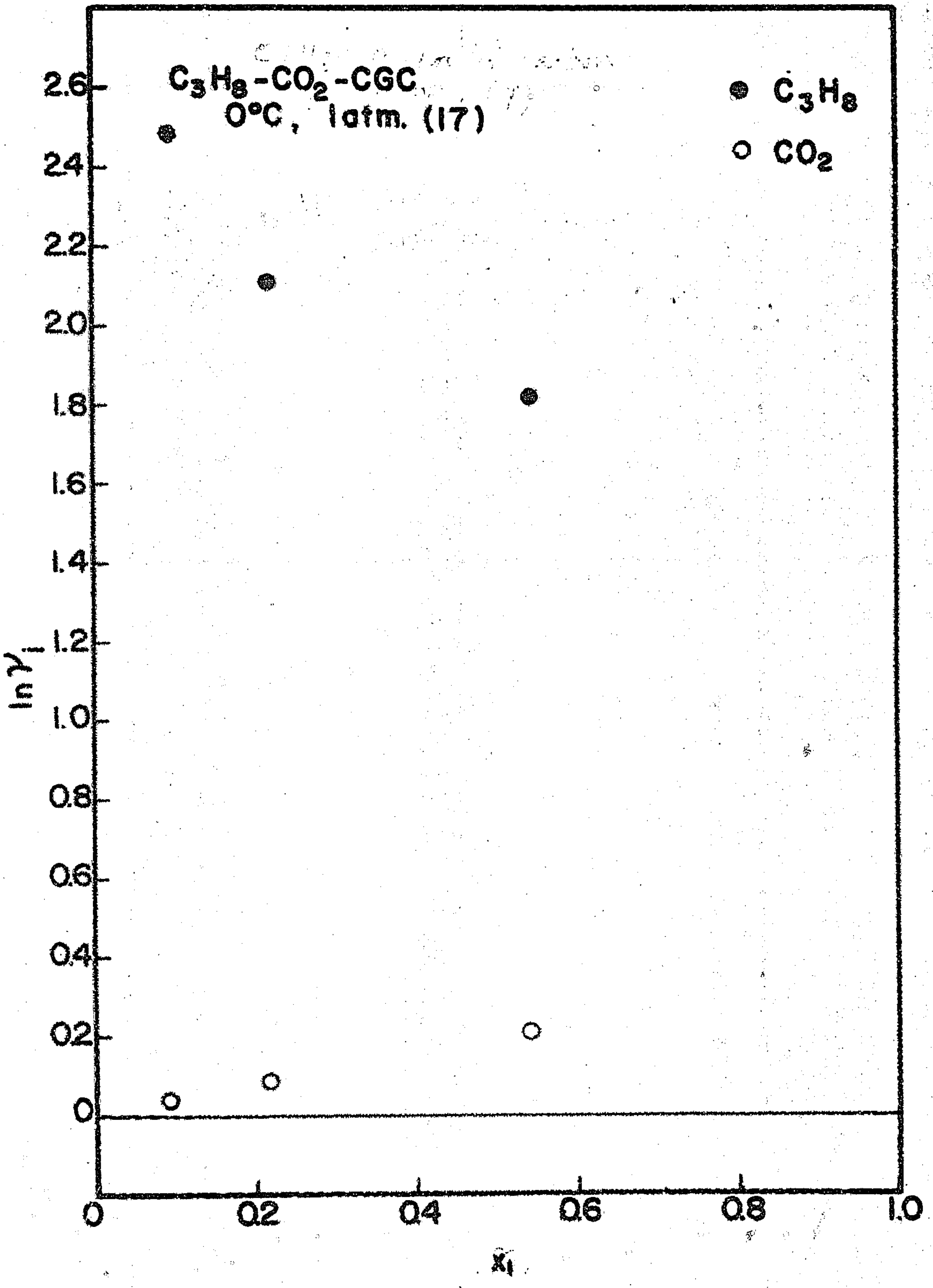


Figure 12 – CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (METHOD OF MYERS et al. (13))

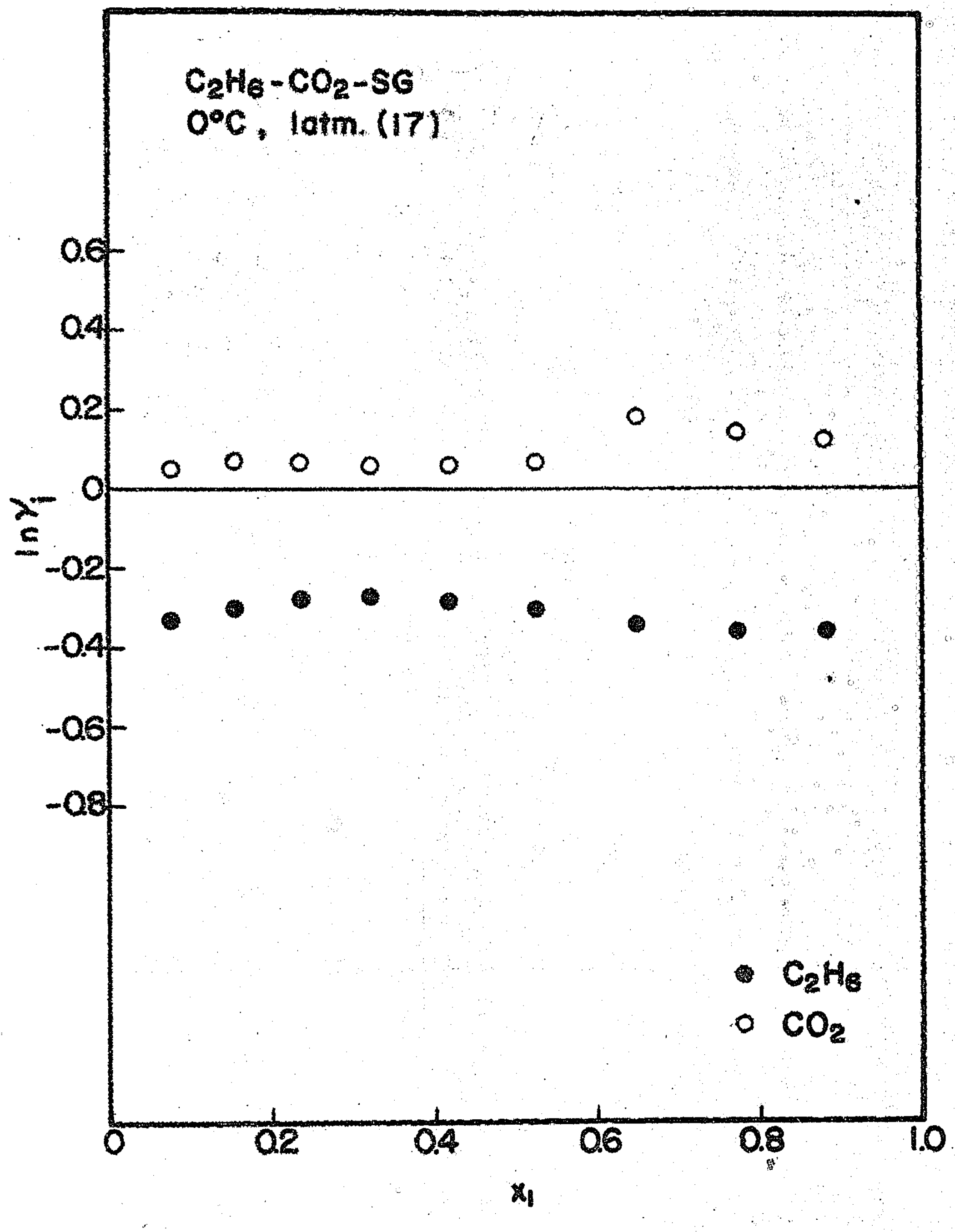


Figure 13 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (METHOD OF MYERS et al. (13))

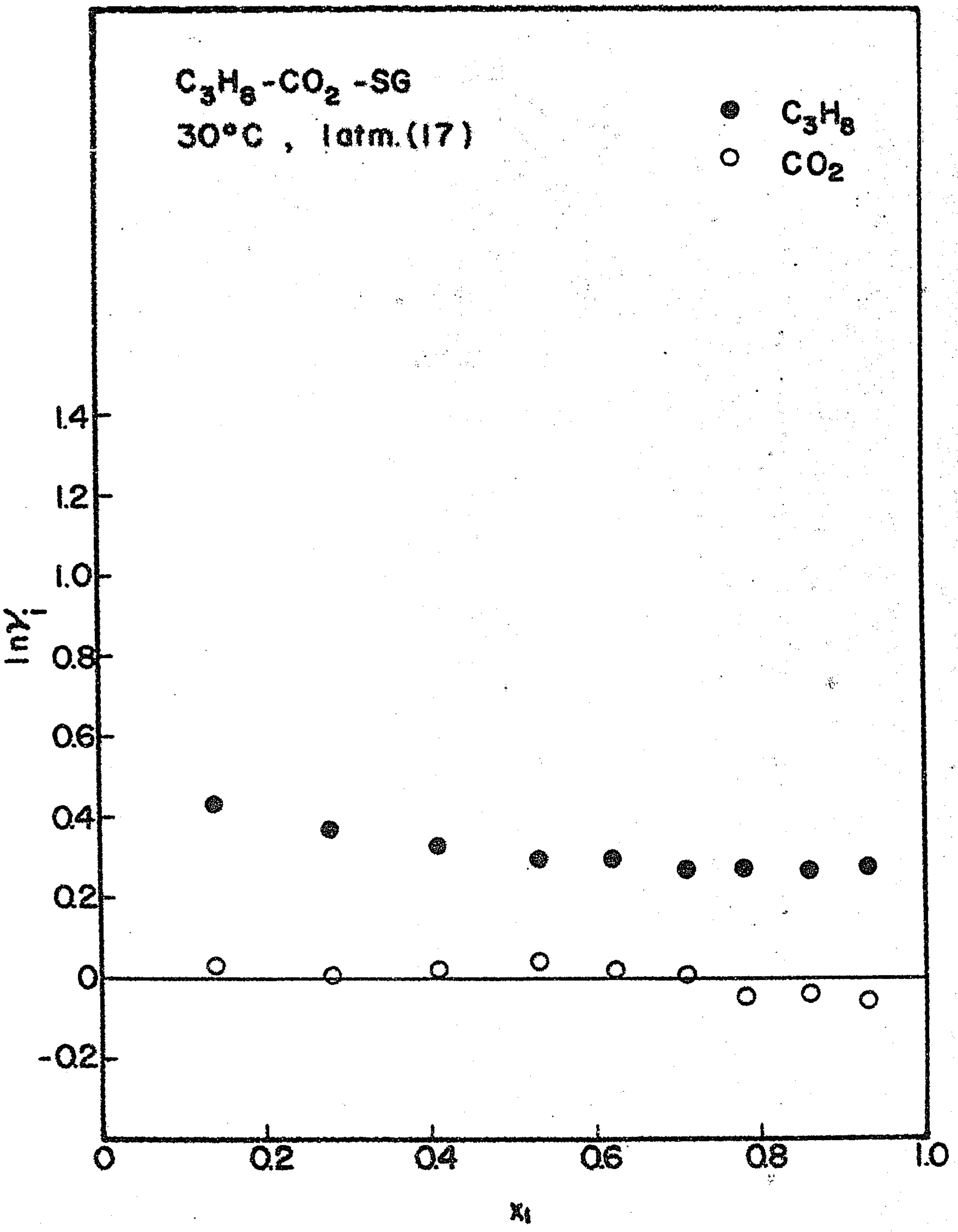


Figure 14 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (METHOD OF MYERS et al.(13))

b. Stoichiometric method: This method was suggested by Jelinek (17), and is based on an approach proposed by Argersinger, et al. (21) for use with ion-exchange equilibria. It may be described as follows:

Stoichiometric relations are written for the adsorption of each gas at a total pressure π:

Gas A: n_1° A (gas) + Surface = n_1° A (Adsorbed)

Gas B: n_2° B (gas) + Surface = n_2° B (Adsorbed)

Subtracting these two equations, we obtain a replacement reaction for a binary system at constant total pressure π.

$$n_1^\circ \text{ A (gas)} + n_2^\circ \text{ B (ads.)} = n_1^\circ \text{A(ads.)} + n_2^\circ \text{ B (gas)} \qquad (68)$$

An equilibrium constant is then defined for this relation in the usual manner,

$$K = \frac{(a_2)_g^{n_2^\circ} \; (a_1)_a^{n_1^\circ}}{(a_1)_g^{n_1^\circ} \; (a_2)_a^{n_2^\circ}} \qquad (69)$$

where $(a_1)_g$ and $(a_2)_g$ are thermodynamic activities of the two components A and B, respectively, in the gas phase, and $(a_1)_a$ and $(a_2)_a$ their activities in the adsorbed phase.

If perfect gas behavior in the gas phase is assumed, then

$$(a_1)_g = y_1 , \text{ and } (a_2)_g = y_2 \tag{70}$$

In the adsorbed phase, the standard state for each component is taken as pure adsorbate at total pressure π,

$$(a_1)_a = \gamma_1 x_1 \text{ and } (a_2)_a = \gamma_2 x_2 \tag{71}$$

These definitions are now substituted into Equation (67) to give

$$K = \frac{(y_2)^{n_2^\circ} (\gamma_1 x_1)^{n_1^\circ}}{(y_1)^{n_1^\circ} (\gamma_2 x_2)^{n_2^\circ}} = \overline{K} \frac{(\gamma_1)^{n_1^\circ}}{(\gamma_2)^{n_2^\circ}} \tag{72}$$

$\overline{K}$ is defined as

$$\overline{K} = \left(\frac{x_1}{y_1}\right)^{n_1^\circ} \left(\frac{y_2}{x_2}\right)^{n_2^\circ} \tag{73}$$

Thus $\overline{K}$ is readily calculated from experimental values of x and y and the pure gas isotherms.

In logarithmic form, Equation (72) is written

$$\ln K - \ln \overline{K} = n_1^\circ \ln \gamma_1 - n_2^\circ \ln \gamma_2 \tag{74}$$

The differential of this equation, at constant T and π, is

$$- d \ln \overline{K} = n_1^\circ \, d \ln \gamma_1 - n_2^\circ \, d \ln \gamma_2 \tag{75}$$

Combining Equations (75) and (30), one obtains

$$n_1^\circ \, d \ln \gamma_1 = - \frac{n_1^\circ x_2}{n_2^\circ x_1 + n_1^\circ x_2} \, d \ln \overline{K} \tag{76}$$

$$n_2^\circ \, d \ln \gamma_2 = \frac{n_2^\circ x_1}{n_2^\circ x_1 + n_1^\circ x_2} \, d \ln \overline{K} \tag{77}$$

A new variable Z is introduced in order to simplify the solution. Z is defined as

$$Z = \frac{n_2^\circ x_1}{n_2^\circ x_1 + n_1^\circ x_2}, \text{ and } Z - 1 = - \frac{n_1^\circ x_2}{n_2^\circ x_1 + n_1^\circ x_2} \tag{78}$$

Making this substitution, Equations (76) and (77) become

$$- n_1^\circ \, d \ln \gamma_1 = (1 - Z) \, d \ln \overline{K} \tag{79}$$

$$n_2^\circ \, d \ln \gamma_2 = Z \, d \ln \overline{K} \tag{80}$$

These equations may be integrated with the boundary conditions

$$\text{B. C. 1} \qquad x_1 = 1, \quad Z = 1; \quad \gamma_1 = 1 \tag{81}$$

$$\text{B. C. 2} \qquad x_2 = 1, \quad Z = 1; \quad \gamma_2 = 1 \tag{82}$$

However, since $\overline{K}$ is indeterminate according to Equation (73) when $x_1 = 0$ or 1, the right hand side of Equations (79) and (80) must be integrated by parts

$$n_1^\circ \int_1^{\gamma_1} d \ln \gamma_1 = (Z - 1) \ln \overline{K} - \int_1^Z \ln \overline{K} \, d Z \tag{83}$$

$$n_2^\circ \int_{\gamma_2}^1 d \ln \gamma_2 = - Z \ln \overline{K} - \int_Z^0 \ln \overline{K} \, d Z \tag{84}$$

The integrated forms of these equations are

$$n_1^\circ \ln \gamma_1 = (Z - 1) \ln \overline{K} - \int_1^Z \ln \overline{K}\, d Z \tag{85}$$

$$-n_2^\circ \ln \gamma_2 = - Z \ln \overline{K} + \int_0^Z \ln \overline{K}\, d Z \tag{86}$$

Upon adding Equations (85) and (86) one obtains

$$n_1^\circ \ln \gamma_1 - n_2^\circ \ln \gamma_2 = - \ln \overline{K} + \int_0^1 \ln \overline{K}\, d Z \tag{87}$$

Comparing this equation with Equation (74), it is seen that

$$\ln K = \int_0^1 \ln \overline{K}\, d Z \tag{88}$$

This integral may be evaluated graphically, by plotting $\ln \overline{K}$ versus Z, as calculated from experimental data.

This method was applied to the following equilibrium data:

Systems						
No.	Comp't. 1	Comp't. 2	Adsorbent	Temp.	Pressure	Ref.
B-1	O_2	CO	Silica Gel	0°C	1 atm	(3)
B-2	CH_4	C_2H_6	Activated Carbon	20°C	750 mm Hg	(8)
B-3	C_3H_8	C_4H_{10}	Activated Carbon	20°C	750 mm Hg	(8)
B-4	N_2	Ar	Silica Gel	89.5°K	250 mm Hg	(20)
B-5	N_2	Ar	Silica Gel	111°K	250 mm Hg	(20)
B-6	C_2H_4	CO_2	Col. "G" Carbon	0°C	1 atm	(17)
B-7	C_2H_4	CO_2	Col. "G" Carbon	30°C	1 atm	(17)
B-8	C_2H_6	CO_2	Col. "G" Carbon	0°C	1 atm	(17)
B-9	C_2H_6	CO_2	Col. "G" Carbon	30°C	1 atm	(17)
B-10	C_3H_6	CO_2	Col. "G" Carbon	0°C	1 atm	(17)
B-11	C_3H_6	CO_2	Col. "G" Carbon	30°C	1 atm	(17)
B-12	C_3H_8	CO_2	Col. "G" Carbon	0°C	1 atm	(17)
B-13	C_3H_8	CO_2	Col. "G" Carbon	30°C	1 atm	(17)
B-14	C_2H_4	CO_2	Silica Gel	0°C	1 atm	(17)
B-15	C_2H_4	CO_2	Silica Gel	30°C	1 atm	(17)
B-16	C_2H_6	CO_2	Silica Gel	0°C	1 atm	(17)
B-17	C_2H_6	CO_2	Silica Gel	30°C	1 atm	(17)
B-18	C_3H_6	CO_2	Silica Gel	0°C	1 atm	(17)
B-19	C_3H_6	CO_2	Silica Gel	30°C	1 atm	(17)
B-20	C_3H_8	CO_2	Silica Gel	0°C	1 atm	(17)
B-21	C_3H_8	CO_2	Silica Gel	30°C	1 atm	(17)

The summary of the results is shown in Table 2. These results are also presented in Tables 16-36 (Appendix C) and Figures 15-35.

Table 2

Summary of Calculation of Adsorbed Phase Activity Coefficients by Stoichiometric Method (17)

System	Adsorbed Phase Activity Coefficients	Reference
B-1	The smallest γ_1 is about 0.914 at $x_1 = 0.193$ and the smallest γ_2 is also about 0.914 at $x_1 = 0.653$. γ_1 increases with increasing x_1 and γ_2 decreases with increasing x_1. $\gamma_1 \to 1$ as $x_1 \to 1$ and $\gamma_2 \to 1$ as $x_1 \to 0$.	(3)
B-2	Only half the range of x is covered. γ_1 increases with increasing x_1 and γ_2 decreases with increasing x_1. The smallest γ_1 is about 0.015 at $x_1 = 0.026$, the smallest γ_2 is about 0.606 at $x_1 = 0.342$. $\gamma_2 \to 1$ as $x_1 \to 0$ and $\gamma_1 \to 1$ as $x_1 \to 1$.	(8)
B-3	$\gamma_1 \to 1$ as $x_1 \to 1$ and $\gamma_2 \to 1$ as $x_1 \to 0$. The maximum value of γ_1 is about 1.041 at $x_1 = 0.68$ and the corresponding minimum value of γ_2 is about 0.939.	(8)
B-4	$\gamma_1 \to 1$ as $x_1 \to 1$ and $\gamma_2 \to 1$ as $x_1 \to 0$. γ_1 increases with increasing x_1 and γ_2 decreases with increasing x_1. The smallest γ_1 is about 0.514 at $x_1 = 0.062$ and the smallest γ_2 is about 0.697 at $x_1 = 0.925$.	(20)

Table 2 (Continued)

System	Adsorbed Phase Activity Coefficients	Reference
B-5	$\gamma_1 \to 1$ as $x_1 \to 1$ and $\gamma_2 \to 1$ as $x_1 \to 0$. γ_1 increases with increasing x_1 and γ_2 decreases with increasing x_1. The smallest γ_1 is about 0.712 at $x_1 = 0.097$ and the smallest γ_2 is about 0.819 at $x_1 = 0.928$.	(20)
B-6	$\gamma_1 \to 1$ as $x_1 \to 1$ and $\gamma_2 \to 1$ as $x_1 \to 0$. $\gamma_1 \to 3.46$ as $x_1 \to 0$ and $\gamma_2 \to 1.116$ as $x_1 \to 1$. The minimum value of $\gamma_1 = 0.9802$ at $x_1 = 0.545$ and the corresponding maximum value of $\gamma_2 = 1.22$.	(17)
B-7	$\gamma_1 \to 1$ as $x_1 \to 1$ and $\gamma_2 \to 1$ as $x_1 \to 0$. $\gamma_1 \to 4.05$ as $x_1 \to 0$ and $\gamma_2 \to 0.497$ as $x_1 \to 1$. The minimum value of γ_1 is about 0.887 and the corresponding maximum value of γ_2 is about 1.222 at $x_1 = 0.6$	(17)
B-8	$\gamma_1 \to 1$ as $x_1 \to 1$ and $\gamma_2 \to 1$ as $x_1 \to 0$. $\gamma_1 \to 5.58$ as $x_1 \to 0$ and $\gamma_2 \to 0.223$ as $x_1 \to 1$. The minimum value of γ_1 is about 0.887 and the corresponding maximum value of γ_2 is about 1.272 at $x_1 = 0.62$.	(17)
B-9	$\gamma_1 \to 1$ as $x_1 \to 1$ and $\gamma_2 \to 1$ as $x_1 \to 0$. $\gamma_1 \to 1.82$ as $x_1 \to 0$ and $\gamma_2 \to 0.122$ as $x_1 \to 1$. The minimum value of γ_1 is about 0.678 and the corresponding maximum value of γ_2 is about 1.062 at $x_1 = 0.23$.	(17)

Table 2 (Continued)

