Rev. Téc. Ing., Univ. Zulia
Vol.2 , N°1 y 2 , 1979

CORRELATION OF EXCESS VOLUMES OF MIXING OF LIQUIDS BY MEANS OF THE CLAUSIUS EQUATION OF STATE

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ABSTRACT

The Clausius equation of state was modified in two ways for calculating excess volumes of mixing (V^E) of liquids . In one modification , the three parameters of the equation were made temperature dependent and were calculated from vapor pressure and saturated liquid and vapor densities of the pure component. In another modification , one of the parameters , Ω_c, of the equation was treated as temperature independent and was assigned a value given by the original equation , while the other two parameters were considered temperature dependent and were determined from vapor pressure and saturated liquid density of the pure component . The Clausius equation was then used with appropriate mixing parameters to calculate V^E.

The results obtained compared well with the available data, although the shapes of V^E vs x curves are somewhat different. The systems studied include nitrogen-argon, nitrogen-oxygen, argon-oxygen, benzene-hexane and benzene-toluene.

RESUMEN

La ecuación de estado de Clausius ha sido modificada de dos maneras para el cálculo de los volúmenes de exceso de mezcla de líquidos (V^E). En la primera modificación, los tres parámetros de la ecuación se consideraron dependientes de la temperatura y fueron calculados a partir de la presión de vapor y la densidad a saturación de la fase líquida y vapor correspondiente al compuesto puro. En la otra modificación uno de los parámetros, Ω_c, de la ecuación se consideró independiente de la temperatura y se le asignó el valor dado por la ecuación original, mientras que los otros dos parámetros se consideraron dependientes de la temperatura y se determinaron a partir de la presión de vapor y la densidad del líquido a saturación del compuesto puro. La ecuación de Clausius con los parámetros de mezcla adecuados se utilizó entonces para calcular V^E.

Los resultados obtenidos comparan bien con los datos disponibles, aunque la forma de las curvas V^E vs x difieren en cierta manera. Los sistemas estudiados fueron nitrógeno-argón, nitrógeno-oxígeno, argón-oxígeno, benceno-hexano y benceno-tolueno.

INTRODUCTION

The change of volume that accompanies the mixing of liquids is a property which is important in determining liquid densities of industrial products and intermediate streams, which are used in the design of storage and separation equipment, and in the determination of exact quantities involved in sales. It is also valuable for evaluating the pressure dependence of the liquid activity coefficient, γ, which is useful in providing the correction term for correlating and testing iso-thermal vapor-liquid equilibrium data.

In an ideal solution, there is no volume change upon mixing of liquids at constant temperature and pressure. Thus $\Delta V^M = 0 = V^E$. In this presentation, the excess volume will be used rather than ΔV^M.

For a mixture of real liquid, V^E per mole of the mixture is given by:

$$V^E = V - \sum_{i=1}^{n} x_i \underline{V}_i \qquad \text{(constant } T, P) \tag{1}$$

where $\underline{V}$ is the molar volume of component i in its pure state.

According to the Euler's theorem, the molal volume is given by

$$V = \sum_{i=1}^{n} x_i \bar{V}_i \qquad \text{(constant } T, P) \tag{2}$$

Combining these two equations gives

$$V^E = \sum_{i=1}^{n} x_i (\bar{V}_i - \underline{V}_i) \tag{3}$$

The partial molal volume $\bar{V}_i$ is defined as

$$\bar{V}_i = \left(\frac{\partial V_T}{\partial n_i}\right)_{T,P,n_j (i \neq j)} \tag{4}$$

At any composition the volume change upon mixing is directly related to the partial molal volumes of the components. Since experimental data are usually not available at the conditions needed for carrying out the determination of all the partial derivatives, the most convenient method for establishing the quantity $\overline{V}_i$ is the use of a suitable equation of state. Unfortunately none of the existing equations of state in their original form [17] can be used to represent satisfactorily the liquid state without any restrictions or modifications.

The need to modify the equations of state in order to derive better expressions for liquid volumes and their partial properties has been recognized. For example, the Redlich - Kwong equation of state has been modified in several ways to improve its capability for data representation [4,5,17].

In this work, the Clausius equation [6] was used with the temperature dependent parameters for deriving the partial molal volumes.

In the original form of the Clausius equation [6],

$$\left(P + \frac{a}{T(V + c)^2}\right)(V - b) = RT \tag{5}$$

The parameters a, b and c can be expressed in terms of the critical properties as follows:

$$a = \Omega_a V_c^2 P_c T_c / Z_c^2 \tag{6}$$

$$b = \Omega_b V_c \left(4 - \frac{1}{Z_c}\right) \tag{7}$$

$$c = {}_c V_c (3/Z_c - 8) \tag{8}$$

To improve the equation's ability to represent the desired thermodynamic properties, it has been suggested that the parameters a, b and c should not be taken as universal constants but as variables [8,9]. They vary with substances and are temperature dependent. As part of this work, two different approaches have been proposed. In an earlier part of this work Ω_a, Ω_b and Ω_c were treated as temperature dependent [8,9] and were established from data on vapor pressures and saturated liquid and vapor densities of the pure components. This mode of operation is described herein as Clausius I. The ability of the equation (Clausius I) to represent the thermodynamic properties was critically evaluated. From the conclusions it was further suggested that by treating Ω_a and Ω_b as temperature dependent [9], while taking Ω_c as temperature independent, would actually improve the calculation results. This proposed approach, that the equation with only two temperature dependent parameters, is referred in this presentation as Clausius II. The parameters Ω_a and Ω_b were then determined from vapor pressures and saturated liquid densities of the pure components. Comprehensive discussions that support the development of the latter modified procedure (Clausius II) are given elsewhere [9].

In this study the objective was set as amplifying the applicability of the previously reported procedures [8,9] for modifying the Clausius equation of state to the calculations of V^E. The equation was used to establish the quantity $\bar{V}_i$ for each compound in the mixture. These values were subsequently used to calculate V^E for the binary mixture.

EQUATIONS FOR EVALUATING THE PARTIAL MOLAL VOLUMES

The partial molal volume of component i in a mixture of n components is defined by

$$\bar{V}_i = - \frac{\left(\frac{\partial P}{\partial n_i}\right)_{T,\, V_T,\, n_j (i \neq j)}}{\left(\frac{\partial P}{\partial V}\right)_{T,\, n_j (\text{all } i)}} \tag{9}$$

Combining equation (9) with equations (5 - 8) gives

$$\overline{V}_i = \frac{\dfrac{RT}{V-b}\left(\dfrac{1+b_i}{V-b}\right) - \dfrac{2\sum_j^n x_j a_{ij} - ac_i/(V+c)}{T(V+c)^2}}{\dfrac{RT}{(V-b)^2} - \dfrac{2a}{T(V+c)^3}} \tag{10}$$

where V is the molar volume of the liquid mixture. The mixing rules reported previously [5,8,9] were also used in this work for calculating the mixing characteristics associated with the Clausius equation.

RESULTS AND DISCUSSION

Based on the proposed procedures the parameters Ω_a, Ω_b and Ω_c were established for the pure components nitrogen [7], argon [7], oxygen [19], toluene [16], benzene [3] and hexane [16] from the available saturation properties at the temperature of interest. A trial and error procedure was used to determine the values of the three parameter for satisfying the three condition in Clausius I.

$$V_\ell\text{, calc.} = V_\ell\text{, exp.} \tag{11}$$

$$V_v\text{, calc.} = V_v\text{, exp.} \tag{12}$$

$$f_v\text{, calc.} = f_\ell\text{, calc.} \tag{13}$$

However, equation (12) was not used in Clausius II since Ω_c was treated as a universal constant. Description of the procedures was given previously [8,9]. The calculated values are listed in Table 1 under the titles Clausius I (Ω_a, Ω_b and Ω_c are temperature dependent) and Clausius II (Ω_a , Ω_b are temperature dependent while Ω_c is proposed to be universal constant at *0.125*) .

It has been our experience that the deviations between the calculated and experimental values of V^E could be reduced when the parameters of the equation of state were established from reliable pure component properties together with the measured set of data . On the other hand the uncertainty in the experimentally determined saturated V_v values (such as that of toluene) was not only reflected in the numerical values of the parameters , but also affected the convergence of the calculation . Consequently, the values of V_v calculated by means of the correlation of Thodos et al. was used . This is the only exception of this investigation.