System	Adsorbed Phase Activity Coefficients	Reference
B-10	$\gamma_1 \rightarrow 1$ as $x_1 \rightarrow 1$ and $\gamma_2 \rightarrow 1$ as $x_1 \rightarrow 0$. γ_1 decreases with increasing x_1 and γ_2 increases with increasing x_1. $\gamma_1 \rightarrow 2.48$ as $x_1 \rightarrow 0$ and $\gamma_2 \rightarrow 2.64$ as $x_1 \rightarrow 1$.	(17)
B-11	$\gamma_1 \rightarrow 1$ as $x_1 \rightarrow 1$ and $\gamma_2 \rightarrow 1$ as $x_1 \rightarrow 0$. $\gamma_1 \rightarrow 1.434$ as $x_1 \rightarrow 0$ and $\gamma_2 \rightarrow 0.074$ as $x_1 \rightarrow 1$. The minimum value of γ_1 is about 0.803 and the corresponding maximum value of γ_2 is about 1.38 at $x_1 = 0.71$.	(17)
B-12	$\gamma_1 \rightarrow 1$ as $x_1 \rightarrow 1$ and $\gamma_2 \rightarrow 1$ as $x_1 \rightarrow 0$. $\gamma_1 \rightarrow 6.06$ as $x_1 \rightarrow 0$ and $\gamma_2 \rightarrow 1.03$ as $x_1 \rightarrow 1$. The minimum value of γ_1 is about 0.942 and the corresponding maximum value of γ_2 is about 1.252 at $x_1 = 0.54$.	(17)
B-13	$\gamma_1 \rightarrow 1$ as $x_1 \rightarrow 1$ and $\gamma_2 \rightarrow 1$ as $x_1 \rightarrow 0$. $\gamma_1 \rightarrow 3.67$ as $x_1 \rightarrow 0$ and $\gamma_2 \rightarrow 0.223$ as $x_1 \rightarrow 1$. The minimum value of γ_1 is about 0.712 and the corresponding maximum value of γ_2 is about 1.185 at $x_1 = 0.44$.	(17)
B-14	$\gamma_1 \rightarrow 1$ as $x_1 \rightarrow 1$ and $\gamma_2 \rightarrow 1$ as $x_1 \rightarrow 0$. $\gamma_1 \rightarrow 3.32$ as $x_1 \rightarrow 0$ and $\gamma_2 \rightarrow 0.905$ as $x_1 \rightarrow 1$. The minimum value of γ_1 is about 0.961 and the corresponding maximum value of γ_2 is about 1.105 at $x_1 = 0.32$.	(17)

Table 2 (Continued)

System	Adsorbed Phase Activity Coefficients	Reference
B-15	$\gamma_1 \rightarrow 1$ as $x_1 \rightarrow 1$ and $\gamma_2 \rightarrow 1$ as $x_1 \rightarrow 0$. $\gamma_1 \rightarrow 1.03$ as $x_1 \rightarrow 0$ and $\gamma_2 \rightarrow 0.802$ as $x_1 \rightarrow 1$. The minimum value of γ_1 is about 0.914 and the corresponding maximum value of γ_2 is about 1.02 at $x_1 = 0.36$.	(17)
B-16	$\gamma_1 \rightarrow 1$ as $x_1 \rightarrow 1$ and $\gamma_2 \rightarrow 1$ as $x_1 \rightarrow 0$. $\gamma_1 \rightarrow 4.14$ as $x_1 \rightarrow 0$ and $\gamma_2 \rightarrow 1.127$ as $x_1 \rightarrow 1$. γ_1 decreases with increasing x_1 and γ_2 increases with increasing x_1.	(17)
B-17	$\gamma_1 \rightarrow 1$ as $x_1 \rightarrow 1$ and $\gamma_2 \rightarrow 1$ as $x_1 \rightarrow 0$. $\gamma_1 \rightarrow 2.14$ as $x_1 \rightarrow 0$ and $\gamma_2 \rightarrow 1.03$ as $x_1 \rightarrow 1$. γ_1 decreases with increasing x_1 and γ_2 increases with increasing x_1.	(17)
B-18	$\gamma_1 \rightarrow 1$ as $x_1 \rightarrow 1$ as $\gamma_2 \rightarrow 1$ as $x_1 \rightarrow 0$. $\gamma_1 \rightarrow 3.06$ as $x_1 \rightarrow 0$ and $\gamma_2 \rightarrow 0.719$ as $x_1 \rightarrow 1$. The minimum value of γ_1 is about 0.905 and the corresponding maximum value of γ_2 is about 1.246 at $x_1 = 0.56$.	(17)
B-19	$\gamma_1 \rightarrow 1$ as $x_1 \rightarrow 1$ as $\gamma_2 \rightarrow 1$ as $x_1 \rightarrow 0$. $\gamma_1 \rightarrow 1.77$ as $x_1 \rightarrow 0$ and $\gamma_2 \rightarrow 0.786$ as $x_1 \rightarrow 1$. The minimum value of γ_1 is about 0.961 and the corresponding maximum value of γ_2 is about 1.162 at $x_1 = 0.66$.	(17)

Table 2 (Continued)

System	Adsorbed Phase Activity Coefficients	Reference
B-20	$\gamma_1 \rightarrow 1$ as $x_1 \rightarrow 1$ as $\gamma_2 \rightarrow 1$ as $x_1 \rightarrow 0$. $\gamma_1 \rightarrow 1.52$ as $x_1 \rightarrow 0$ and $\gamma_2 \rightarrow 0.97$ as $x_1 \rightarrow 1$. The minimum value of γ_1 is about 0.97 and the corresponding maximum value of γ_2 is about 1.083 at $x_1 = 0.43$.	(17)
B-21	$\gamma_1 \rightarrow 1$ as $x_1 \rightarrow 1$ as $\gamma_2 \rightarrow 1$ as $x_1 \rightarrow 0$. $\gamma_1 \rightarrow 1$ as $x_1 \rightarrow 0$ and $\gamma_2 \rightarrow 0.496$ as $x_1 \rightarrow 1$. The minimum value of γ_1 is about 0.896 and the corresponding maximum value of γ_2 is about 1.02 at $x_1 = 0.495$.	(17)

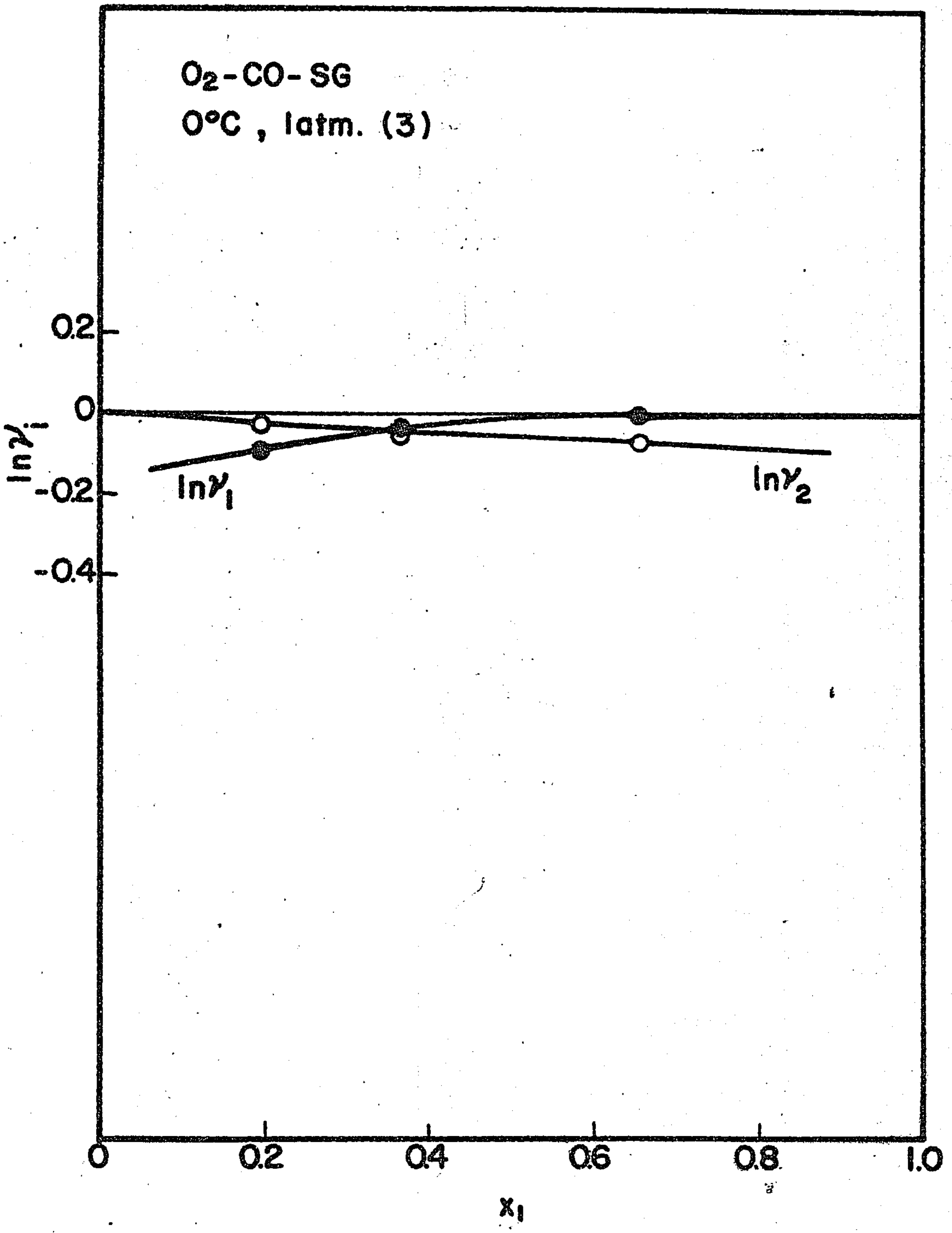


Figure 15 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (STOICHIOMETRIC METHOD (17))

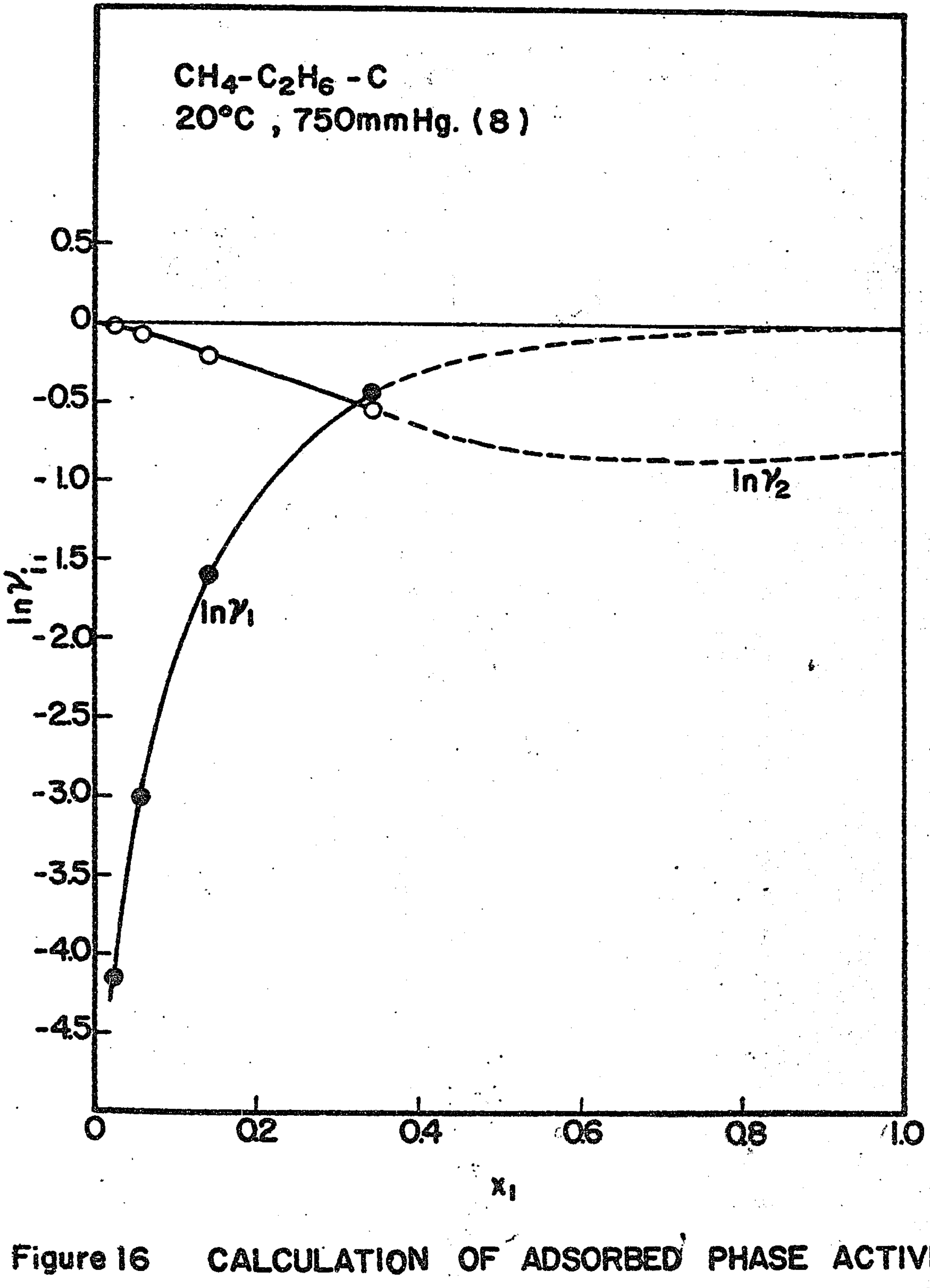


Figure 16 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (STOICHIOMETRIC METHOD (17))

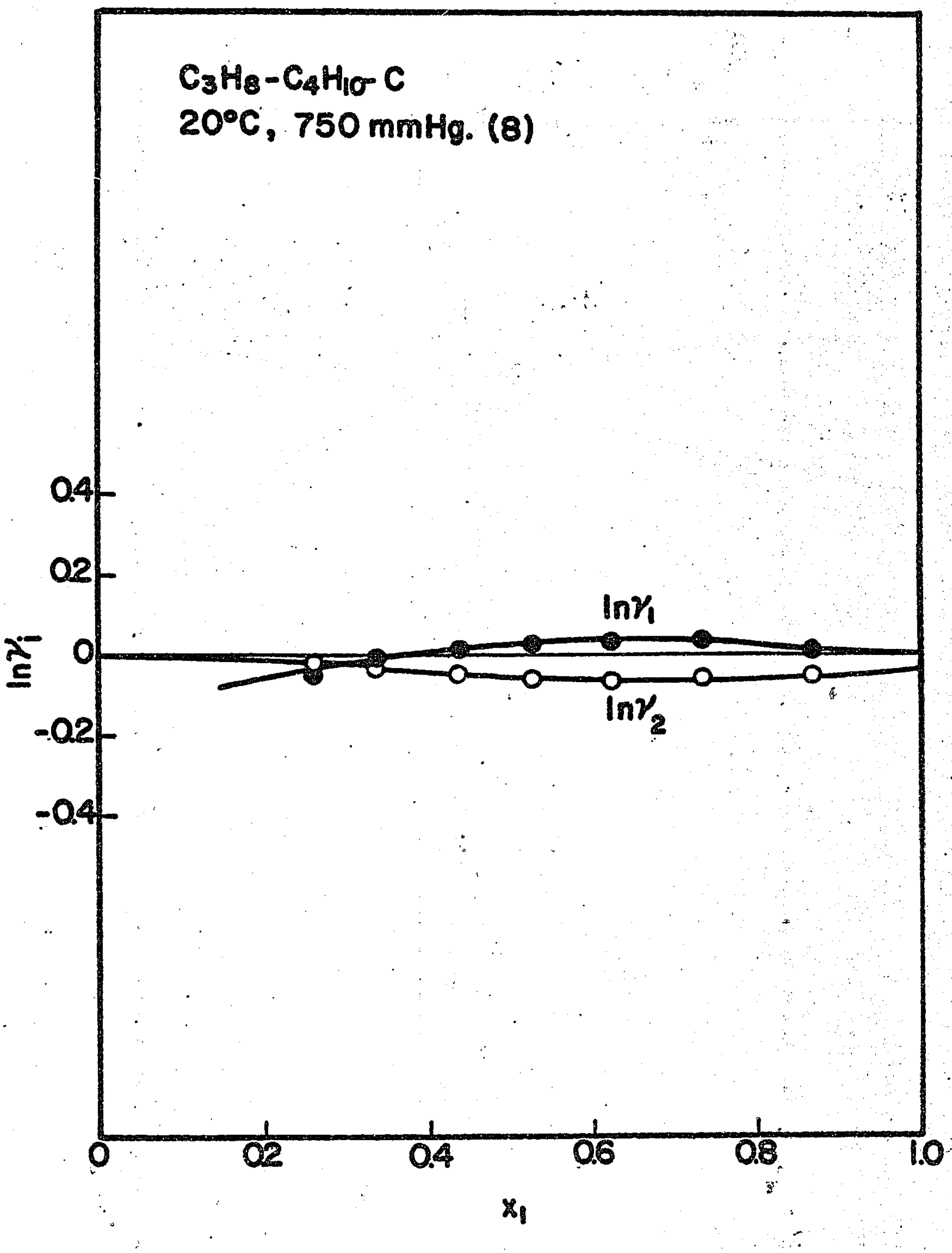


Figure 17 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (STOICHIOMETRIC METHOD(17))

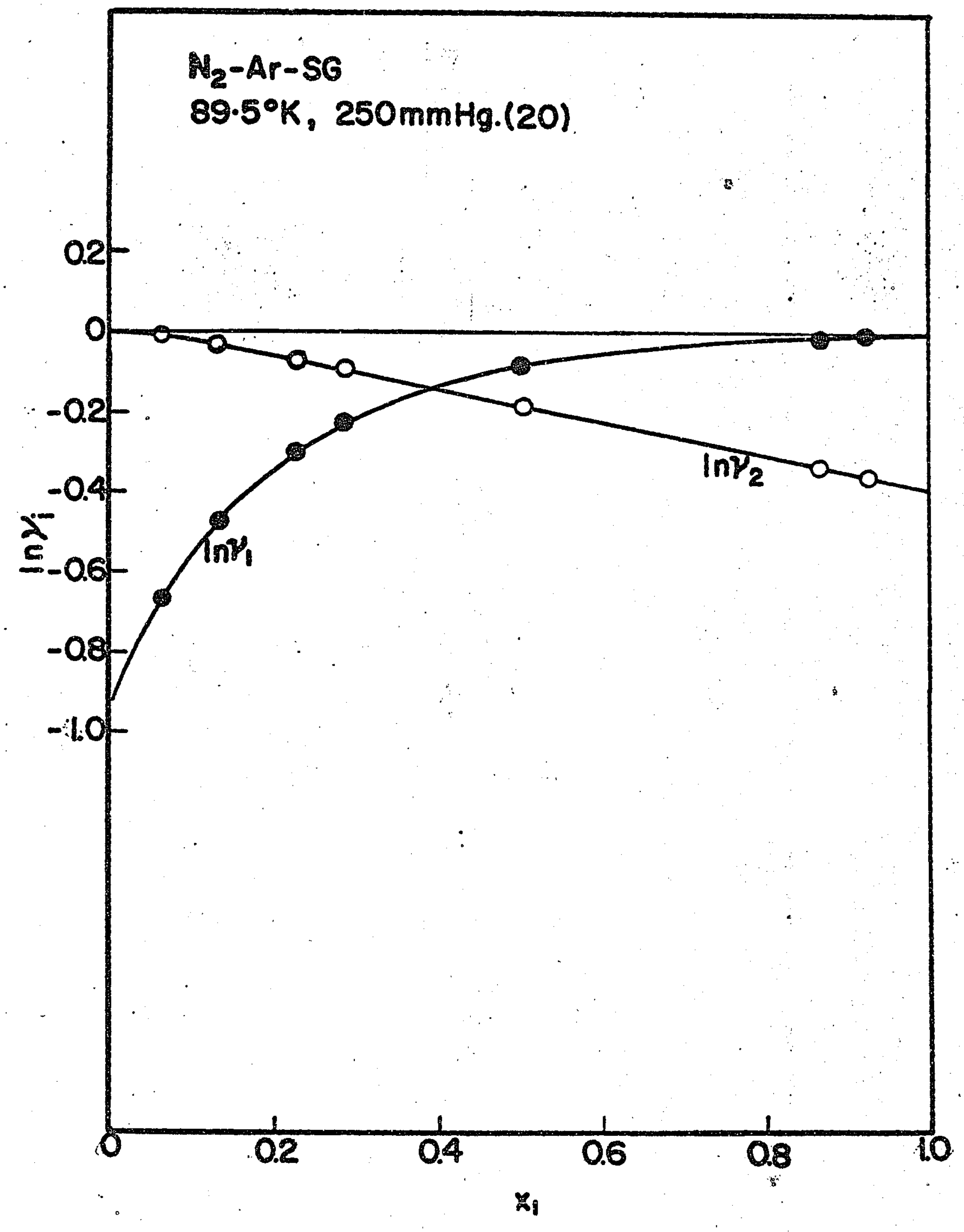


Figure 18 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (STOICHIOMETRIC METHOD(17))

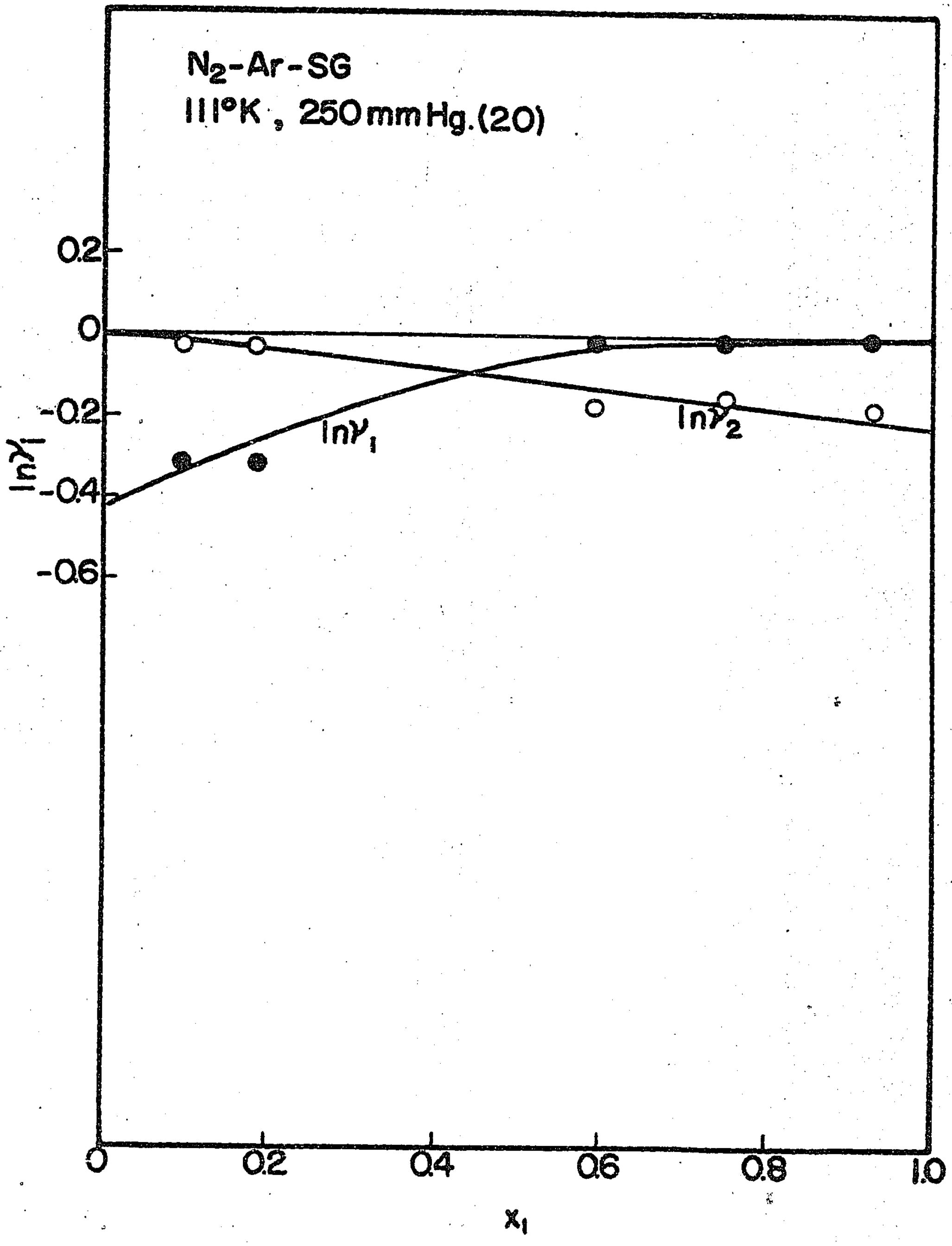


Figure 19 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (STOICHIOMETRIC METHOD (17))

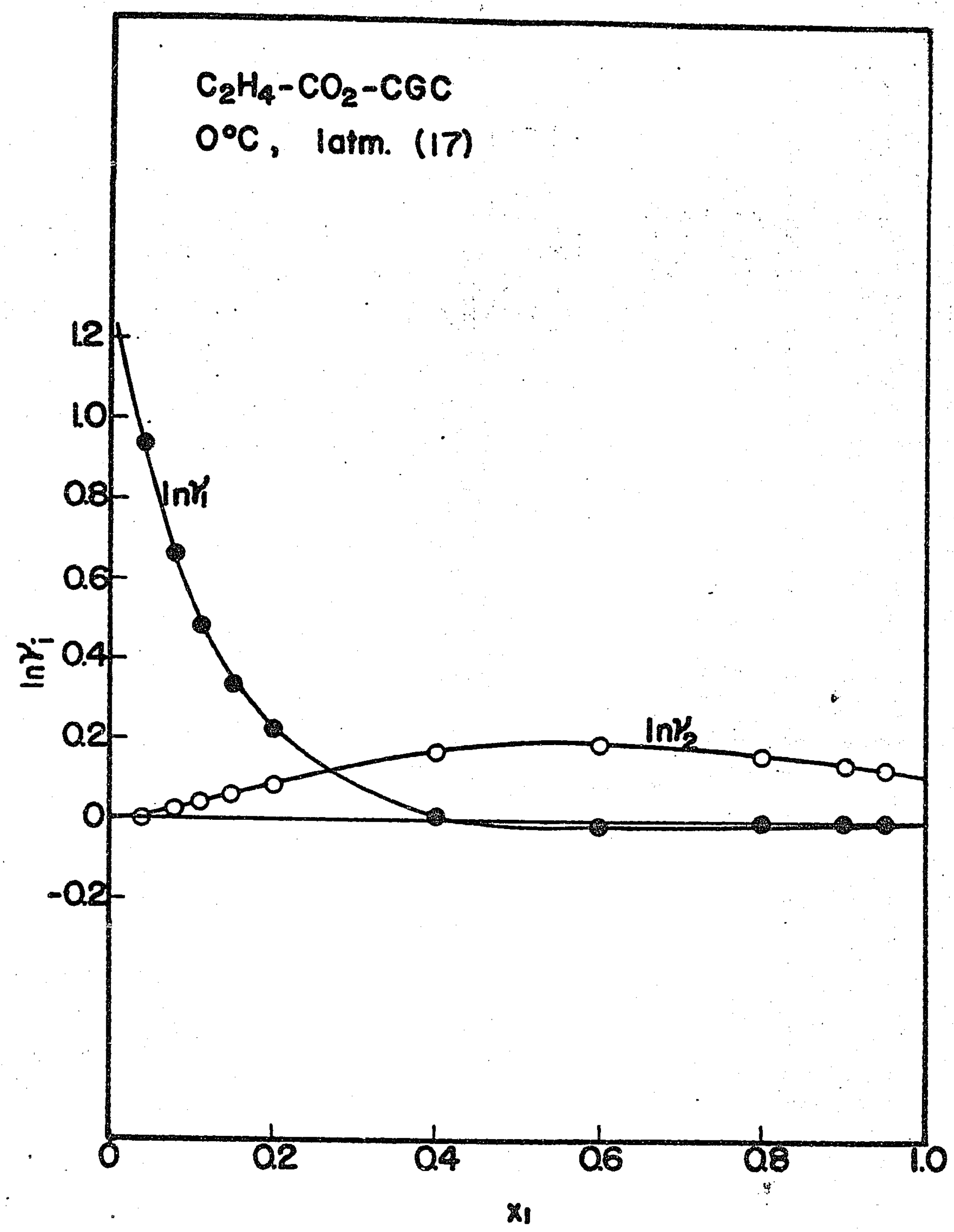


Figure 20 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (STOICHIOMETRIC METHOD(17))

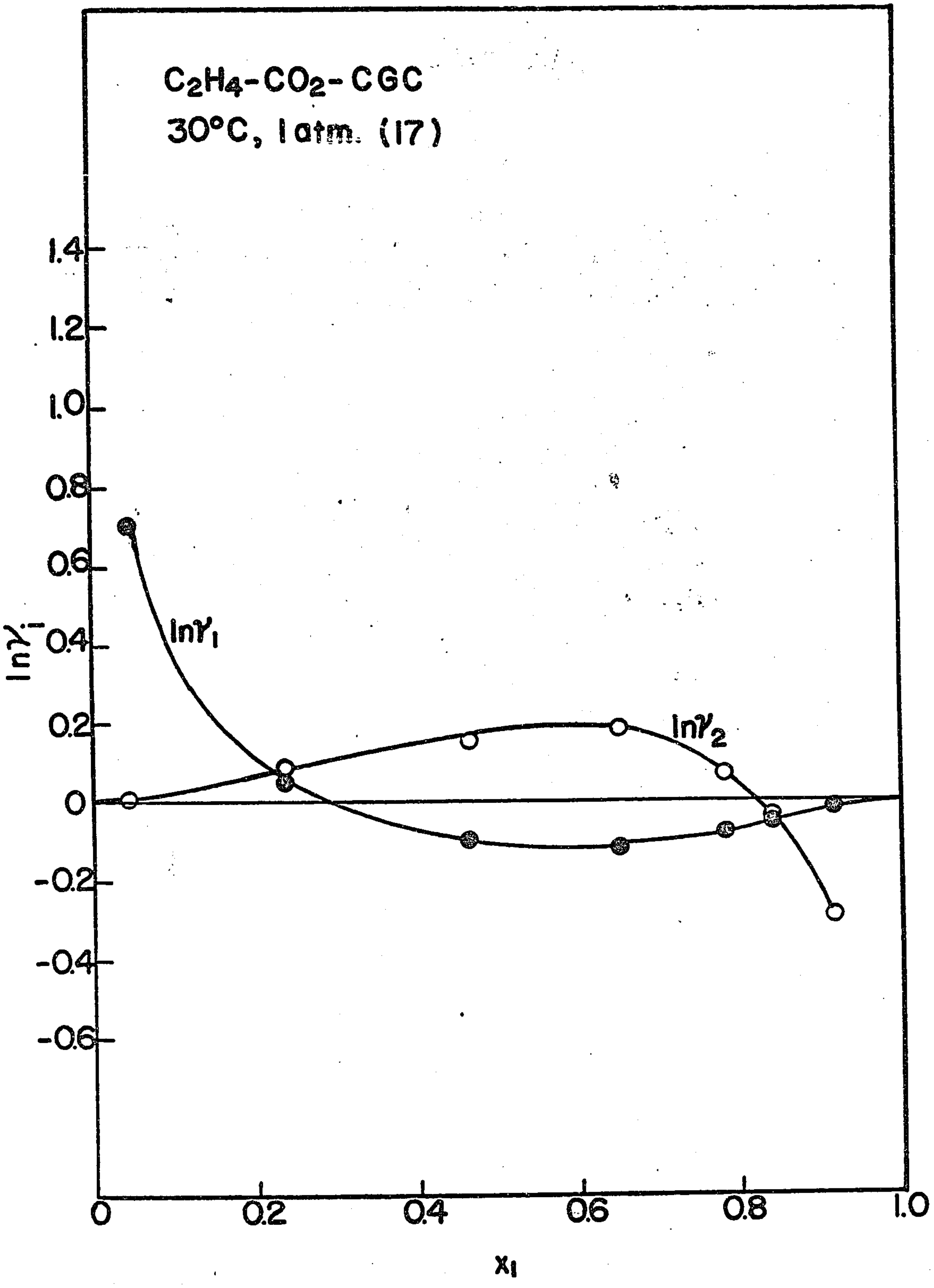


Figure 21 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (STOICHIOMETRIC METHOD(17))

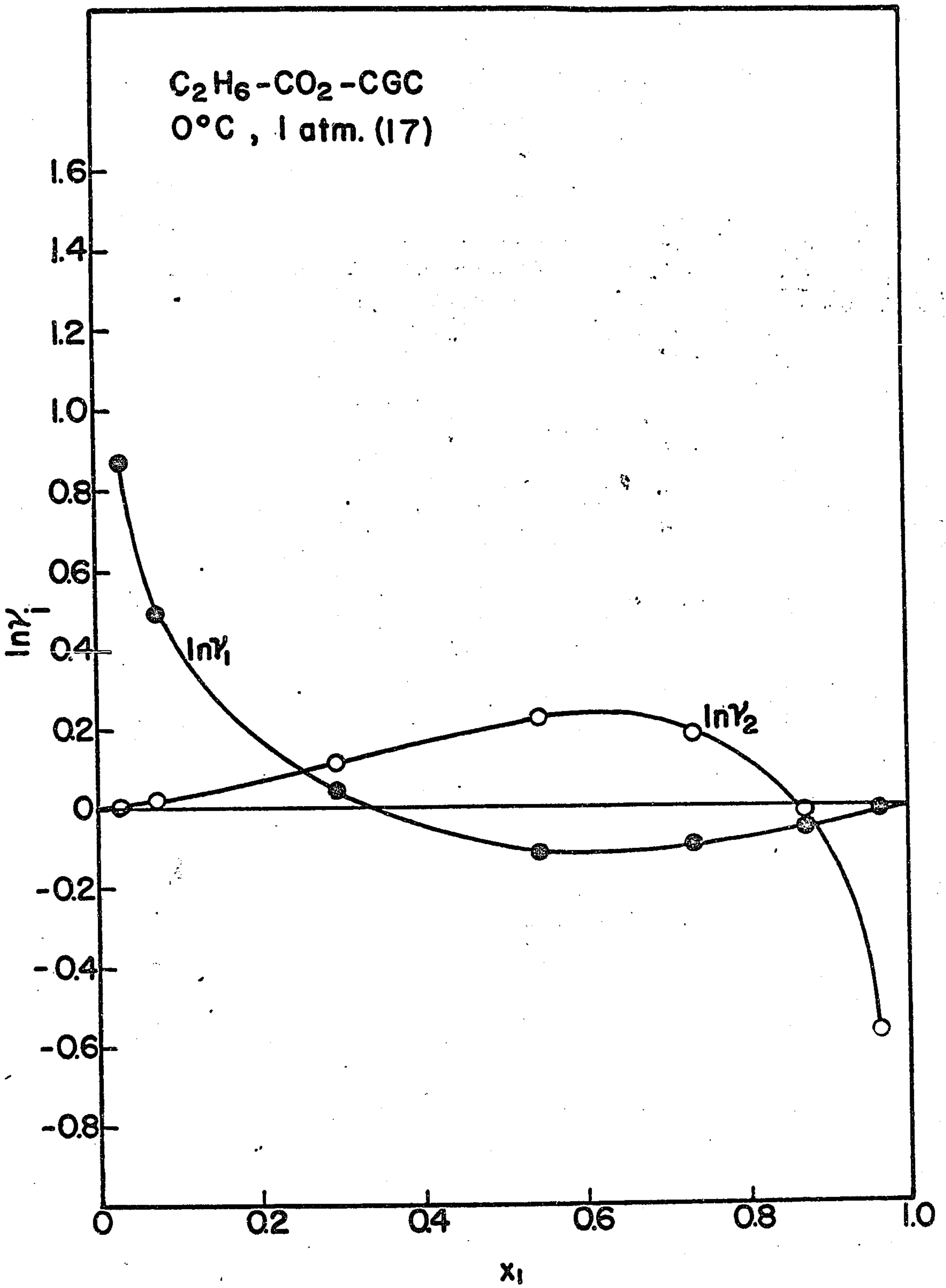


Figure 22 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (STOICHIOMETRIC METHOD (17))

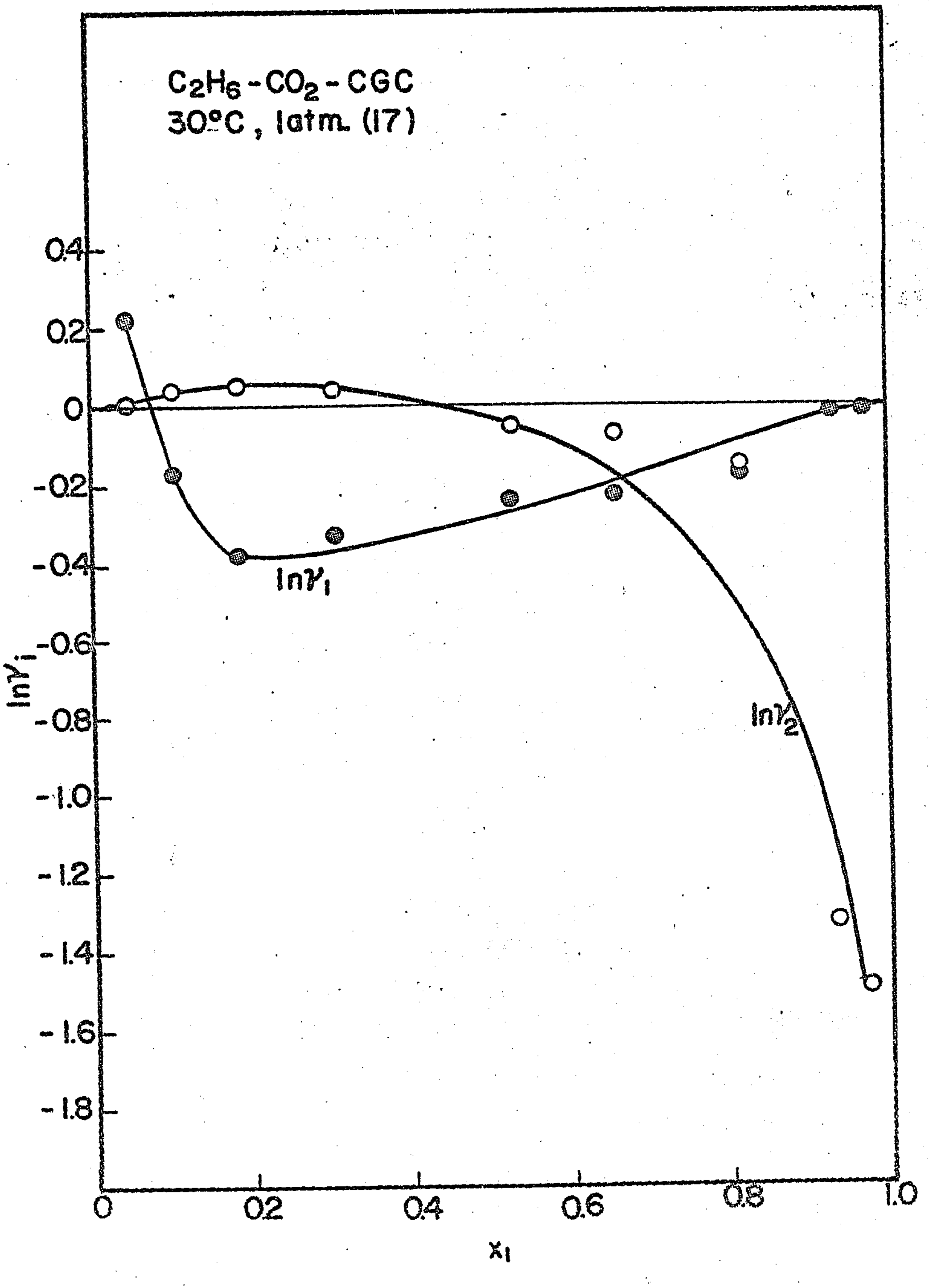


Figure 23 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (STOICHIOMETRIC METHOD (17))

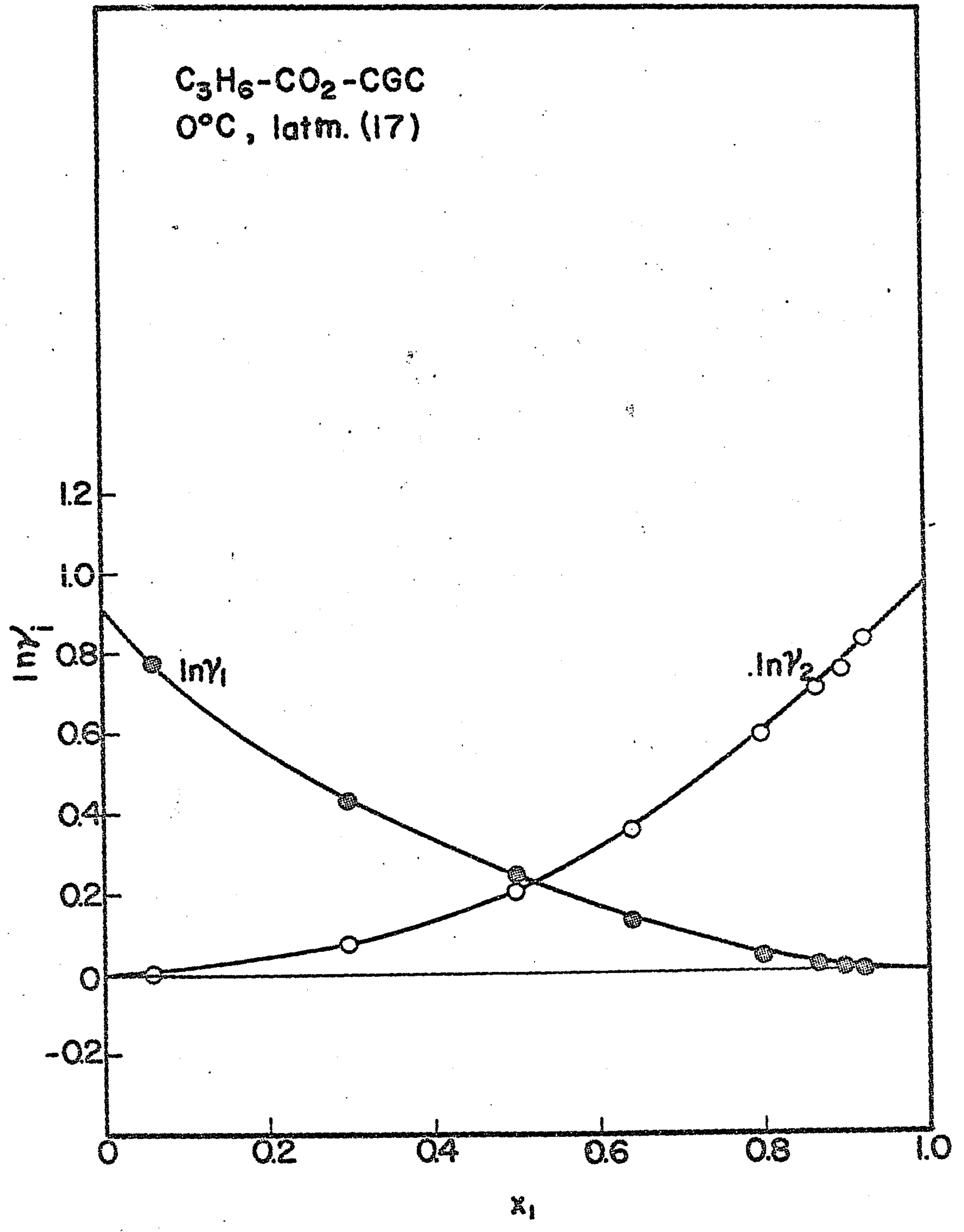


Figure 24 CALCULATION OF ADSORBE PHASE ACTIVITY COEFFICIENTS (STOICHIOMETRIC METHOD (17))

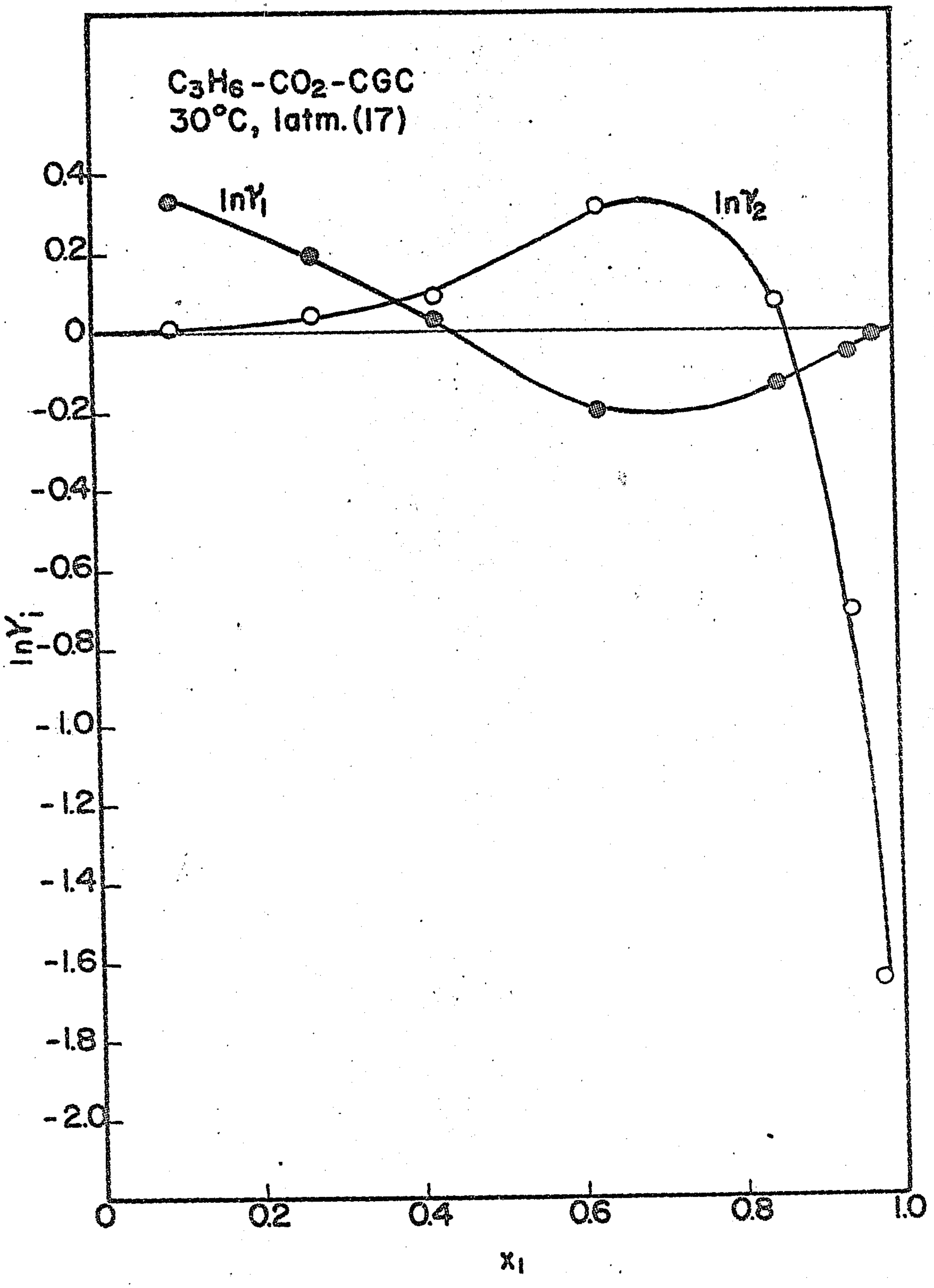


Figure 25 CALCULATION OF ADSOBED PHASE ACTIVITY COEFFICIENTS (STOICHIOMETRIC METHOD(17))