In this investigation the excess volumes of mixing values for five binary systems ; nitrogen - argon [13] at 83.78 K, argon - oxygen [11,14] at 83.82 K , nitrogen - oxygen [14] at 83.82 K , benzene - hexane [10,15] and benzene - toluene [12] at 298.15 K were calculated and compared with the experimental data. The comparison was depicted in Fig. 1 - 5 and summarized in Table 2 . The experimental data were used to establish the binary interaction parameter, k_{ij} in such a manner that the sum of the absolute differences between the calculated and the experimental values is minimum . If more than one set of data are reported , the value of k_{ij} were calculated in the same manner using all the available data.

For the system benzene - hexane, the higher average absolute deviation may be due to the low precision of the data as indicated by Battino [2] . The results for the five system investigated are comparable in terms of the average absolute deviation although the shape of V^E *vs* x curves is somewhat different. This may be due to the in - accuracy of the experimental data. It is also possible that the proposed procedures could be further modified.

In addition , it is noticeable that the numerical values of k_{ij} varies with the properties it derives from [8,9] . Therefore, it may not be feasible to use k_{ij} values obtained from one property of mixing for the calculation of other properties of mixing, For this reason, it is desirable to have at least one reliable data point determined experimentally for the evaluation of the required k_{ij} for the excess property concerned.

Finally, for the present purpose of representing V^E, the use of the saturated vapor volume is avoided when the parameters Ω_a and Ω_b of the Clausius equation of state were treated as temperature dependent while asigning to Ω_c a constant value . The equation still produces comparable representation of excess volumes of mixing for the systems investigated.

TABLE 1

Values of the Clausius Equation Parameters

		Clausius I			Clausius II*	
Component	T, K	Ω_a	Ω_b	Ω_c	Ω_a	Ω_b
Nitrogen	83.82	0.35688	0.49518	0.07316	0.41146	0.44156
Argon	83.82	0.23093	0.55785	0.00001	0.36718	0.46695
	90.00	0.35120	0.53305	0.09180	0.38147	0.45950
Oxygen	83.85	0.33995	0.53700	0.09390	0.37485	0.51170
	90.00	0.35120	0.53305	0.09180	0.38810	0.50200
Benzene	298.15	0.29710	0.92484	0.03560	0.44615	0.80638
Hexane	298.15	0.47933	1.55840	0.11360	0.50054	1.51670
Toluene	298.15	0.27670	0.13992	0.0500	0.46410	1.20944

* $\Omega_c = 0.125$

TABLE 2

Comparison of calculated V^E values with available data in the literature

		CLAUSIUS I			CLAUSIUS II				
System	Temp, K	$\lvert\Delta V^E\rvert_{av}^{*}$	%**	k_{ij}	$\lvert\Delta V^E\rvert_{av}^{*}$	%**	k_{ij}	N° of data point.	Reference.
Nitrogen-argon	83.78	0.007	5.1	0.021	0.005	4.1	0.014	8	13
Argon-oxygen	83.82	0.006	7.3	0.013	0.004	4.5	0.012	8	13
	90	0.007	6.7	0.012	0.005	4.9	0.011	12	11,14
Nitrogen-oxygen	83.82	0.007	2.9	0.002	0.003	0.9	0.012	7	14
Benzene-hexane	298.15	0.087	30.8	0.000	0.057	20.2	0.003	15	10,15
Benzene-toluene	298.15	0.004	10.0	0.00	0.003	5.5	-0.0095	23	12

$$*\lvert\Delta V^E\rvert_{av} = \frac{\sum \lvert V^E_{exp} - V^E_{calc}\rvert}{N}$$

$$** \ \% = \frac{\sum \left\lvert \dfrac{V^E_{exp} - V^E_{calc}}{V^E_{exp}} \right\rvert \times 100}{N}$$

NOMENCLATURE

a , b , c	Parameters of the Clausius Equation of state
f	Fugacity
k_{ij}	Binary interaction constant $k_{ij} = 1 - T_{cij}/(T_{ci}T_{cj})^{0.5}$
N	Number of data points
P	Pressure
R	Gas constant
T	Temperature
V	Volume
$\underline{V}_i$	Molar volume of component i in the pure liquid state at given T , P conditions
x	Liquid mole fraction
Z	Compressibility factor
Ω_a , Ω_b , Ω_c	Parameters of Clausius equation of state
Δ	Difference

Subscripts

c	Critical state
i , j	Components identification
T	Total property
ℓ	Liquid
v	Vapor