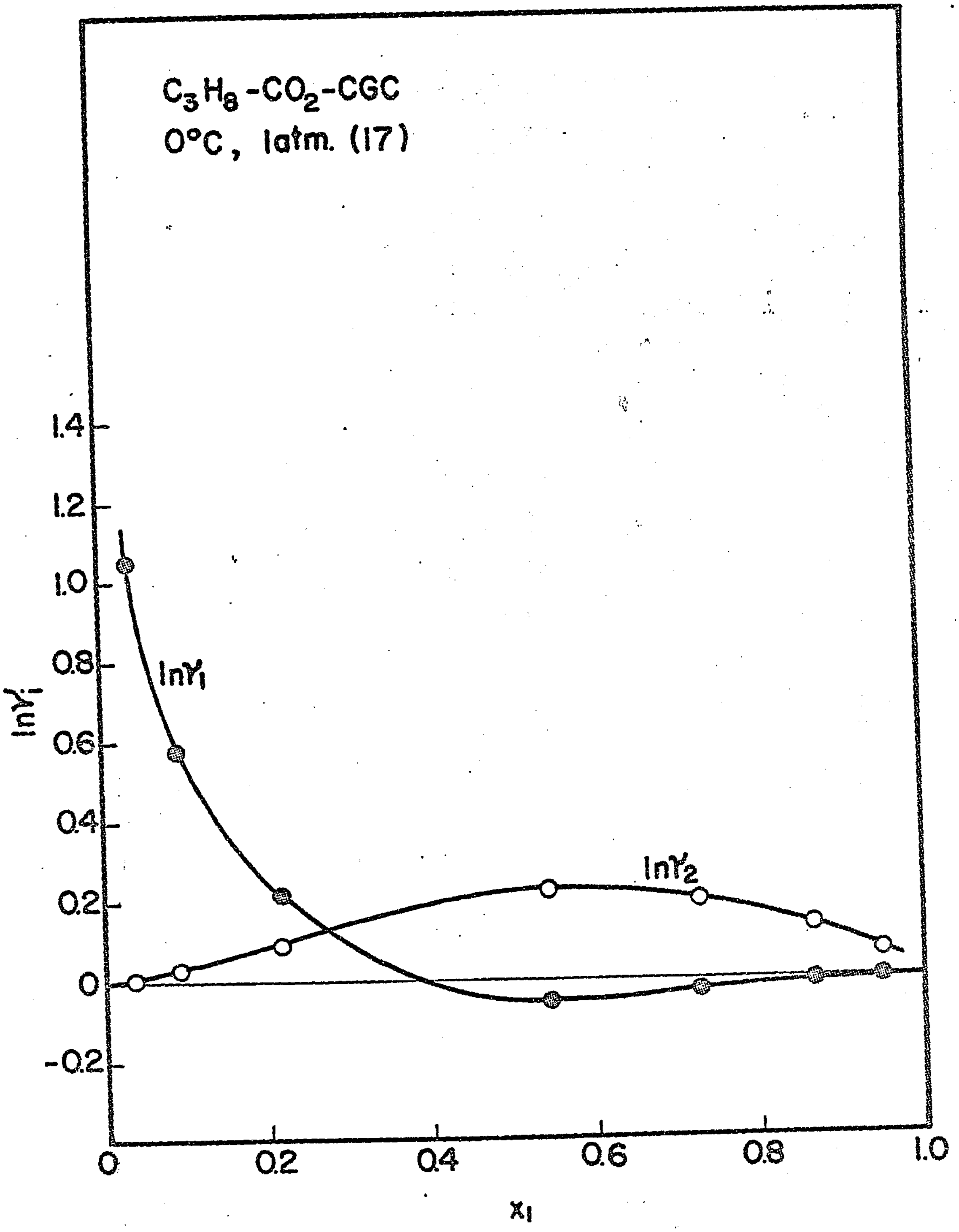


Figure 26 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (STOICHIOMETRIC METHOD (17))

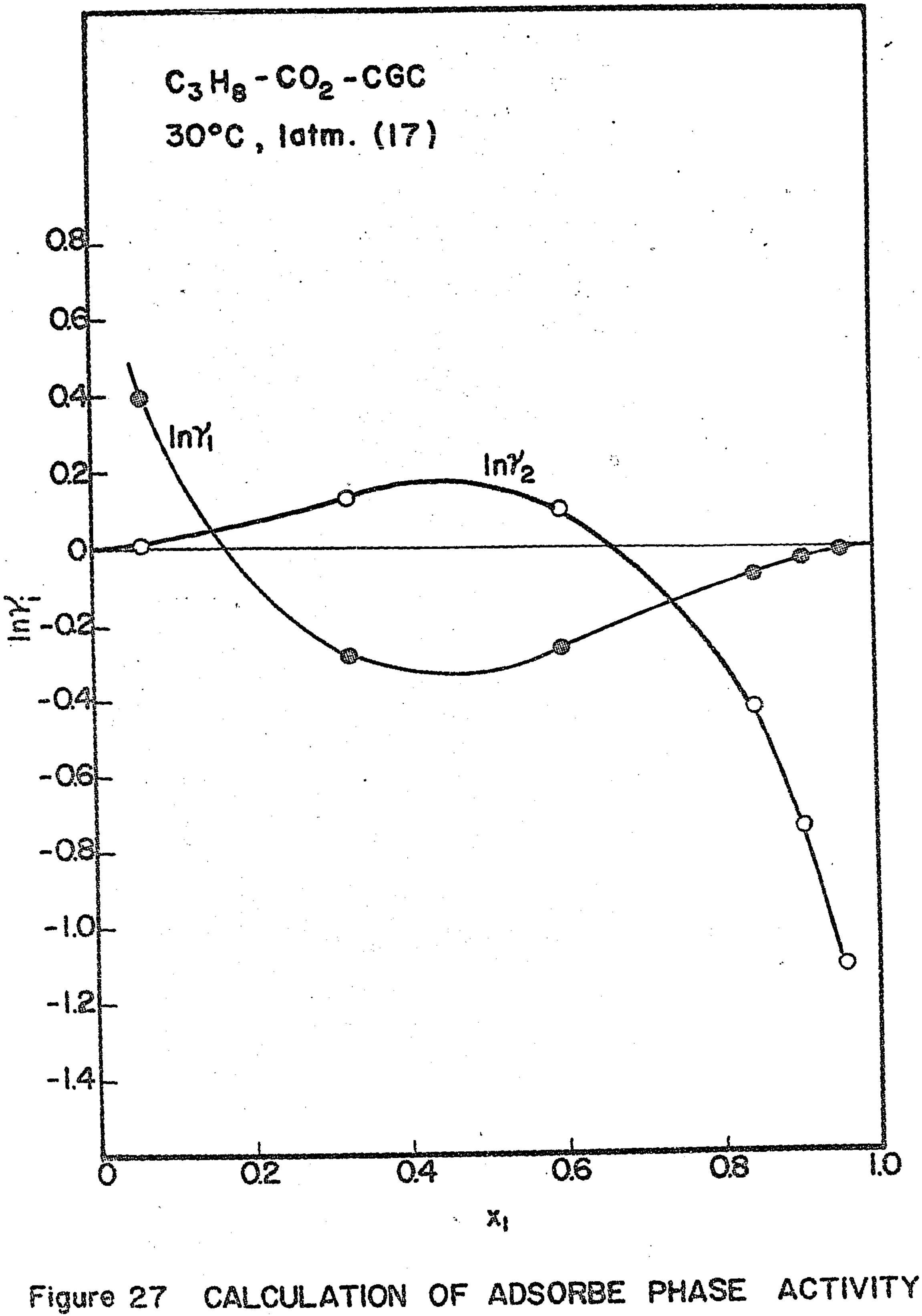


Figure 27 CALCULATION OF ADSORBE PHASE ACTIVITY COEFFICIENTS (STOICHIOMETRIC METHOD(17))

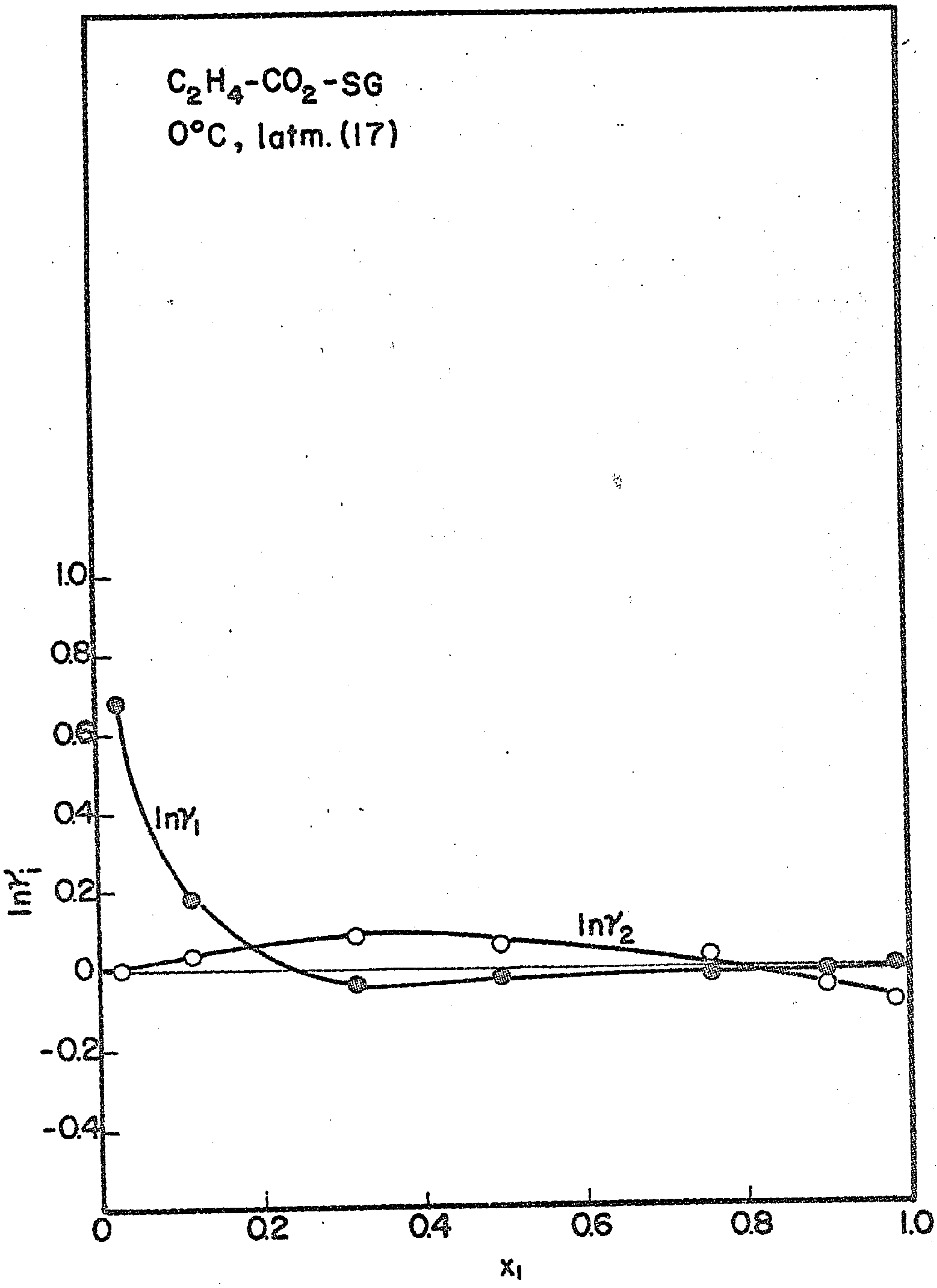


Figure 28 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (STOICHIOMETRIC METHOD (17))

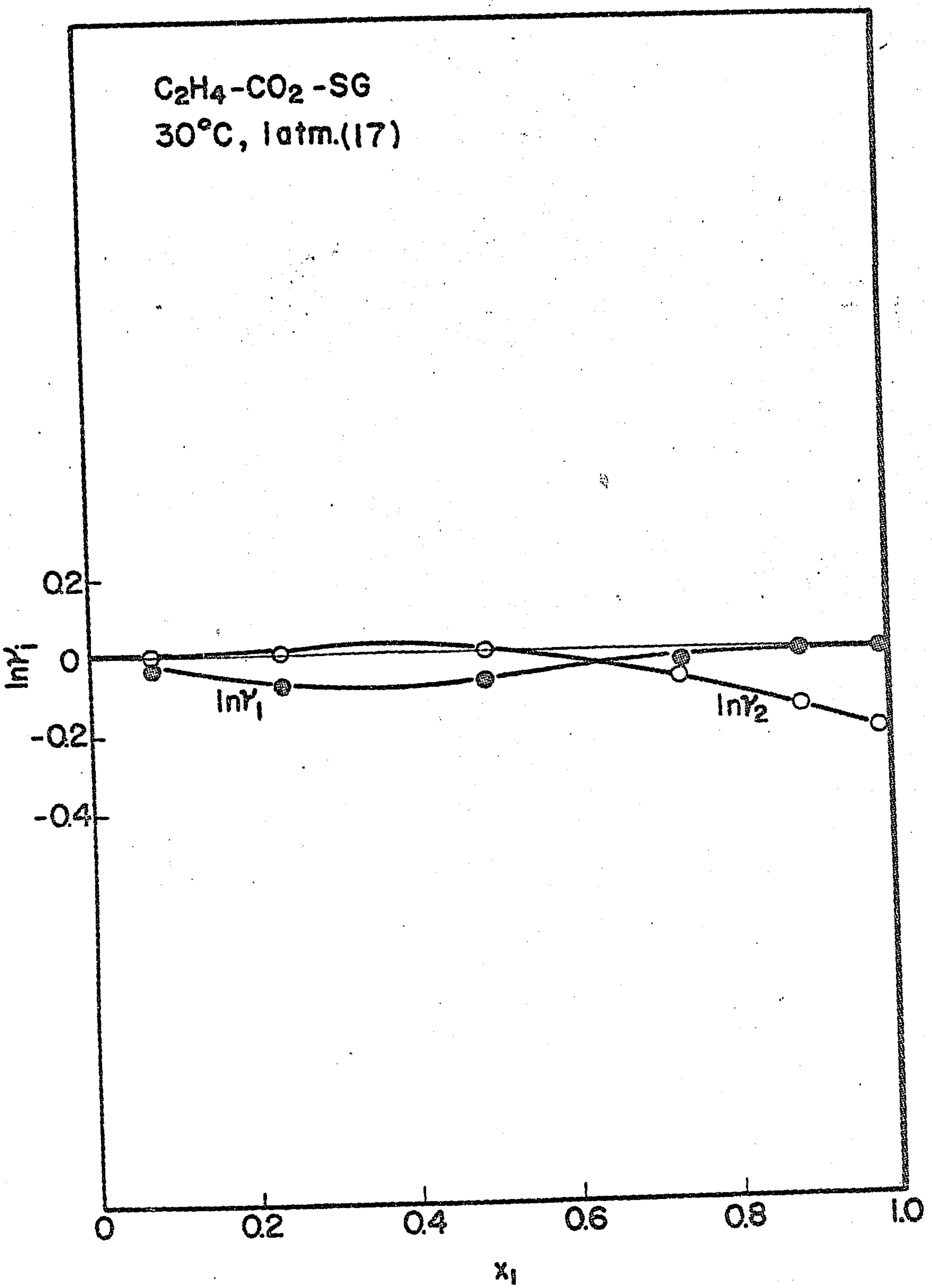


Figure 29 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (STOICHIOMETRIC METHOD (17))

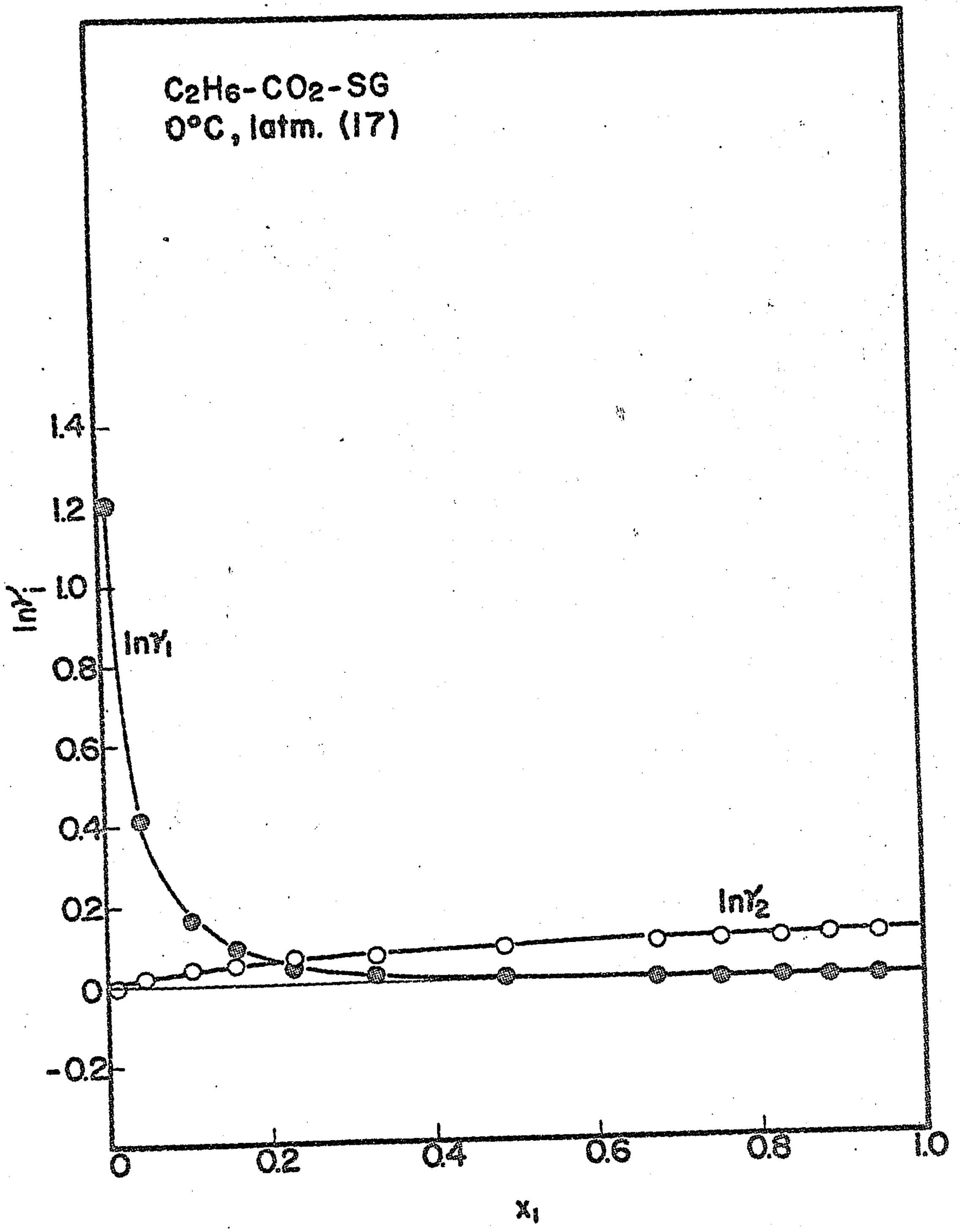


Figure 30 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (STOICHIOMETRIC METHOD (17))

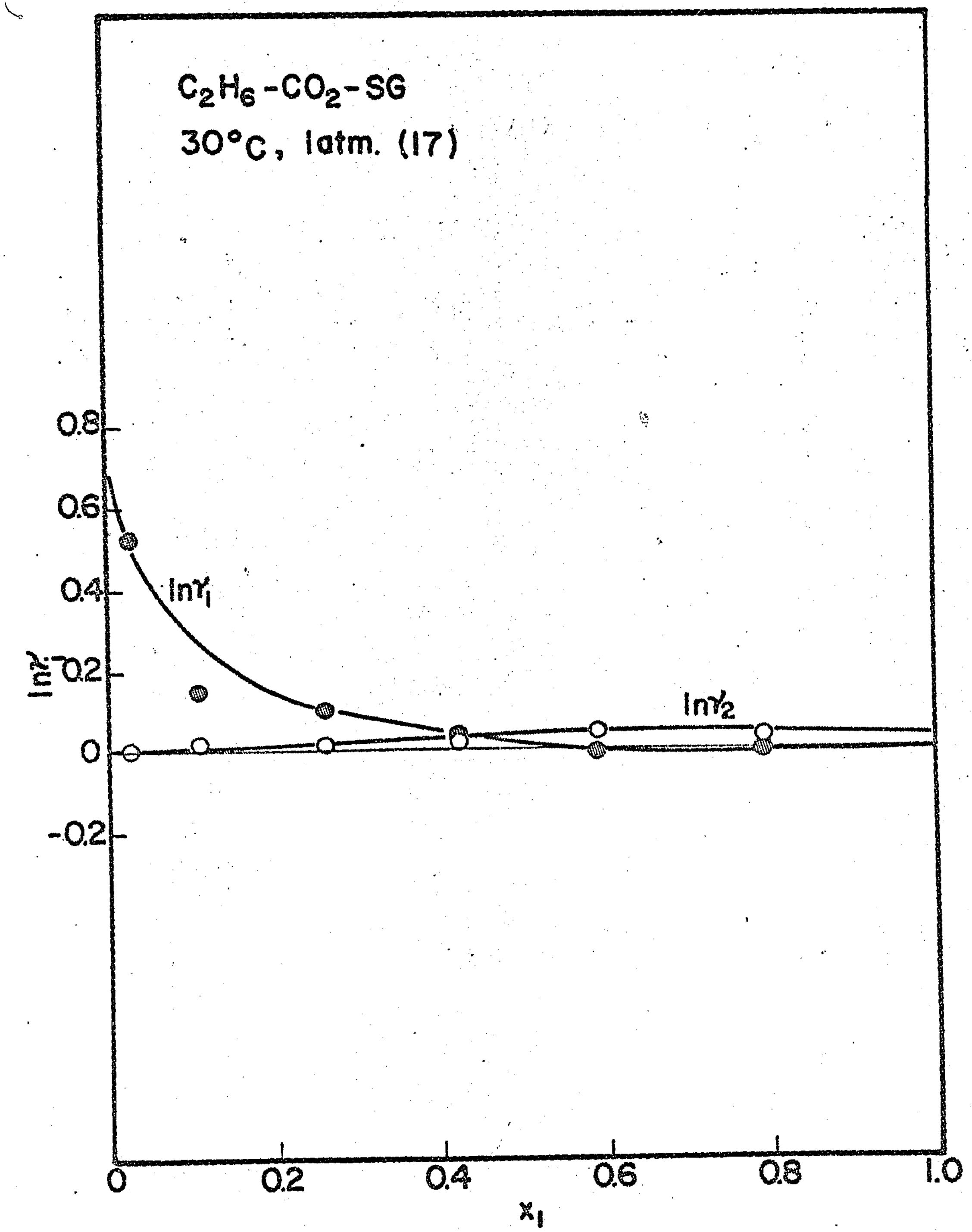


Figure 31 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (STOICHIOMETRIC METHOD (17))

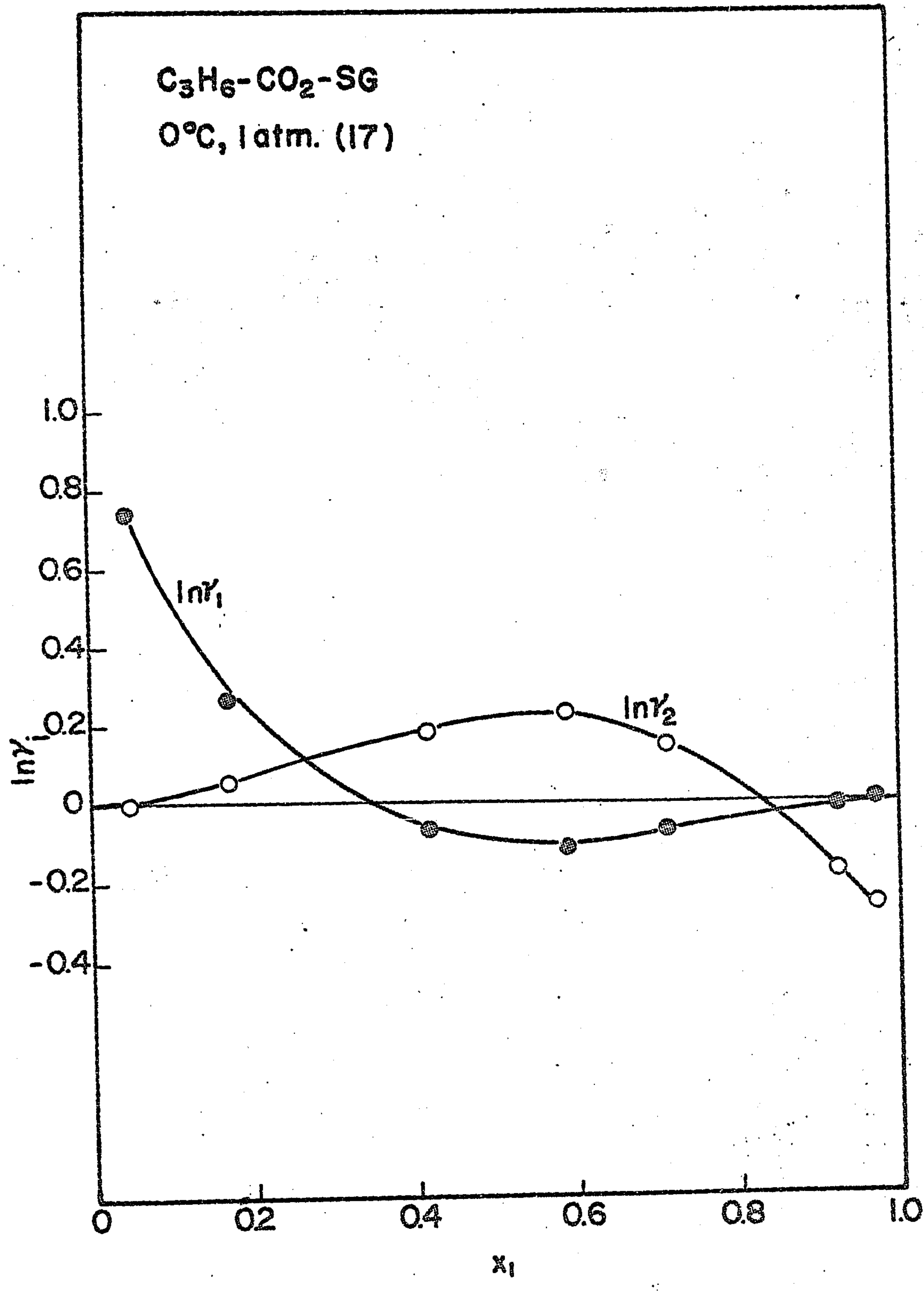


Figure 32 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (STOICHIOMETRIC METHOD (17))

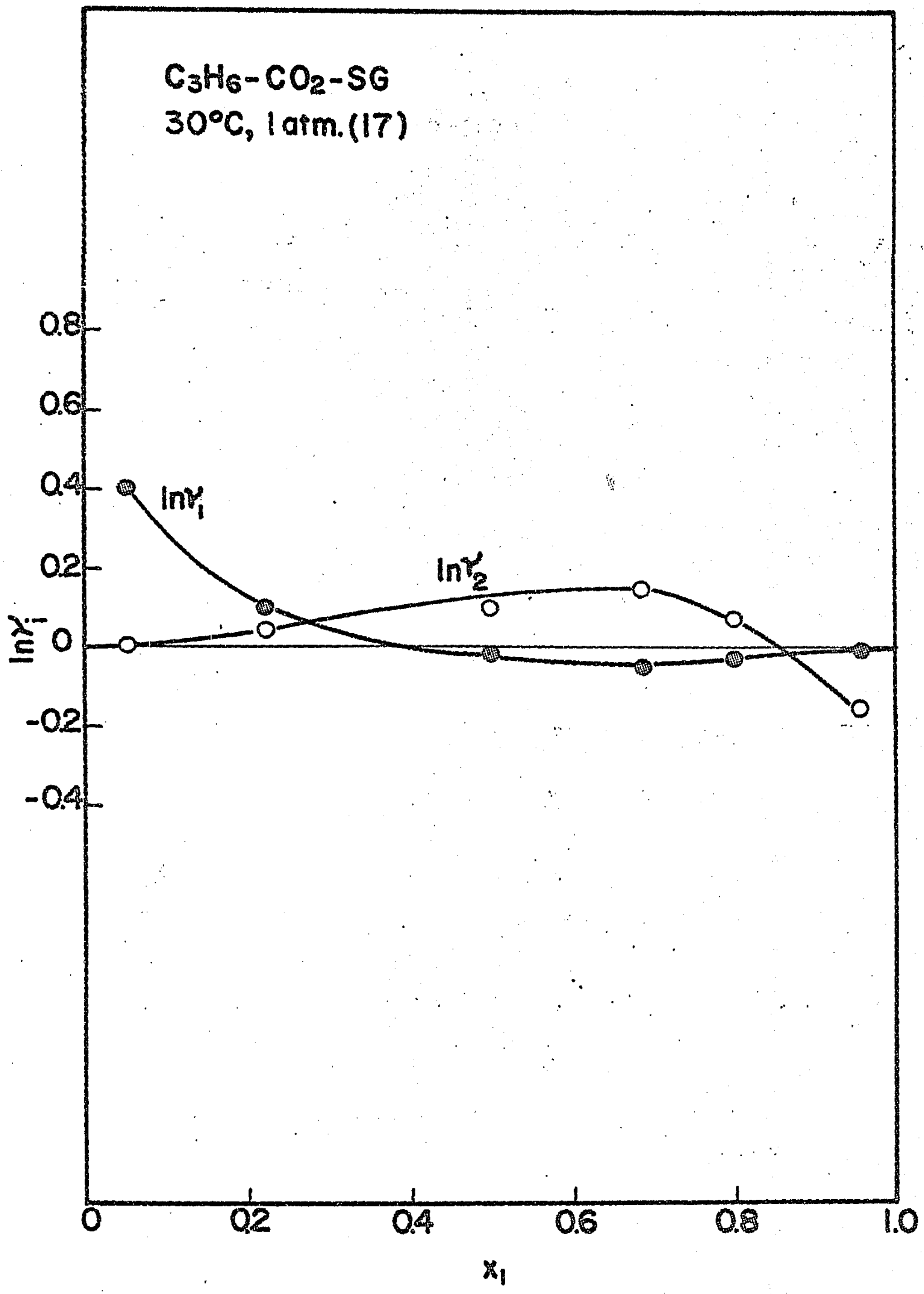


Figure 33 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (STOICHIOMETRIC METHOD (17))

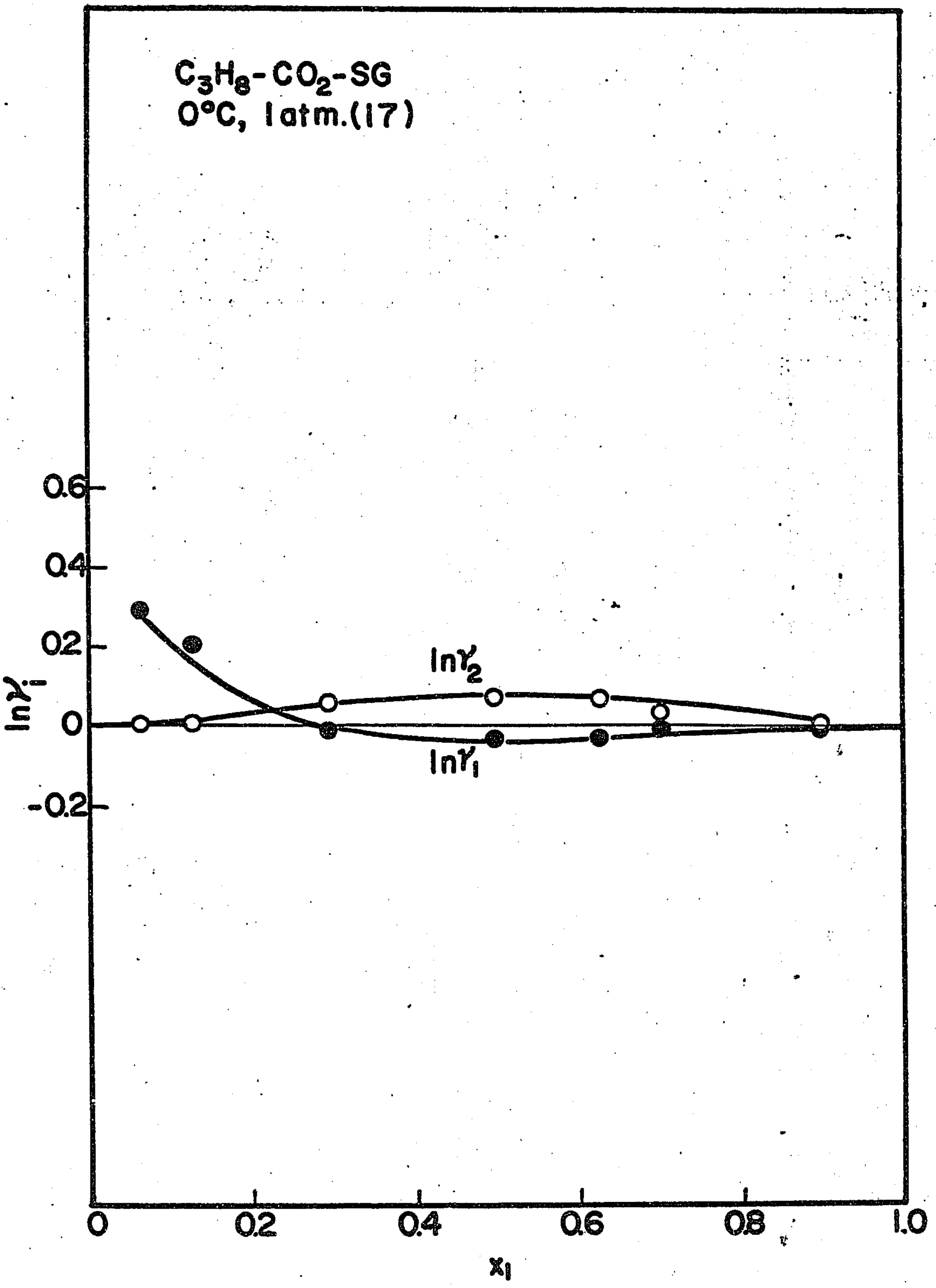


Figure 34 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (STOICHIOMETRIC METHOD (17))

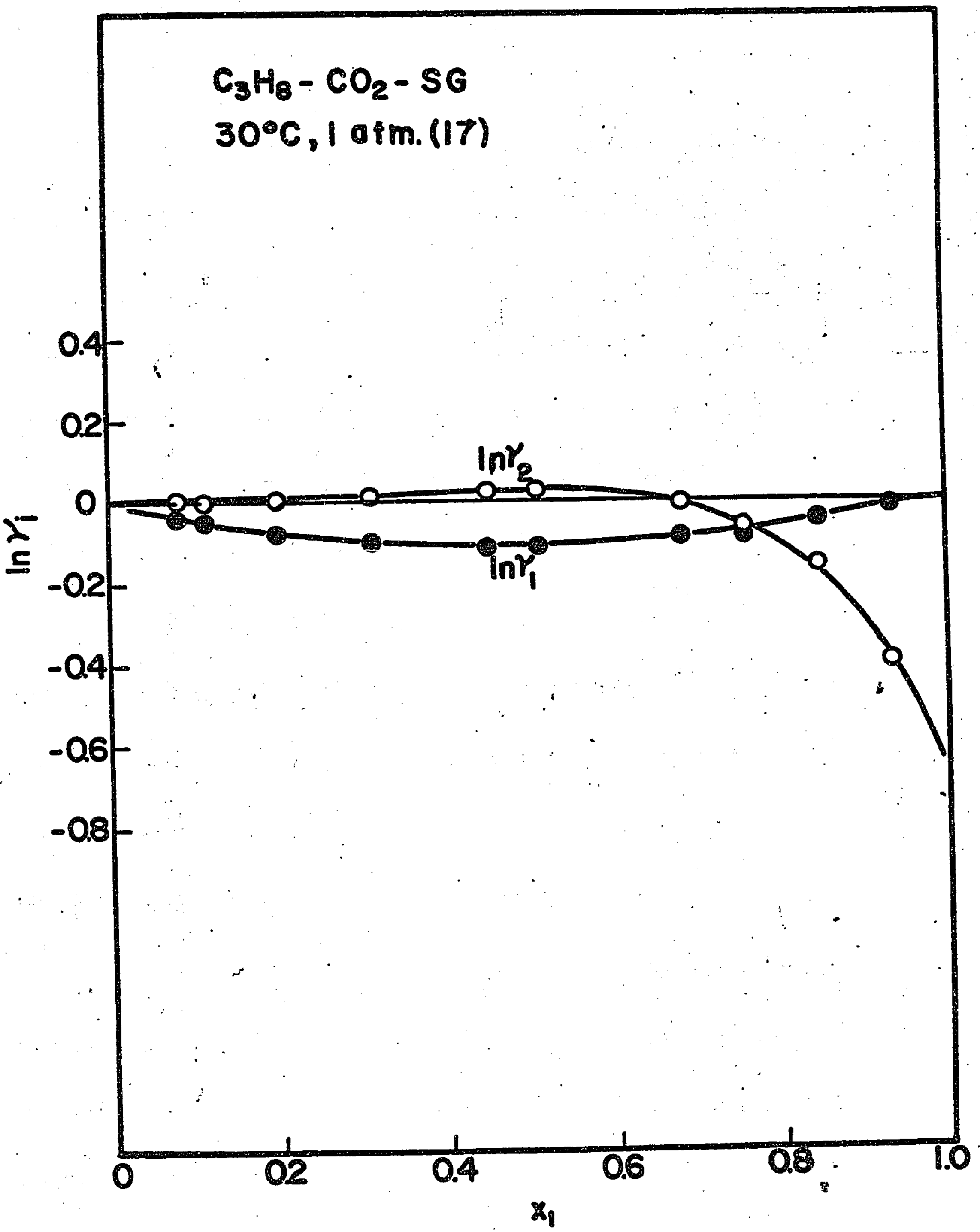


Figure 35 CALCULATION OF ADSORBED PHASE ACTIVITY COEFFICIENTS (STOICHIOMETRIC METHOD (17))

B. Discussion

The following conclusions can be drawn from the results of the above calculations:

(1) Very accurate equilibrium data are required for these calculations, and sometimes extrapolation is needed to construct the curve for graphical integration. Therefore, calculating errors are always involved during curve fittings, extrapolation and graphical integrations. The analysis of errors which is involved in the method of Myers and Prausnitz for calculating the adsorbed phase activity coefficients is discussed in Appendix D.

(2) From the results of the calculations, it is easily seen that the adsorbed phase activity coefficients of many systems are far from unity. Thus, the conclusion of Myers and Prausnitz, that the calculated activity coefficients were found to be equal to unity within the experimental error, needs to be modified.

(3) Examining the results of the method of Myers and Prausnitz, the values of adsorbed phase activity coefficients of many systems (see Figure 6 and Figures 9 - 14) are not consistent with the derived Gibbs-Duhem equation if the system is treated as a binary one (i.e. the third component - solid is not considered). The methods

generally employed for testing the thermodynamic consistency of binary vapour-liquid equilibrium data (28) might be used for this purpose. Among these methods, the visual test proposed by Lu (29) would be the simplest and quickest one. It may be seen, from a log γ vs. x plot, whether or not the data are thermodynamically consistent according to the Gibbs-Duhem equation for a binary system. The visual test method may be summarized as follows:

(a) At $x_1 = 0.5$

$$\log \gamma_1 \approx \frac{1}{4} (\log \gamma_2)_{x_1 = 1}$$

$$\log \gamma_2 \approx \frac{1}{4} (\log \gamma_1)_{x_1 = 0}$$

(b) $(\log \gamma_1)_{x_1 = 0.25} \approx (\log \gamma_2)_{x_1 = 0.75}$

(c) If $(\log \gamma_1)_{x_1 = 0} \gtreqless (\log \gamma_2)_{x_1 = 1}$

then $\log (\gamma_1)_{x_1 = 0.5} \lesseqgtr (\log \gamma_2)_{x_1 = 0.5}$

(d) Both log γ curves approach their zero values with a horizontal tangency

(e) The two areas bounded by the log γ curves and the $x_1 = 0$ and $x_1 = 1$ lines should be identical

(f) If there is a minimum or a maximum on one of the log γ curves, there should be a corresponding maximum or minimum on the other curve at the same composition.

(g) If there is no maximum or minimum, both log γ curves should be on the same side of the log $\gamma = 0$ line.

(h) At $x_1 = 0.5$, the slopes of the log γ curves should be equal but opposite in sign.

Obviously, the results shown in Figure 6 and Figures 9 - 14 do not satisfy the necessary conditions of the test listed above. There is no way of correlating the data since no common character could be found among these results. This difficulty may be due to the effect of the adsorbent.

(4) Although the results of Myers and Prausnitz's method are inconsistent with the Gibbs-Duhem equation when the system was treated as a binary one, they at least could provide information concerning the adsorbed phase behavior. It was found that using any value of γ on the smoothed $\ln \gamma_1$ vs. x_1 plot, one might calculate the gas phase compositions y_1 and y_2 corresponding to a given value of the adsorbed phase compositions x_1 and x_2 by means of Equation (19). For the system tested, an error of 25% with respect to the experimental value of y_1 was observed (see Appendix D).

(5) The stoichiometric relation (Equation (68)), which was used as a starting point for calculating the adsorbed phase activity coefficients by Jelinek, has a doubtful basis (ion-exchange). Since he did not point out whether his method is empirical or not, at total pressure π, the pure component adsorption amount n_1° and n_2° can no longer be used instead of n_1 and n_2, respectively. The Gibbs-Duhem equation was inserted already in the derivation of the method. Therefore, consistent results were to be expected. Furthermore, the values of γ's, calculated by stoichiometric method, cannot be used to calculate back the gas phase composition y from the given adsorbed phase composition x by means of Equation (19). Thus, the method cannot be employed to correlate and interpret the equilibrium data.

VI CONCLUSIONS AND RECOMMENDATIONS

The principal conclusions and recommendations included in the above discussion may be summarized as follows:

(1) The applications of classical solution thermodynamics to the mixed-gas adsorption have been extensively reviewed.

(2) Three recently proposed methods for predicting the binary equilibria are equivalent to each other provided that n_1° is equal to n_2° at the same spreading pressure.

(3) It was found that the residual term by which the three methods differ is of little significance for all systems tested. Therefore, the semi-empirical method of Cook and Basmadjian for predicting binary equilibria is equivalent to the ideal adsorbed solution method of Myers and Prausnitz, regardless of whether or not $(n_1^\circ)_\phi$ is equal to $(n_2^\circ)_\phi$.

(4) The adsorbed phase activity coefficients for eleven systems were investigated by Myers and Prausnitz's method, and the adsorbed phase activity coefficients for twenty-one systems were investigated by the so-called stoichiometric method proposed by Jelinek.

(5) The adsorbed phase activity coefficients of many systems are not even near unity. Thus, the conclusion made by Myers and Prausnitz, that the calculated activity coefficients were found to be

equal to unity within the experimental error, needs to be modified.

(6) The values of activity coefficients of many systems, calculated by Myers and Prausnitz's method, are not consistent with the derived Gibbs-Duhem equation when the system is treated as a binary one. There is no way of correlating the data since no common character could be found among these values. This handicap may be due to the different solid effect for different binary gas mixtures, since the adsorbent was assumed to be inert for this method.

(7) The effect of the type of solid on the adsorbed molecules is considerable. A correlation may be obtained if a number of systems, each of them measured on a different kind of adsorbent at the same temperature and pressure, are investigated. Further proof of the solid effect is needed for future work.

(8) The error inherent in the method of Myers and Prausnitz, for calculating the adsorbed phase activity coefficients, was estimated, for the system C_3H_6 - CO_2 - C, 0°C, 1 atm., to be about 25% with respect to the experimental value of y when the calculated γ's were used to calculate back the value of y corresponding to a given value of x by using Equation (19).

(9) The predicted result of binary equilibria, by means of the ideal adsorbed solution method of Myers et al., is also shown in Figure 40. It is easily seen that the value of y, calculated from $\ln \gamma_i$ vs. x_1 plot, is closer than that by the ideal adsorbed solution method.