Superscripts

E	Excess property
M	Property change on mixing
-	Partial molal quantity

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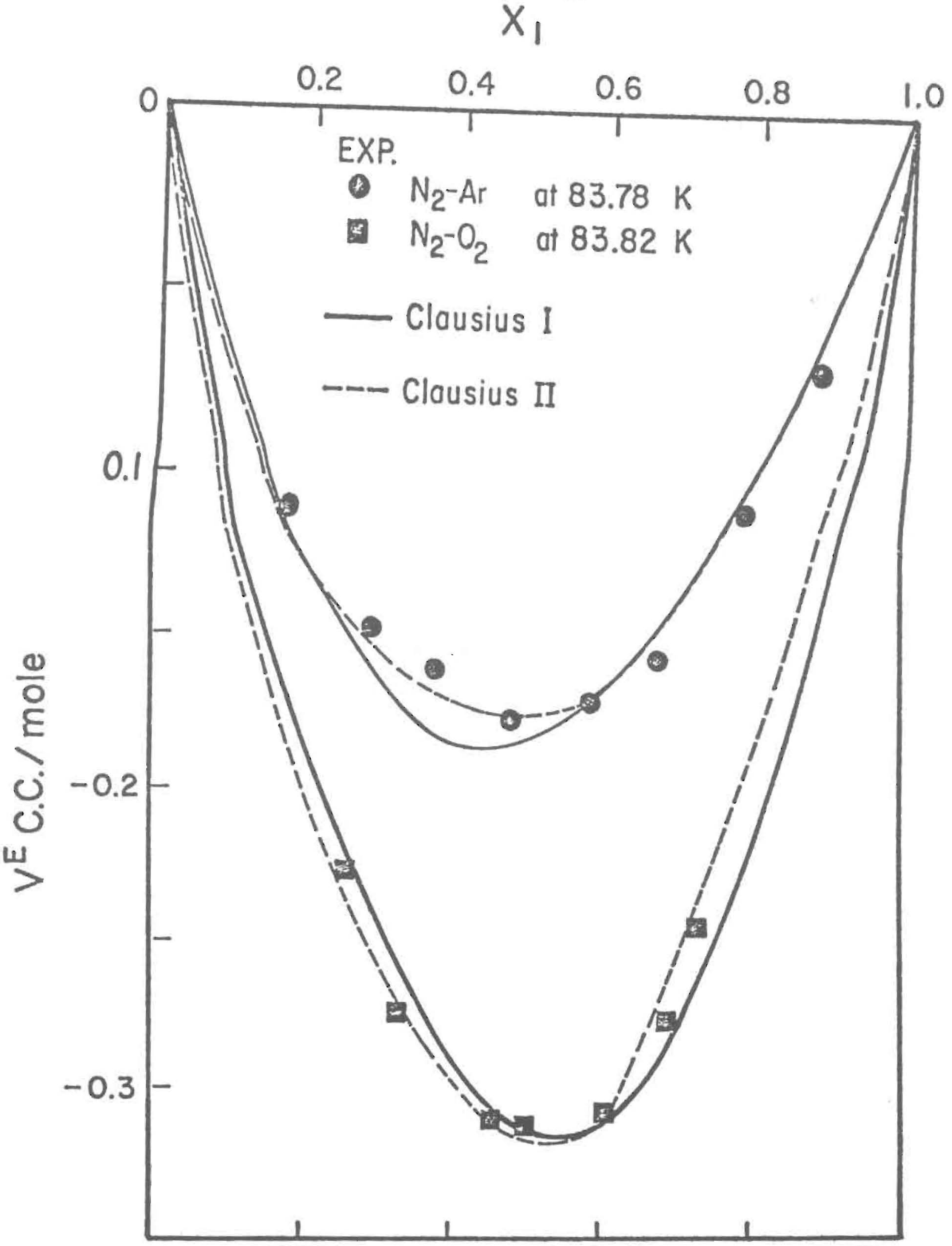
CAPTION OF FIGURES

Figure 1 :	Comparison of experimental and Calculated Values of excess volumes of mixing of nitrogen - argon and nitrogen - oxigen at 83.78 and 83.82 K.
Figure 2 :	Comparison of experimental and Calculated Values of excess volumes of mixing of argon - oxygen at 83.82 K.
Figure 3 :	Comparison of experimental and Calculated Values of excess volumes of mixing of argon - oxygen at 90 K.
Figure 4 :	Comparison of experimental and Calculated Values of excess volumes of mixing of benzene - hexane at 298.15 K.
Figure 5 :	Comparison of experimental and Calculated Values of excess volumes of mixing of benzene - toluene.