(10) A doubtful stoichiometric relation was used as the starting point for calculating the adsorbed phase activity coefficients by the so-called stoichiometric method of Jelinek. Consistent curves of $\ln \gamma_1$ and $\ln \gamma_2$ were obtained but this is probably due to the fact that the Gibbs-Duhem equation was inserted already in the derivation. Furthermore, the values of γ's, calculated by this method, cannot be used to calculate back the gas phase composition from the given adsorbed phase composition by means of Equation (19). Thus, the method cannot be employed to correlate and interpret the equilibrium data.

(11) It is suggested that the future adsorption investigations include the study of solid effect as well as the vapour-liquid equilibria and P V T of gas mixtures.

Appendix A

Specific Molar Area Ratio of Adsorbates

Table 3

Specific Molar Area Ratio of Adsorbed Molecules

System	$\phi A/RT$	P_1°	P_2°	n_1°	n_2°	a_1°/a_2°
$C_2H_4 - CO_2 - C$ 0° C (17)	1	7.4	57.3	0.702	0.696	0.991
	2	22.3	153.0	1.157	1.348	1.165
	3	47.5	273.5	1.639	1.968	1.201
	5	122.5	610.0	2.390	3.279	1.372
$C_2H_6 - CO_2 - C$ 30° C (17)	1	4.9	181.0	0.730	0.753	1.032
	2	12.5	465.0	1.235	1.596	1.292
	3	25.7	758.0	1.520	2.282	1.501
$C_3H_6 - CO_2 - C$ 0° C (17)	2	5.2	153.0	1.640	1.348	0.822
	4	12.0	446.0	2.700	2.700	1.000
	6	21.5	810.0	3.042	3.108	1.022
$C_3H_8 - CO_2 - C$ 0° C (17)	1	2.0	57.3	1.160	0.696	0.600
	2	4.9	153.0	1.980	1.348	0.681
	3.	7.5	273.5	2.660	1.968	0.740
	5	15.0	610.0	3.053	3.279	1.074
$C_2H_6 - CO_2 - SG$ 0° C (17)	0.2	86.5	45.0	0.171	0.170	0.994
	0.6	318.0	160.0	0.523	0.498	0.952
	1.0	587.5	300.0	0.845	0.832	0.985
$C_3H_8 - CO_2 - SG$ 30° C (17)	0.2	47.5	144.7	0.141	0.187	1.326
	0.5	153.0	381.0	0.393	0.456	1.160
	0.8	275.0	639.8	0.632	0.732	1.158

Table 3 (Continued)

System	$\phi A/RT$	P_1°	P_2°	n_1°	n_2°	a_1°/a_2°
N_2 - Ar - SG 89.5° K (20)	100	24.8	17.3	74.6	73.4	0.984
	200	50.0	45.2	85.8	97.0	1.131
	300	98.4	115.0	98.7	127.4	1.291
	400	235.0	245.0	116.6	159.2	1.365
	500	525.0	448.0	135.9	184.1	1.355
N_2 - Ar - SG 111° K (20)	100	30.0	56.0	44.1	52.6	1.193
	200	145.0	240.0	73.8	89.8	1.217
	250	270.0	389.0	87.7	106.1	1.210
C_3H_8 - C_4H_{10} - C 20° C (8, 24)	50	7.7	3.8	27.3	31.5	1.154
	100	28.0	10.8	45.5	41.1	0.903
	200	150.0	74.9	73.1	69.5	0.951
	300	500.0	259.0	89.9	84.2	0.937
CH_4 - C_2H_6 - C 20° C (8, 24)	10	276.0	15.0	8.7	11.0	1.264
	30	1075.0	45.0	22.9	20.5	0.896
	50	2160.0	85.0	34.9	29.0	0.831
	70	3560.0	160.0	45.0	39.8	0.884
	90	5275.0	250.0	53.9	48.1	0.893
O_2 - CO - SG 0° C (3)	10	262.0	138.0	10.1	10.0	0.990
	20	527.0	276.0	19.8	19.5	0.985
	30	792.0	421.0	29.0	29.0	1.000
CH_4 - C_4H_{10} - C 20° C (8, 24)	50	2160.0	3.8	34.9	31.5	0.903
	100	6250.0	10.8	57.9	41.1	0.710

Table 3 (Continued)

System	ØA/RT	P_1°	P_2°	n_1°	n_2°	a_1°/a_2°
C_2H_4 - C_3H_6 - C 0° C (17)	2	22.3	5.2	1.157	1.640	1.417
	4	80.5	12.0	2.044	2.700	1.321
	6	175.3	21.5	2.743	3.042	1.109
C_2H_4 - C_3H_8 - C 0° C (17)	1	7.4	2.0	0.702	1.160	1.652
	2	22.3	4.9	1.157	1.980	1.711
	3	47.5	7.5	1.639	2.660	1.623
	5	122.5	15.0	2.390	3.053	1.277
C_2H_6 - C_4H_{10} - C 20° C (8, 24)	50	85.0	3.8	29.0	31.5	1.086
	70	160.0	5.0	39.8	34.4	0.864
	100	300.0	10.8	52.0	41.1	0.790
CH_4 - C_3H_8 - C 20° C (8, 24)	50	2160.0	7.7	34.9	27.3	0.782
	100	6250.0	28.0	57.9	45.5	0.786
C_2H_6 - C_3H_8 - C 20° C (8, 24)	50	85.0	7.7	29.0	27.3	0.941
	70	160.0	13.5	39.8	35.0	0.879
	100	300.0	28.0	52.0	45.5	0.875
CO_2 - C_3H_8 - C 20° C (8, 24)	1	62.0	10.0	0.73	0.83	1.138
	3	290.0	57.0	2.04	1.78	0.873
	5	619.0	142.0	3.31	2.53	0.765
	6	815.0	205.0	3.95	2.925	0.741

Appendix B

Calculation of Residue

Table 4

Calculation of Residue

System	Temperature	Spreading Pressure	Residue R	$\left[R/\int_0^{n_1^\circ} \ln\left(\frac{P_1^\circ}{P_2^\circ}\right) dn^\circ\right] x100\%$
CH_4 - C_2H_6 - C (8, 24)	20° C	18.3	0	0
C_2H_6 - CO_2 - SG (17)	0° C	1.245	0	0
O_2 - CO - SG (3)	0° C	28.9	0	0
H_2 - CO - C (23)	150° K	15.2	0	0
CO_2 - C_3H_8 - C (8, 24)	20° C	378.0	65	22.8
H_2 - N_2 - C (23)	77.4° K	364.0	-102.8	21.1
N_2 - CO - C (23)	130° K	414.0	-10.7	10.9

Appendix C

Calculation of Adsorbed Phase Activity Coefficients

Table 5

Calculation of Adsorbed Phase Activity Coefficients by the Method of Myers and Prausnitz (13)

System: Oxygen (1) and carbon monoxide (2) on silica gel at 0° C, π = 760 mm Hg (3)

y_1	y_2	x_1	x_2	$\frac{A\phi}{RT}$	P_1°	P_2°	γ_1	γ_2	$\ln\gamma_1$	$\ln\gamma_2$
0.3029	0.6971	0.1918	0.8082	46.3129	1225	657	0.9798	0.9976	-0.021	-0.002
0.5146	0.4854	0.3635	0.6365	41.4388	1095	587	0.9826	0.9874	-0.017	-0.012
0.7699	0.2301	0.6514	0.3486	35.5564	939	505	0.9566	0.9934	-0.044	-0.007

Table 6

Calculation of Adsorbed Phase Activity Coefficients
by the Method of Myers and Prausnitz (13)

System: Methane (1) and Ethane (2) on active carbon at 20° C, π = 750 mm Hg (8)

x_1	x_2	y_1	y_2	$\frac{A\phi}{RT}$	P_1°	P_2°	γ_1	γ_2	$\ln \gamma_1$	$\ln \gamma_2$
0.3952	0.6048	0.934	0.066	51.137	2230	92	0.8055	0.9015	-0.216	-0.103
0.3423	0.6577	0.917	0.083	55.542	2520	102	0.8137	0.9403	-0.205	-0.062
0.1480	0.8520	0.755	0.245	85.463	4850	230	0.7994	0.9502	-0.224	-0.051
0.1407	0.8593	0.749	0.251	86.733	4980	235	0.8124	0.9447	-0.208	-0.056
0.0593	0.9407	0.511	0.489	116.521	8050	400	0.8135	0.9877	-0.205	-0.012
0.0467	0.9533	0.481	0.519	119.700	8145	425	0.9611	0.9736	-0.039	-0.026
0.0251	0.9749	0.269	0.731	139.933	11000	570	0.7405	0.9998	-0.299	-0.001

Table 7

Calculation of Adsorbed Phase Activity Coefficients by the Method of Myers and Prausnitz (13)

System: Propane (1) - Butane (2) - Active Carbon at 20° C, 750 mm Hg (8)

y_1	y_2	x_1	x_2	$\frac{A\phi}{RT}$	P_1°	P_2°	γ_1	γ_2	$\ln\gamma_1$	$\ln\gamma_2$
0.495	0.505	0.263	0.737	398.278	1228.0	730.5	1.150	0.704	0.1398	-0.3509
0.628	0.372	0.339	0.661	397.018	1215.0	720.5	1.144	0.586	0.1310	-0.5344
0.725	0.275	0.437	0.563	395.833	1206.0	715.0	1.032	0.512	0.0295	-0.6694
0.816	0.184	0.527	0.473	394.516	1194.5	705.0	0.972	0.414	-0.0284	-0.8818
0.851	0.149	0.622	0.378	393.921	1190.0	700.0	0.862	0.422	-0.1485	-0.8627
0.917	0.083	0.735	0.265	392.787	1053.5	695.0	0.888	0.338	-0.1187	-1.0847
0.950	0.050	0.868	0.132	392.116	999.0	688.0	0.821	0.413	-0.1972	-0.8843

Table 8

Calculation of Adsorbed Phase Activity Coefficients by the Method of Myers and Prausnitz (13)

System: Nitrogen (1) - Argon (2) - Silica Gel at 89.5°K, 250 mm Hg (20)

y_1	y_2	x_1	x_2	$\frac{A\phi}{RT}$	P_1°	P_2°	γ_1	γ_2	$\ln \gamma_1$	$\ln \gamma_2$
0.030	0.970	0.063	0.937	413.605	263.5	266.0	0.452	0.973	-0.7941	-0.0274
0.081	0.919	0.132	0.868	420.554	279.0	279.0	0.550	0.949	-0.5978	-0.0524
0.179	0.821	0.226	0.774	428.185	298.0	293.0	0.664	0.905	-0.4095	-0.0998
0.243	0.757	0.287	0.713	431.365	304.0	297.5	0.696	0.892	-0.3620	-0.1143
0.494	0.506	0.501	0.499	436.288	317.5	307.7	0.776	0.824	-0.2536	-0.1936
0.894	0.106	0.867	0.133	429.493	300.5	294.5	0.858	0.677	-0.1532	-0.3901
0.940	0.060	0.922	0.078	427.583	297.1	291.3	0.858	0.660	-0.1532	-0.4155

Table 9

Calculation of Adsorbed Phase Activity Coefficients by the Method of Myers and Prausnitz (13)

System: Nitrogen (1) and Argon (2) on Silica Gel at 111°K, π = 250 mm Hg (20)

y_1	y_2	x_1	x_2	$\frac{A\phi}{RT}$	P_1°	P_2°	γ_1	γ_2	$\ln \gamma_1$	$\ln \gamma_2$
0.1	0.9	0.19	0.81	214.60	174	278	0.756	0.999	-0.279	-0.001
0.2	0.8	0.31	0.69	222.34	183	300	0.881	0.966	-0.126	-0.034
0.3	0.7	0.41	0.59	230.54	215	325	0.851	0.913	-0.161	-0.091
0.4	0.6	0.50	0.50	236.14	230	342	0.870	0.877	-0.139	-0.131
0.5	0.5	0.586	0.414	240.24	240	355	0.889	0.851	-0.117	-0.161
0.6	0.4	0.67	0.33	243.14	248	367	0.903	0.826	-0.102	-0.191
0.7	0.3	0.759	0.241	245.54	252	378	0.915	0.823	-0.088	-0.194
0.8	0.2	0.841	0.159	247.64	256	385	0.929	0.817	-0.073	-0.202
0.9	0.1	0.922	0.078	249.54	258	396	0.946	0.820	-0.055	-0.198

Table 10

Calculation of Adsorbed Phase Activity Coefficients by the Method of Myers and Prausnitz (13)

System: Ethylene (1) - Carbon Dioxide (2) - Col. "G" Carbon at 0°C, 1 atm (17)

y_1	y_2	x_1	x_2	$\frac{\phi A}{RT}$	P_1°	P_2°	γ_1	γ_2	$\ln \gamma_1$	$\ln \gamma_2$
0.0719	0.9281	0.0439	0.9561	5.541	149.0	719.0	8.354	1.026	2.1223	0.0295
0.1427	0.8573	0.1799	0.8201	5.537	148.7	714.5	4.054	1.112	1.3987	0.1043
0.4156	0.5844	0.5913	0.4087	6.439	203.0	945.0	2.631	1.150	0.9670	0.1397
0.7165	0.2835	0.8390	0.1610	7.292	262.8	1230.0	2.470	1.088	0.9042	0.0861
0.8749	0.1251	0.9255	0.0745	7.670	293.8	1235.0	2.445	1.040	0.8920	0.0392

Table 11

Calculation of Adsorbed Phase Activity Coefficients by the Method of Myers and Prausnitz (13)

System: Ethane (1) - Carbon Dioxide (2) - Col. "G" Carbon at 30° C, 1 atm (17)

y_1	y_2	x_1	x_2	$\frac{\phi A}{RT}$	P°_1	P°_2	γ_1	γ_2	$\ln \gamma_1$	$\ln \gamma_2$
0.1	0.9	0.36	0.64	3.702	40	974	5.277	1.097	1.661	0.0925
0.2	0.8	0.57	0.43	4.403	58	1180	4.597	1.198	1.523	0.1807
0.3	0.7	0.70	0.30	5.020	80	1355	4.071	1.308	1.404	0.2682
0.4	0.6	0.79	0.21	5.583	100	1500	3.848	1.445	1.348	0.3680
0.5	0.5	0.85	0.15	6.091	126	1655	3.548	1.530	1.265	0.4250
0.6	0.4	0.885	0.115	6.536	149	1771	3.457	1.492	1.240	0.4000
0.7	0.3	0.92	0.08	6.914	173	1877	3.342	1.518	1.205	0.4176
0.8	0.2	0.95	0.05	7.221	196	1961	3.265	1.550	1.182	0.4382
0.9	0.1	0.974	0.026	7.454	211	2019	3.328	1.447	1.201	0.3679

Table 12

Calculation of Adsorbed Phase Activity Coefficients by the Method of Myers and Prausnitz (13)

System: Propylene (1) and Carbon Dioxide (2) on Col. "G" Carbon at 0°C, π = atm (17)

y_1	y_2	x_1	x_2	$\frac{A\phi}{RT}$	P_1°	P_2°	γ_1	γ_2	$\ln \gamma_1$	$\ln \gamma_2$
0.1	0.9	0.413	0.587	6.514	25	906	7.361	1.290	1.996	0.255
0.2	0.8	0.705	0.295	7.746	36.5	1138	5.912	1.813	1.777	0.593
0.3	0.7	0.881	0.119	9.286	55.5	1424	4.661	3.141	1.539	1.144
0.4	0.6	0.945	0.055	11.016	80	1745	4.024	4.752	1.391	1.558
0.5	0.5	0.965	0.035	12.870	130	2087	3.030	5.204	1.109	1.649
0.6	0.4	0.979	0.021	14.796	191	2436	2.440	5.941	0.892	1.782

Table 13

Calculation of Adsorbed Phase Activity Coefficients by the Method of Myers and Prausnitz (13)

System: Propane (1) - Carbon Dioxide (2) - Col. "G" Carbon at 0°C, 1 atm (17)

y_1	y_2	x_1	x_2	$\frac{\phi A}{RT}$	P_1°	P_2°	γ_1	γ_2	$\ln\gamma_1$	$\ln\gamma_2$
0.0284	0.9716	0.0920	0.9080	5.814	19.5	780	12.031	1.043	2.4849	0.0392
0.0486	0.9514	0.2158	0.7842	6.068	20.7	844.3	8.269	1.092	2.1126	0.0862
0.1189	0.8811	0.5409	0.4591	7.167	27.0	1175.0	6.188	1.241	1.8229	0.2151
0.2253	0.7747	0.7266	0.2734	8.690						
0.4024	0.5976	0.8653	0.1347	10.647		(too far to extrapolate)				
0.4902	0.5098	0.9097	0.0903	11.439						
0.6500	0.3500	0.9489	0.0511	12.633						

Table 14

Calculation of Adsorbed Phase Activity Coefficients by the Method of Myers and Prausnitz (13)

System: Ethane (1) and Carbon Dioxide (2) on Silica Gel at 0°C, π = 1 atm (17)

y_1	y_2	x_1	x_2	$\frac{\phi A}{RT}$	P°_1	P°_2	γ_1	γ_2	$\ln \gamma_1$	$\ln \gamma_2$
0.1	0.9	0.076	0.924	2.0015	1387	698	0.721	1.061	-0.3271	0.0582
0.2	0.8	0.155	0.845	1.9238	1322	665	0.742	1.081	-0.2984	0.0770
0.3	0.7	0.235	0.765	1.8733	1277	644	0.760	1.080	-0.2744	0.0769
0.4	0.6	0.320	0.680	1.8288	1240	624	0.766	1.075	-0.2665	0.0681
0.5	0.5	0.416	0.584	1.7888	1206	608	0.757	1.070	-0.2783	0.0676
0.6	0.4	0.525	0.475	1.7528	1173	593	0.741	1.079	-0.2997	0.0768
0.7	0.3	0.649	0.351	1.7253	1152	582	0.712	1.116	-0.3396	0.0190
0.8	0.2	0.771	0.229	1.6968	1128	570	0.699	1.165	-0.3581	0.1489
0.9	0.1	0.880	0.119	1.6718	1108	559	0.702	1.143	-0.3538	0.1310

Table 15

Calculation of Adsorbed Phase Activity Coefficients by the Method of Myers and Prausnitz (13)

System: Propane (1) and Carbon Dioxide (2) on Silica Gel at 30°C, π = 1 atm (17)

y_1	y_2	x_1	x_2	$\frac{\phi A}{RT}$	P_1°	P_2°	γ_1	γ_2	$\ln \gamma_1$	$\ln \gamma_2$
0.1	0.9	0.14	0.86	0.9756	351.0	766.0	1.547	1.038	0.4382	0.0380
0.2	0.8	0.28	0.72	1.0208	374.0	835.0	1.451	1.011	0.3715	0.0099
0.3	0.7	0.41	0.59	1.0745	396.0	875.0	1.404	1.031	0.3368	0.0295
0.4	0.6	0.53	0.47	1.1335	424.0	925.0	1.353	1.049	0.3031	0.0487
0.5	0.5	0.62	0.38	1.1947	454.0	977.0	1.350	1.024	0.3001	0.0248
0.6	0.4	0.71	0.29	1.2560	485.0	1029.0	1.324	1.019	0.2776	0.0196
0.7	0.3	0.78	0.22	1.3142	515.0	1079.0	1.324	0.960	0.2776	-0.0408
0.8	0.2	0.86	0.14	1.3642	540.0	1120.0	1.309	0.969	0.2700	-0.0314
0.9	0.1	0.93	0.07	1.3967	555.0	1146.0	1.325	0.947	0.2800	-0.0544

Table 16

Calculation of Adsorbed Phase Activity Coefficients

by Stoichiometric Method (17)

System: Oxygen (1) - Carbon Monoxide (2) - Silica Gel at 0° C, 1 atm (3)

(n_1° = 1.2513 n_2° = 2.1826 mg. mols/gm)

x_1	y_1	$\ln\overline{K}$	Z	$\int_0^Z \ln\overline{K}\,dZ$	$\int_Z^1 \ln\overline{K}\,dZ$	$\ln\gamma_1$	$\ln\gamma_2$
0.1918	0.3029	-0.8945	0.2927	-0.2147	-0.7493	-0.0932	-0.0216
0.3635	0.5146	-1.0265	0.4990	-0.4121	-0.5510	-0.0301	-0.0459
0.6514	0.7699	-1.1087	0.7652	-0.7034	-0.2606	-0.0002	-0.0664

$$\ln K = \int_0^1 \ln\overline{K}\,dZ = -0.9640$$

Table 17

Calculation of Adsorbed Phase Activity Coefficients by Stoichiometric Method (17)

System: Methane (1) - Ethane (2) - Active Carbon at 20°C, 750 mm Hg (8)

(n_1° = 0.8103 n_2° = 3.3103 mg-mols/gm)

x_1	y_1	$\ln \overline{K}$	Z	$\int_0^Z \ln \overline{K}\, dZ$	$\int_Z^1 \ln \overline{K}\, dZ$	$\ln \gamma_1$	$\ln \gamma_2$
0.0251	0.269	-2.8750	0.0952	-0.2285	-5.9688	-4.1558	-0.0137
0.0593	0.511	-3.9660	0.2048	-0.6008	-5.5965	-3.0145	-0.0639
0.1407	0.749	-5.6000	0.4008	-1.5474	-4.6499	-1.5974	-0.2106
0.3423	0.917	-7.6505	0.6801	-3.3981	-2.7992	-0.4342	-0.5453

$$\ln K = \int_0^1 \ln \overline{K}\, dZ = -6.1973$$

Table 18

Calculation of Adsorbed Phase Activity Coefficients by Stoichiometric Method (17)

System: Propane (1) and Butane (2) on Active Carbon at 20° C, π = 750 mm Hg (8)

(n_1° = 4.240 n_2° = 3.951 mg-mols/gm)

x_1	y_1	$\ln \overline{K}$	Z	$\int_0^Z \ln \overline{K} \, dZ$	$\int_Z^1 \ln \overline{K} \, dZ$	$\ln \gamma_1$	$\ln \gamma_2$
0.263	0.495	-4.7978	0.2495	-1.1103	-3.7824	-0.0428	-0.0220
0.339	0.628	-4.8849	0.3233	-1.4847	-3.4080	-0.0106	-0.0309
0.437	0.725	-4.9718	0.4197	-1.9657	-2.9270	+0.0104	-0.0464
0.527	0.816	-5.5838	0.5093	-2.4349	-2.4578	+0.0279	-0.0605
0.622	0.851	-5.0063	0.6052	-2.9564	-1.9363	+0.0387	-0.0666
0.735	0.917	-5.5239	0.7210	-3.5820	-1.3107	+0.0370	-0.0533
0.868	0.950	-4.2176	0.8597	-4.2789	-0.6138	+0.0134	-0.0429

$$\ln K = \int_0^1 \ln \overline{K} \, dZ = -4.8927$$

Table 19

Calculation of Adsorbed Phase Activity Coefficients by Stoichiometric Method (17)

System: Nitrogen (1) and Argon (2) on Silica Gel at 89.5°K, π = 250 mm Hg (20)

(n_1° = 5.268 n_2° = 7.143 mg-mols/gm)

x_1	y_1	$\ln \overline{K}$	Z	$\int_0^Z \ln \overline{K}\, dZ$	$\int_Z^1 \ln \overline{K}\, dZ$	$\ln \gamma_1$	$\ln \gamma_1$
0.063	0.030	4.1554	0.0835	0.4026	0.3127	-0.6635	-0.0078
0.132	0.081	2.9803	0.1710	0.7205	-0.0052	-0.4699	-0.0295
0.226	0.179	1.8000	0.2836	0.9841	-0.2688	-0.2958	-0.0663
0.287	0.243	1.2350	0.3531	1.0897	-0.3744	-0.2227	-0.0915
0.501	0.494	-0.1400	0.5765	1.2061	-0.4908	-0.0819	-0.1802
0.867	0.894	-1.6400	0.8984	0.9076	-0.1923	-0.0049	-0.3333
0.922	0.940	-1.8200	0.9413	0.8281	-0.1128	-0.0011	-0.3558

$$\ln K = \int_0^1 \ln \overline{K}\, dZ = 0.7153$$

Table 20

Calculation of Adsorbed Phase Activity Coefficients by Stoichiometric Method (17)

System: Nitrogen (1) and Argon (2) on Silica Gel at 111°K, π = 250 mm Hg (20)

($n_1^\circ = 3.83$ $n_2^\circ = 4.07$ mg-mols/gm)

x_1	y_1	$\ln \overline{K}$	Z	$\int_0^Z \ln \overline{K} \, dZ$	$\int_Z^1 \ln \overline{K} \, dZ$	$\ln \gamma_1$	$\ln \gamma_2$
0.097	0.047	2.994	0.102	0.397	1.501	-0.310	-0.0226
0.183	0.093	3.025	0.192	0.672	1.226	-0.318	-0.0224
0.593	0.517	1.222	0.607	1.421	0.477	-0.00865	-0.167
0.748	0.680	1.335	0.759	1.611	0.287	-0.00914	-0.147
0.927	0.905	1.162	0.931	1.817	0.081	0.000183	-0.171

$$\ln K = \int_0^1 \ln \overline{K} \, dZ = 1.898$$

Table 21

Calculation of Adsorbed Phase Activity Coefficients by Stoichiometric Method (17)

System: Ethylene (1) and Carbon Dioxide (2) on Col. "G" Carbon at 0° C, π = 1 atm (17)

(n_1° = 4.78 n_2° = 3.78 mg-mols/gm)

x_1	y_1	$\ln \overline{K}$	Z	$\int_0^Z \ln \overline{K} \, d Z$	$\int_Z^1 \ln \overline{K} \, d Z$	$\ln \gamma_1$	$\ln \gamma_2$
0.04	0.064	-2.3046	0.0319	-0.1062	2.2526	0.9371	0.0087
0.08	0.093	-0.7736	0.0643	-0.1539	2.3003	0.6327	0.0276
0.11	0.110	0	0.0890	-0.1642	2.3106	0.4834	0.0436
0.15	0.130	0.7717	0.1225	-0.1514	2.2978	0.3390	0.0652
0.20	0.156	1.3900	0.1651	-0.1063	2.2527	0.2285	0.0891
0.40	0.264	2.7584	0.3452	+0.2937	1.8527	0.0097	0.1747
0.60	0.429	2.9490	0.5426	+0.8778	1.2686	-0.0168	0.1916
0.80	0.667	2.7960	0.7598	+1.5014	0.6450	-0.0057	0.1653
0.90	0.819	2.6935	0.8768	+1.8270	0.3194	-0.0026	0.1419
0.95	0.905	2.6582	0.9376	+1.9885	0.1579	-0.0017	0.1337

$$\ln K = \int_0^1 \ln \overline{K} \, d Z = +2.1464$$

Table 22

Calculation of Adsorbed Phase Activity Coefficients by Stoichiometric Method (17)

System: Ethylene (1) - Carbon Dioxide (2) - Col. "G" Carbon at 30°C, 1 atm (17)

($n_1^\circ = 3.46$ $n_2^\circ = 2.29$ mg-mols/gm)

x_1	y_1	$\ln \overline{K}$	Z	$\int_0^Z \ln \overline{K}\, dZ$	$\int_Z^1 \ln \overline{K}\, dZ$	$\ln \gamma_1$	$\ln \gamma_2$
0.0427	0.0510	-0.6352	0.0287	-0.0364	1.8379	0.7095	0.0079
0.2364	0.1451	1.8250	0.1700	0.1151	1.6864	0.0496	0.0852
0.4641	0.3134	2.5000	0.3643	0.5454	1.2561	-0.0963	0.1595
0.6503	0.4230	2.6327	0.5517	1.0324	0.7691	-0.1188	0.1835
0.7820	0.6055	2.2399	0.7036	1.4100	0.3915	-0.0787	0.0725
0.8408	0.7150	1.8934	0.7777	1.5585	0.2430	-0.0514	-0.0376
0.9175	0.8709	1.1992	0.8804	1.7197	0.0818	-0.0178	-0.2899

$$\ln K = \int_0^1 \ln \overline{K}\, dZ = 1.8015$$

Table 23

Calculation of Adsorbed Phase Activity Coefficients

by Stoichiometric Method (17)

System: Ethane (1) - Carbon Dioxide (2) - Col. "G" Carbon at 0°C, 1 atm (17)

(n_1° = 4.95 n_2° = 3.77 mg-mols/gm)

x_1	y_1	$\ln \overline{K}$	Z	$\int_0^Z \ln \overline{K} \, dZ$	$\int_Z^1 \ln \overline{K} \, dZ$	$\ln \gamma_1$	$\ln \gamma_2$
0.0304	0.0313	-0.1493	0.0233	-0.0303	4.1909	0.8760	0.0071
0.0745	0.0528	1.7867	0.0578	0.0076	4.1530	0.4989	0.0254
0.2970	0.1358	4.3980	0.2434	0.6227	3.5379	0.0425	0.1188
0.5446	0.2563	5.5746	0.4766	1.8112	2.3494	-0.1148	0.2243
0.7333	0.4389	5.3354	0.6768	2.9112	1.2494	-0.0960	0.1857
0.8720	0.6767	4.3800	0.8384	3.7082	0.4524	-0.0516	-0.0096
0.9620	0.9407	2.0900	0.9507	4.1021	0.0585	-0.0090	-0.5611

$$\ln K = \int_0^1 \ln \overline{K} \, dZ = 4.1606$$

Table 24

Calculation of Adsorbed Phase Activity Coefficients

by Stoichiometric Method (17)

System: Ethane (1) - Carbon Dioxide (2) - Col. "G" Carbon at 30° C, 1 atm (17)

(n_1° = 4.035 n_2° = 2.285 mg-mols/gm)

x_1	y_1	$\ln \overline{K}$	Z	$\int_0^Z \ln \overline{K} \, dZ$	$\int_Z^1 \ln \overline{K} \, dZ$	$\ln \gamma_1$	$\ln \gamma_2$
0.0477	0.0178	3.8474	0.028	0.0817	4.6431	0.224	0.0114
0.1022	0.0274	5.4881	0.061	0.2357	4.4891	-0.164	0.0448
0.1846	0.0419	6.3521	0.114	0.5901	4.1347	-0.373	0.0590
0.3046	0.0781	6.1364	0.199	1.1211	3.6037	-0.325	0.0439
0.5289	0.1813	5.5828	0.389	2.2661	2.4587	-0.237	-0.0426
0.6576	0.2616	5.4764	0.521	3.0021	1.7227	-0.224	-0.0659
0.8176	0.4399	5.0675	0.717	3.9595	0.7653	-0.166	-0.1430
0.9332	0.8730	1.7382	0.888	4.5696	0.1552	-0.00972	-1.324
0.9742	0.9553	1.3362	0.955	4.6936	0.0312	-0.00716	-1.493

$$\ln K = \int_0^1 \ln \overline{K} \, dZ = 4.7248$$

Table 25

Calculation of Adsorbed Phase Activity Coefficients
by Stoichiometric Method (17)

System: Propylene (1) and Carbon dioxide (2) on Col. "G" Carbon at 0°C, $\pi = 1$ atm (17)

($n_1^\circ = 6.17 \quad n_2^\circ = 3.78$ mg-mols/gm)

x_1	y_1	$\ln \overline{K}$	Z	$\int_0^Z \ln \overline{K} \, dZ$	$\int_Z^1 \ln \overline{K} \, dZ$	$\ln \gamma_1$	$\ln \gamma_2$
0.0611	0.0242	5.8602	0.0382	0.211	10.440	0.777	0.00345
0.2973	0.0917	8.2246	0.2054	1.400	9.251	0.439	0.0765
0.5008	0.1393	9.9484	0.3800	2.987	7.664	0.244	0.2075
0.6418	0.1847	10.7893	0.5226	4.494	6.157	0.132	0.359
0.7994	0.2308	12.7319	0.7089	6.710	3.941	0.0446	0.591
0.8673	0.2854	13.2052	0.7997	7.881	2.770	0.0204	0.711
0.8933	0.3166	13.4014	0.8365	8.371	2.280	0.0134	0.752
0.9231	0.3452	14.1434	0.8800	8.961	1.690	0.0067	0.829

$$\ln K = \int_0^1 \ln \overline{K} \, dZ = 10.651$$

Table 26

Calculation of Adsorbed Phase Activity Coefficients by Stoichiometric Method (17)

System: Propylene (1) - Carbon Dioxide (2) - Col. "G" Carbon at 30° C, 1 atm (17)

($n_1^\circ = 5.06$ $n_2^\circ = 2.29$ mg-mols/gm)

x_1	y_1	$\ln \overline{K}$	Z	$\int_0^Z \ln \overline{K}\, dZ$	$\int_Z^1 \ln \overline{K}\, dZ$	$\ln \gamma_1$	$\ln \gamma_2$
0.0968	0.0362	5.1249	0.0463	0.2136	6.5866	0.3359	0.0103
0.2701	0.0925	5.9206	0.1434	0.7545	6.0457	0.1926	0.0413
0.4253	0.1325	6.8452	0.2509	1.4999	5.3003	0.0341	0.0950
0.6285	0.1660	8.5817	0.4336	2.9884	3.8118	-0.2074	0.3199
0.8502	0.3592	7.6799	0.7198	5.3557	1.4445	-0.1398	0.0752
0.9401	0.6811	5.4591	0.8766	6.4102	0.3900	-0.0561	-0.7096
0.9720	0.9074	3.0814	0.9401	6.6875	0.1127	-0.0142	-1.6554

$$\ln K = \int_0^1 \ln \overline{K}\, dZ = 6.8002$$

Table 27

Calculation of Adsorbed Phase Activity Coefficients
by Stoichiometric Method (17)

System: Propane (1) and Carbon Dioxide (2) on Col. "G" Carbon at 0° C, π = 1 atm (17)

($n_1^\circ = 4.99$ $n_2^\circ = 3.77$ mg-mols/gm)

x_1	y_1	$\ln \overline{K}$	Z	$\int_0^Z \ln \overline{K} \, dZ$	$\int_Z^1 \ln \overline{K} \, dZ$	$\ln \gamma_1$	$\ln \gamma_2$
0.0374	0.0181	3.6859	0.0285	0.0697	8.8211	1.0502	0.0094
0.0920	0.0284	6.1205	0.0711	0.3030	8.5878	0.5817	0.0351
0.2158	0.0488	8.1417	0.1721	1.0363	7.8545	0.2232	0.0968
0.5409	0.1189	10.0195	0.4709	3.8605	5.0303	-0.0543	0.2275
0.7266	0.2253	9.7703	0.6675	5.7726	3.1182	-0.0261	0.1987
0.8653	0.4024	9.4343	0.8292	7.3211	1.5697	-0.0084	0.1331
0.9489	0.6500	9.1424	0.9335	8.2999	0.5909	-0.0034	0.0622

$$\ln K = \int_0^1 \ln \overline{K} \, dZ = 8.8908$$

Table 28

Calculation of Adsorbed Phase Activity Coefficients by Stoichiometric Method (17)

System: Propane (1) - Carbon Dioxide (2) - Col. "G" Carbon at 30° C, 1 atm (17)

($n_1^\circ = 4.34$ $n_2^\circ = 2.29$ mg-mols/gm)

x_1	y_1	$\ln \overline{K}$	Z	$\int_0^Z \ln \overline{K} d Z$	$\int_Z^1 \ln \overline{K} d Z$	$\ln \gamma_1$	$\ln \gamma_2$
0.0604	0.0108	7.01	0.0328	0.1999	8.5112	0.3988	0.0131
0.3233	0.0359	10.27	0.2013	1.7620	6.9491	-0.2888	0.1334
0.5961	0.1109	10.10	0.4378	4.1868	4.5243	-0.2659	0.1026
0.8414	0.3341	8.05	0.7368	6.9141	1.7970	-0.0741	-0.4292
0.9042	0.4890	7.14	0.8328	7.6571	1.0540	-0.0322	-0.7472
0.9567	0.5550	6.23	0.9210	8.2632	0.4479	-0.0102	-1.1033

$$\ln K = \int_0^1 \ln \overline{K} d Z = 8.7111$$

Table 29

Calculation of Adsorbed Phase Activity Coefficients
by Stoichiometric Method (17)

System: Ethylene (1) - Carbon Dioxide (2) - Silica Gel at 0°C, 1 atm (17)

(n_1° = 1.62 n_2° = 1.72 mg-mols/gm)

x_1	y_1	$\ln \overline{K}$	Z	$\int_0^Z \ln \overline{K} d Z$	$\int_Z^1 \ln \overline{K} d Z$	$\ln \gamma_1$	$\ln \gamma_2$
0.0258	0.0599	-1.4259	0.0277	-0.0454	-0.2836	0.6808	0.0034
0.1132	0.1526	-0.5620	0.1193	-0.1348	-0.1942	0.1857	0.0394
0.3172	0.3320	-0.1117	0.3303	-0.1930	-0.1360	-0.0378	0.0908
0.4956	0.5238	-0.1881	0.5106	-0.2103	-0.1187	-0.0164	0.0665
0.7569	0.7820	-0.2406	0.7678	-0.2472	-0.0818	-0.0160	0.0363
0.8991	0.9186	-0.4039	0.9044	-0.2896	-0.0394	-0.0005	-0.0440
0.9812	0.9857	-0.4783	0.9823	-0.3229	-0.0061	0.0015	-0.0854

$$\ln K = \int_0^1 \ln \overline{K} d Z = 0.3290$$

Table 30

Calculation of Adsorbed Phase Activity Coefficients
by Stoichiometric Method (17)

System: Ethylene (1) - Carbon Dioxide (2) - Silica Gel at 30° C, 1 atm (17)

$(n_1^\circ = 0.99 \quad n_2^\circ = 0.84$ mg-mols/gm)

x_1	y_1	$\ln \overline{K}$	Z	$\int_0^Z \ln \overline{K} \, dZ$	$\int_Z^1 \ln \overline{K} \, dZ$	$\ln \gamma_1$	$\ln \gamma_2$
0.0827	0.0867	-0.0600	0.0711	-0.0056	-0.0841	-0.0287	0.0015
0.2410	0.2430	-0.0103	0.2122	-0.0101	-0.0796	-0.0722	0.0094
0.4963	0.5026	-0.0231	0.4553	-0.0119	-0.0778	-0.0659	0.0017
0.7417	0.7764	-0.1280	0.7090	-0.0298	-0.0599	-0.0229	-0.0726
0.8906	0.9121	-0.2150	0.8735	-0.0580	-0.0317	-0.0045	-0.1545
0.9865	0.9901	-0.2642	0.9841	-0.0849	-0.0048	-0.0006	-0.2085

$$\ln K = \int_0^1 \ln \overline{K} \, dZ = -0.0897$$

Table 31

Calculation of Adsorbed Phase Activity Coefficients

by Stoichiometric Method (17)

System: Ethane (1) and Carbon Dioxide (2) on Silica Gel at 0° C, π = 1 atm (17)

($n_1^\circ = 1.046$ $n_2^\circ = 1.716$ mg-mols/gm)

x_1	y_1	$\ln \overline{K}$	Z	$\int_0^Z \ln \overline{K} \, dZ$	$\int_Z^1 \ln \overline{K} \, dZ$	$\ln \gamma_1$	$\ln \gamma_1$
0.0129	0.0671	-1.822	0.0209	-0.0423	-0.4545	1.2100	0.0013
0.0490	0.1043	-0.894	0.0779	-0.1125	-0.3843	0.4200	0.0244
0.1054	0.1622	-0.563	0.1619	-0.1735	-0.3233	0.1720	0.0446
0.1603	0.2138	-0.414	0.2385	-0.2151	-0.2817	0.0921	0.0566
0.2338	0.2970	-0.398	0.3336	-0.2592	-0.2376	0.0529	0.0655
0.3319	0.4161	-0.468	0.4490	-0.3077	-0.1891	0.0204	0.0747
0.4889	0.5640	-0.423	0.6108	-0.3692	-0.1276	0.0119	0.0870
0.6759	0.7228	-0.338	0.7738	-0.4254	-0.0714	0.0031	0.0991
0.7520	0.7808	-0.250	0.8326	-0.4446	-0.0522	0.0016	0.1029
0.8285	0.8474	-0.254	0.8860	-0.4617	-0.0351	0.0010	0.1053
0.8852	0.9053	-0.355	0.9267	-0.4745	-0.0223	0.0007	0.1092
0.9447	0.9546	-0.350	0.9655	-0.4864	-0.0104	0.0002	0.1113

$$\ln K = \int_0^1 \ln \overline{K} \, dZ = -0.4968$$

Table 32

Calculation of Adsorbed Phase Activity Coefficients by Stoichiometric Method (17)

System: Ethane (1) - Carbon Dioxide (2) - Silica Gel at 30°C, 1 atm (17)

($n_1^\circ = 0.54 \quad n_2^\circ = 0.84$ mg-mols/gm)

x_1	y_1	$\ln \overline{K}$	Z	$\int_0^Z \ln \overline{K}\, dZ$	$\int_Z^1 \ln \overline{K}\, dZ$	$\ln \gamma_1$	$\ln \gamma_2$
0.0309	0.0950	-0.6639	0.0471	-0.0348	-0.3493	0.5246	0.0042
0.1115	0.2109	-0.4438	0.1634	-0.0954	-0.2887	0.1530	0.0273
0.2633	0.4095	-0.4244	0.3573	-0.1681	-0.2160	0.1052	0.0196
0.4224	0.5618	-0.3860	0.5322	-0.2257	-0.1584	0.0411	0.0242
0.5916	0.6977	-0.3418	0.6926	-0.2766	-0.1075	-0.0044	0.0475
0.7934	0.8580	-0.3573	0.8565	-0.3311	-0.0530	-0.0031	0.0299

$$\ln K = \int_0^1 \ln \overline{K}\, dZ = -0.3841$$

Table 33

Calculation of Adsorbed Phase Activity Coefficients by Stoichiometric Method (17)

System: Propylene (1) - Carbon Dioxide (2) - Silica Gel at 0° C, 1 atm (17)

($n_1^\circ = 3.41$ $n_2^\circ = 1.72$ mg-mols/gm)

x_1	y_1	$\ln \overline{K}$	Z	$\int_0^Z \ln \overline{K} \, dZ$	$\int_Z^1 \ln \overline{K} \, dZ$	$\ln \gamma_1$	$\ln \gamma_2$
0.0462	0.0822	-2.0314	0.0239	-0.0582	0.5412	0.7403	0.0056
0.1680	0.1831	-0.3249	0.0924	-0.1315	0.6145	0.2667	0.0590
0.4126	0.3285	1.0072	0.2616	-0.0482	0.5312	-0.0623	0.1812
0.5862	0.4621	1.2613	0.4168	0.1336	0.3494	-0.1133	0.2280
0.7102	0.6158	0.9712	0.5793	0.3160	0.1670	-0.0709	0.1434
0.9211	0.9125	0.2112	0.8548	0.4848	-0.0018	-0.0095	-0.1769
0.9701	0.9708	-0.0442	0.9424	0.4909	-0.0079	-0.0016	-0.2612

$$\ln K = \int_0^1 \ln \overline{K} \, dZ = 0.4830$$

Table 34

Calculation of Adsorbed Phase Activity Coefficients by Stoichiometric Method (17)

System: Propylene (1) - Carbon Dioxide (2) - Silica Gel at 30°C, 1 atm (17)

($n_1^\circ = 2.22 \quad n_2^\circ = 0.84$ mg-mols/gm)

x_1	y_1	$\ln \overline{K}$	Z	$\int_0^Z \ln \overline{K} dZ$	$\int_Z^1 \ln \overline{K} dZ$	$\ln \gamma_1$	$\ln \gamma_2$
0.0500	0.0414	0.4264	0.0195	0.0051	1.3111	0.4023	0.0038
0.2208	0.1384	1.1214	0.0968	0.0708	1.2454	0.1048	0.0450
0.4962	0.2941	1.4445	0.2715	0.3041	1.0121	-0.0181	0.1049
0.6826	0.4264	1.5416	0.4487	0.5647	0.7515	-0.0443	0.1512
0.7996	0.5616	1.4418	0.6015	0.8041	0.5121	-0.0282	0.0751
0.9560	0.8615	1.1943	0.8915	1.1980	0.1182	-0.0051	-0.1587

$$\ln K = \int_0^1 \ln \overline{K} dZ = 1.3162$$

Table 35

Calculation of Adsorbed Phase Activity Coefficients by Stoichiometric Method (17)

System: Propane (1) - Carbon Dioxide (2) - Silica Gel at 0°C, 1 atm (17)

(n_1° = 2.63 n_2° = 1.72 mg-mols/gm)

x_1	y_1	$\ln \overline{K}$	Z	$\int_0^Z \ln \overline{K} \, dZ$	$\int_Z^1 \ln \overline{K} \, dZ$	$\ln \gamma_1$	$\ln \gamma_2$
0.0603	0.0751	-0.6046	0.0403	-0.0348	0.1708	0.2855	0.0060
0.1262	0.1435	-0.3723	0.0863	-0.0575	0.1935	0.2029	0.0148
0.2912	0.2689	0.2626	0.2118	-0.0554	0.1914	-0.0059	0.0645
0.4945	0.4570	0.3303	0.3901	-0.0018	0.1378	-0.0242	0.0760
0.6250	0.5865	0.3352	0.5215	0.0436	0.0924	-0.0259	0.0763
0.6997	0.6761	0.2204	0.6038	0.0678	0.0682	-0.0073	0.0380
0.8952	0.8887	0.1226	0.8482	0.1193	0.0167	-0.0007	-0.0089

$$\ln K = \int_0^1 \ln \overline{K} \, dZ = 0.1360$$

Table 36

Calculation of Adsorbed Phase Activity Coefficients

by Stoichiometric Method (17)

System: Propane (1) and Carbon Dioxide (2) on Silica Gel at 30° C, π = 1 atm (17)

(n_1° = 1.396 n_2° = 0.840 mg-mols/gm)

x_1	y_1	$\ln \overline{K}$	Z	$\int_0^Z \ln \overline{K}\, dZ$	$\int_Z^1 \ln \overline{K}\, dZ$	$\ln \gamma_1$	$\ln \gamma_1$
0.0822	0.0470	0.464	0.0511	0.0225	0.3901	-0.0358	0.0018
0.1122	0.0806	0.480	0.0706	0.0317	0.3809	-0.0466	0.0027
0.1994	0.1448	0.520	0.1303	0.0615	0.3511	-0.0722	0.0077
0.3121	0.2231	0.563	0.2145	0.1070	0.3056	-0.0984	0.0157
0.4499	0.3229	0.587	0.3298	0.1733	0.2393	-0.1103	0.0243
0.5100	0.4015	0.585	0.3851	0.2057	0.2069	-0.1097	0.0230
0.6819	0.5667	0.522	0.5633	0.3043	0.1083	-0.0856	-0.0122
0.7610	0.6380	0.454	0.5671	0.3501	0.0625	-0.0667	-0.0616
0.8458	0.7914	0.334	0.7674	0.3936	0.0190	-0.0420	-0.1634
0.9312	0.9263	0.094	0.8907	0.4200	-0.0074	-0.0127	-0.4010

$$\ln K = \int_0^1 \ln \overline{K}\, dZ = 0.4126$$

Appendix D

Sources of Errors in the Calculation of γ

SOURCES OF ERRORS IN THE CALCULATION OF γ BY THE METHOD OF MYERS AND PRAUSNITZ (13)

The total deviation from the actual value of γ is extremely difficult to estimate because of tedious graphical steps involved in the calculations, and the propagation of errors. However, the error in each step can be roughly analysed. The system C_3H_6 - CO_2 - Columbia "G" Carbon at 0° C and 1 atm (17) is taken as an example.

(1) Pure component spreading pressure:

a) Curve fitting: The error of plotting $n°/P_i^\circ$ versus P_i° is trivial. It may be assumed to be ± 2%.

b) Extrapolation: The extrapolation of the curve n_i°/P_i° versus P_i° to zero pressure is required. This is extremely difficult for components of low volatility. The data of C_3H_6 show that the maximum deviation of pure component equilibrium pressure at the same spreading pressure is about 20% at the low pressure region when two different values of n_i°/P_i° (that is, 0.41 and 0.64) are used at zero pressure. In other words, at the same P_i°, the maximum deviation of ϕ_i° would be 20% in the low pressure region (see Figure 36).

c) Graphical integration: The mechanical error of graphical integration is about ± 3%.

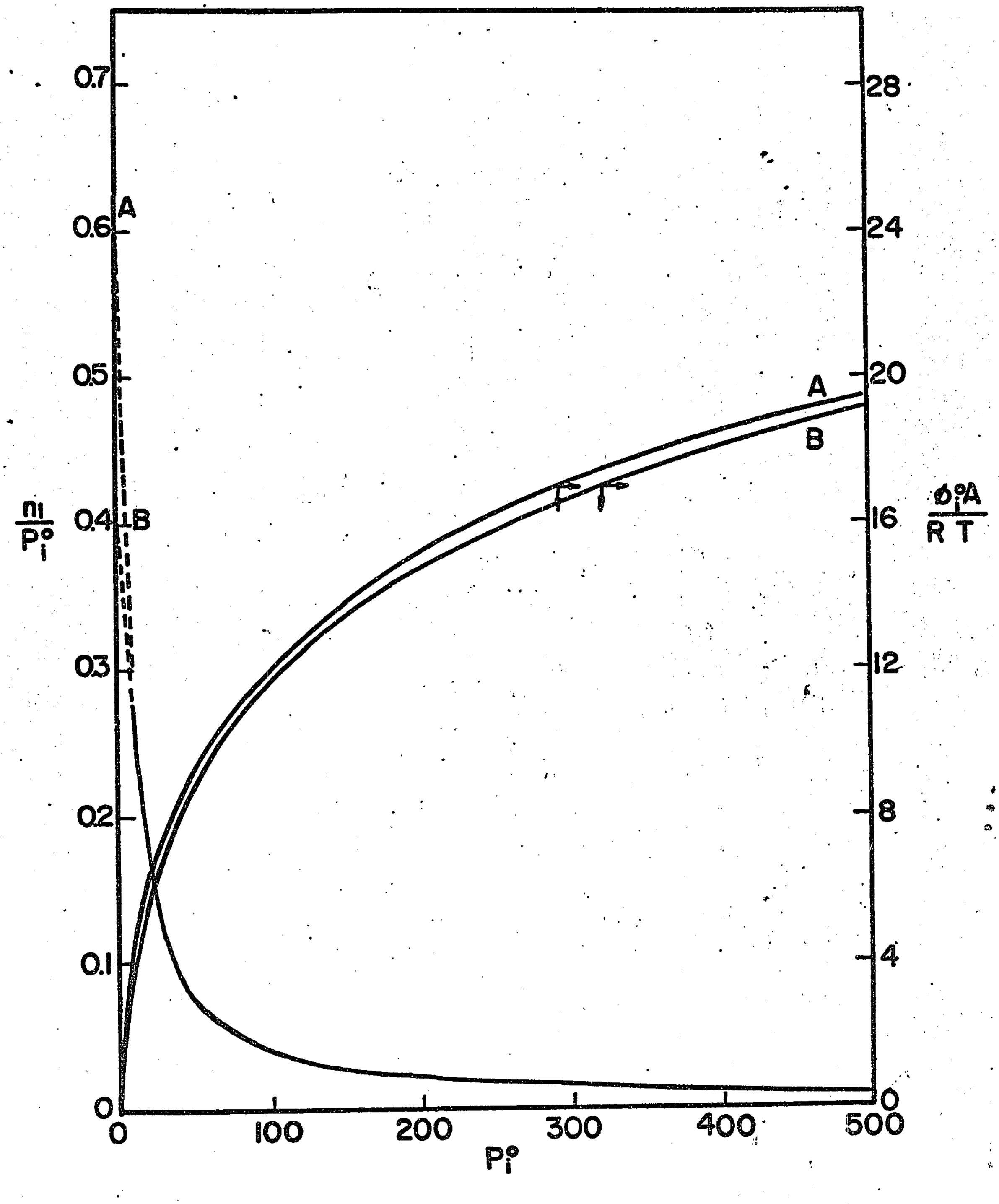


Figure 36 COMPARISON OF TWO DIFFERENT EXTRAPOLATIONS

(2) Binary spreading pressure:

a) Curve fitting: Two curves, n_1/y_1 versus y_1 and n_2/y_2 vs. y_2, are plotted. The scattering of the experimental data for Component 1 (C_3H_6) makes the construction of the curve extremely difficult. Two limiting curves showed ± 27% deviation. After the integration of the curves, the maximum deviations would be ± 10% (see Figures 37 and 38).

b) Extrapolation: Either Equation (66) or Equation (67) could be used according to the actual distribution of the experimental points. Usually, the extrapolating range is small, unless the given data cover only the middle composition range. The error of extrapolation is within ± 5%.

c) Graphical integration: The mechanical error of graphical integration is about ± 3%.

(3) Using Equation (19) to calculate γ:

a) Reading off P_i° from ϕ_i versus P_i° plot: For Component 1 (C_3H_6), the reading error is about ± 1 mm Hg, and the larger error is attributed to the extrapolation to the higher pressure for Component 2 (CO_2) which is about ± 20 mm Hg.

b) The propagration of errors from the above steps to the final value of γ is difficult to estimate.

Since the thermodynamic method can only be used for testing the data consistency but not the data accuracy, there is so far no method

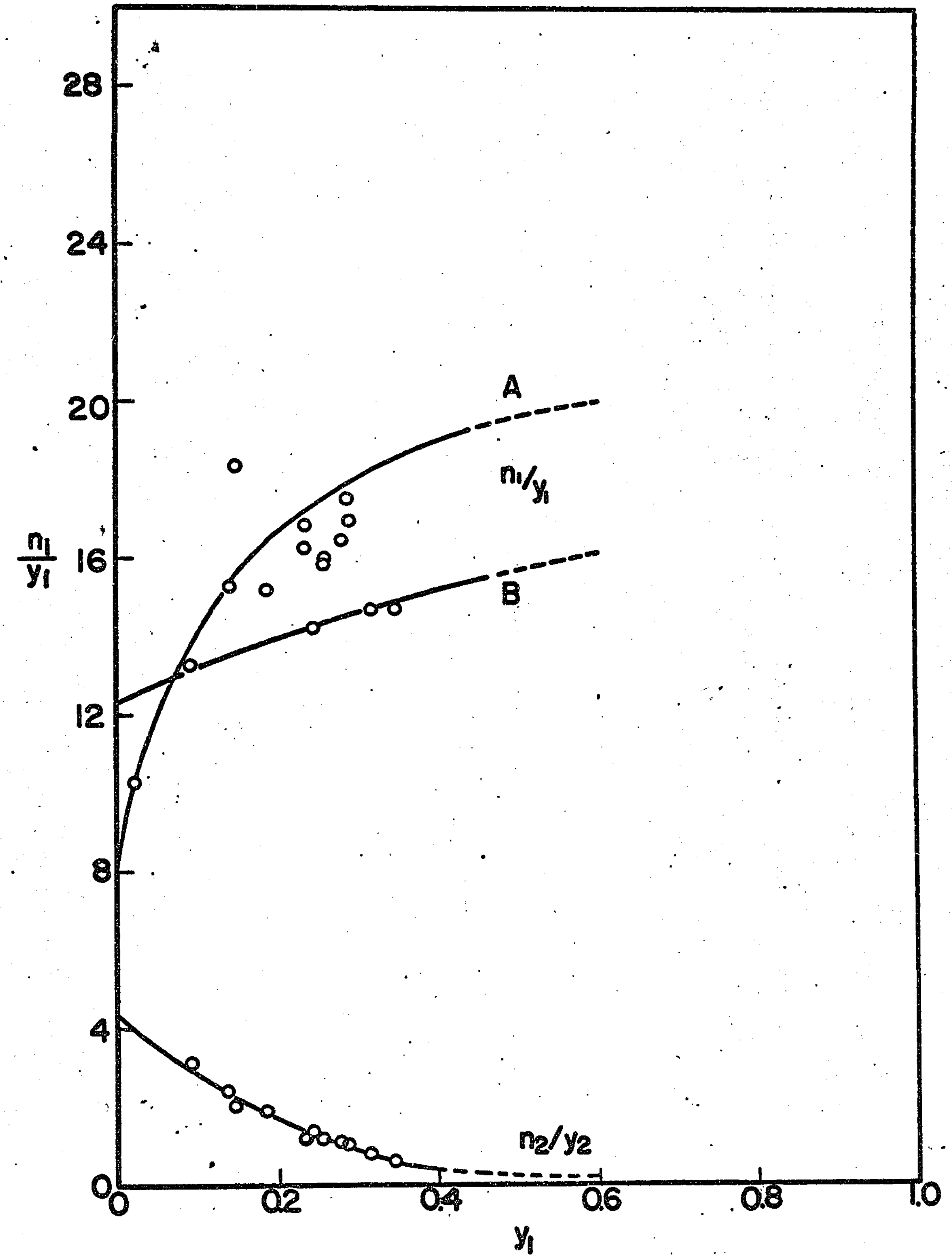


Figure 37 CURVES OF TWO EXTREME CASES

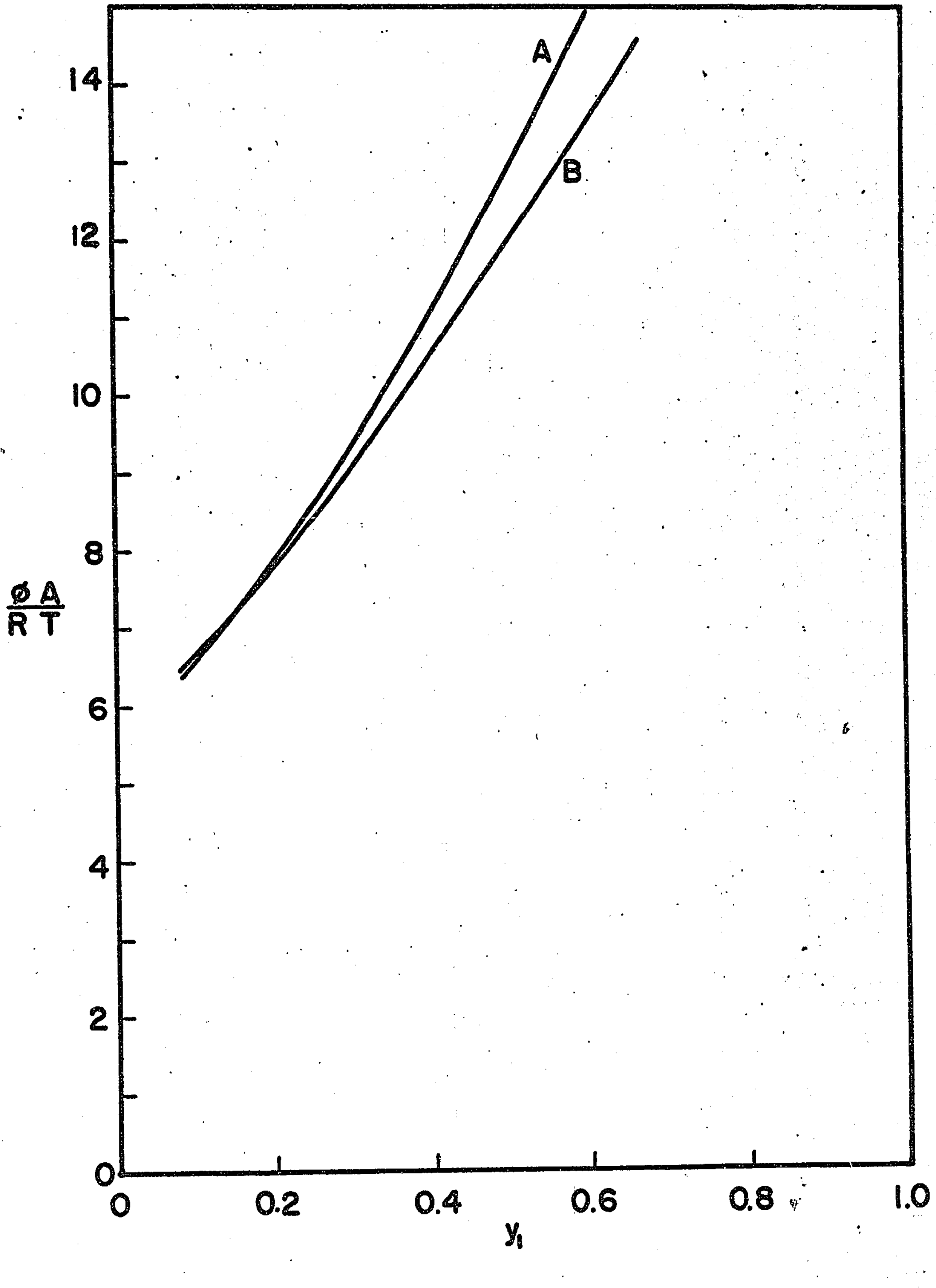


Figure 38 COMPARISON OF INTEGRATION OF TWO EXTREME CURVES

which can be used to test the data accuracy. The above analysis is limited to the study of errors inherent in the graphical method. As to the total error of calculation, it may be estimated by using the values on the smoothing curve (Figure 39) and substituting into Equation (19) to calculate back. The results are then compared to the experimental data. The maximum final error is seen to be about 25% (Figure 40). (Excluding the point at $x_1 = 0.95$, the maximum error observed is about 25% (at $x_1 = 0.8$). At $x_1 = 0.95$, the reliability of $P_2^\circ(\phi)$ is doubtful due to the extrapolation procedure).

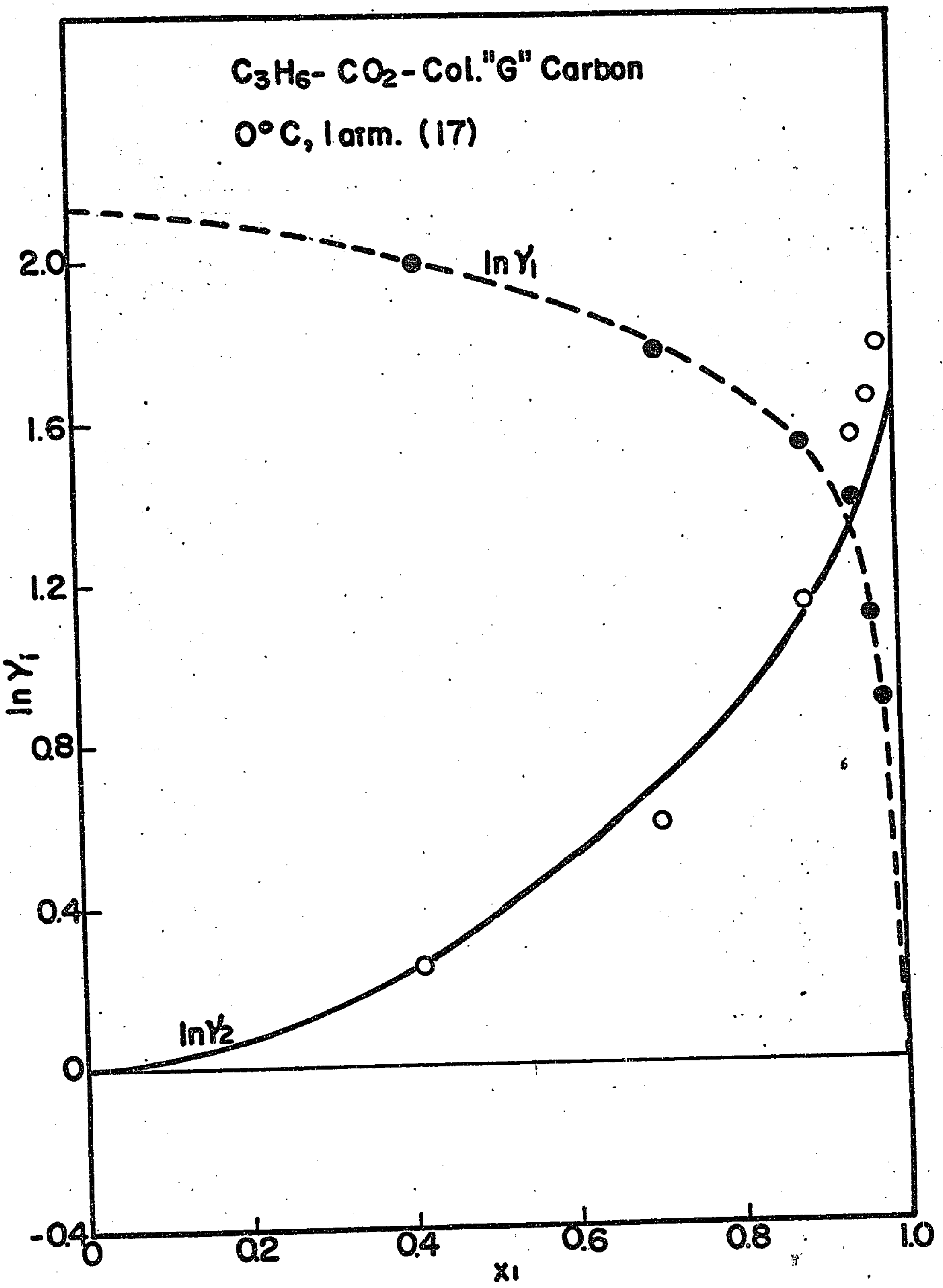
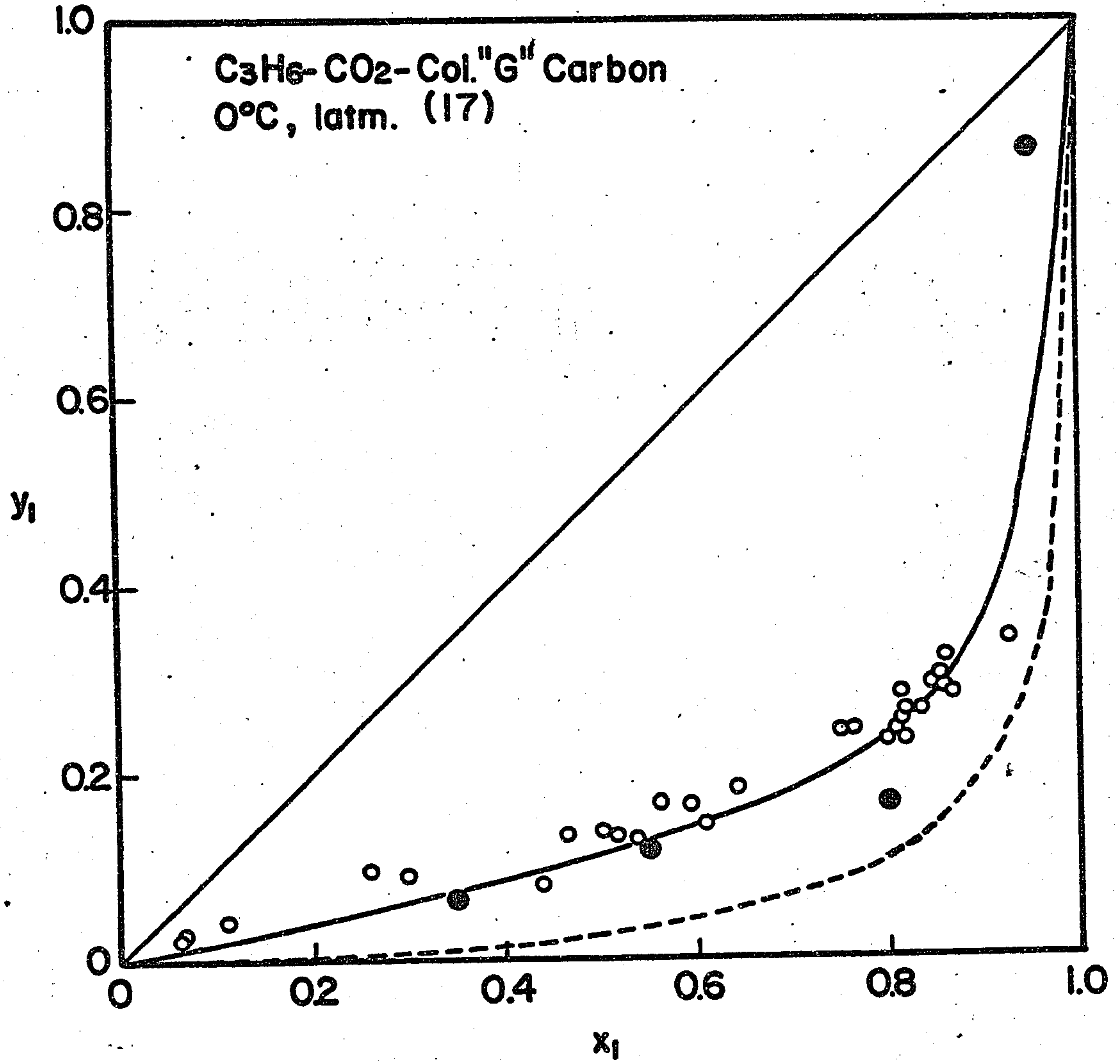


Figure 39 SMOOTHING CURVES OF ln γ_1 AND ln γ_2



● CALCULATED VALUE FROM $\ln\gamma_1$ vs. x_1 PLOT

—— SMOOTHED EXPERIMENTAL DATA

---- CALCULATED VALUES FROM IDEAL ADSORBED SOLUTION METHOD

Figure 40 TOTAL ERROR OF CALCULATION OF γ

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