X_1
0
0.2
0.4
0.6
0.8
1.0
EXP.
● N_2-Ar at 83.78 K
■ N_2-O_2 at 83.82 K
—— Clausius I
---- Clausius II
0.1
-0.2
-0.3
V^E C.C./mole

Figure 1

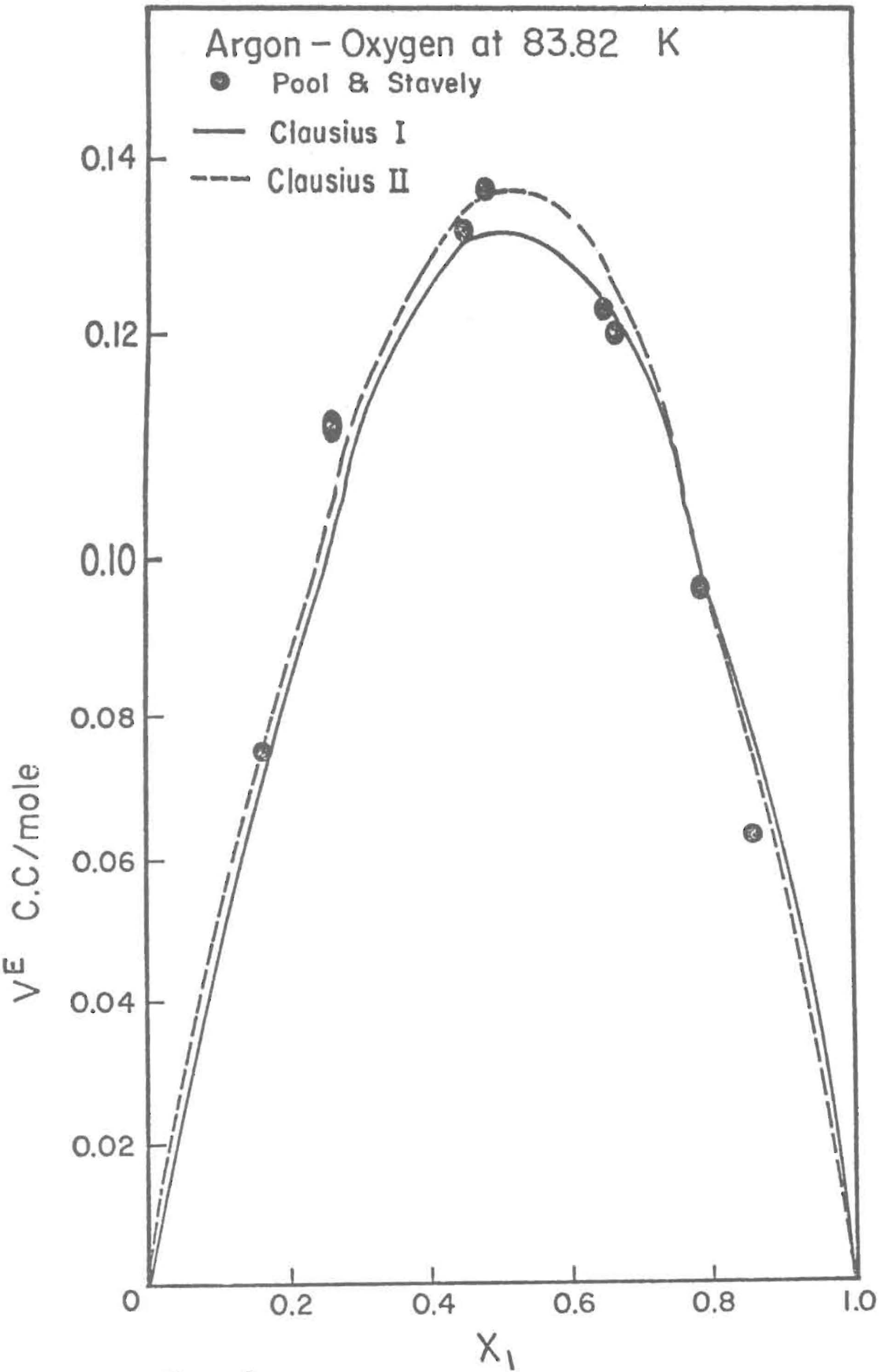
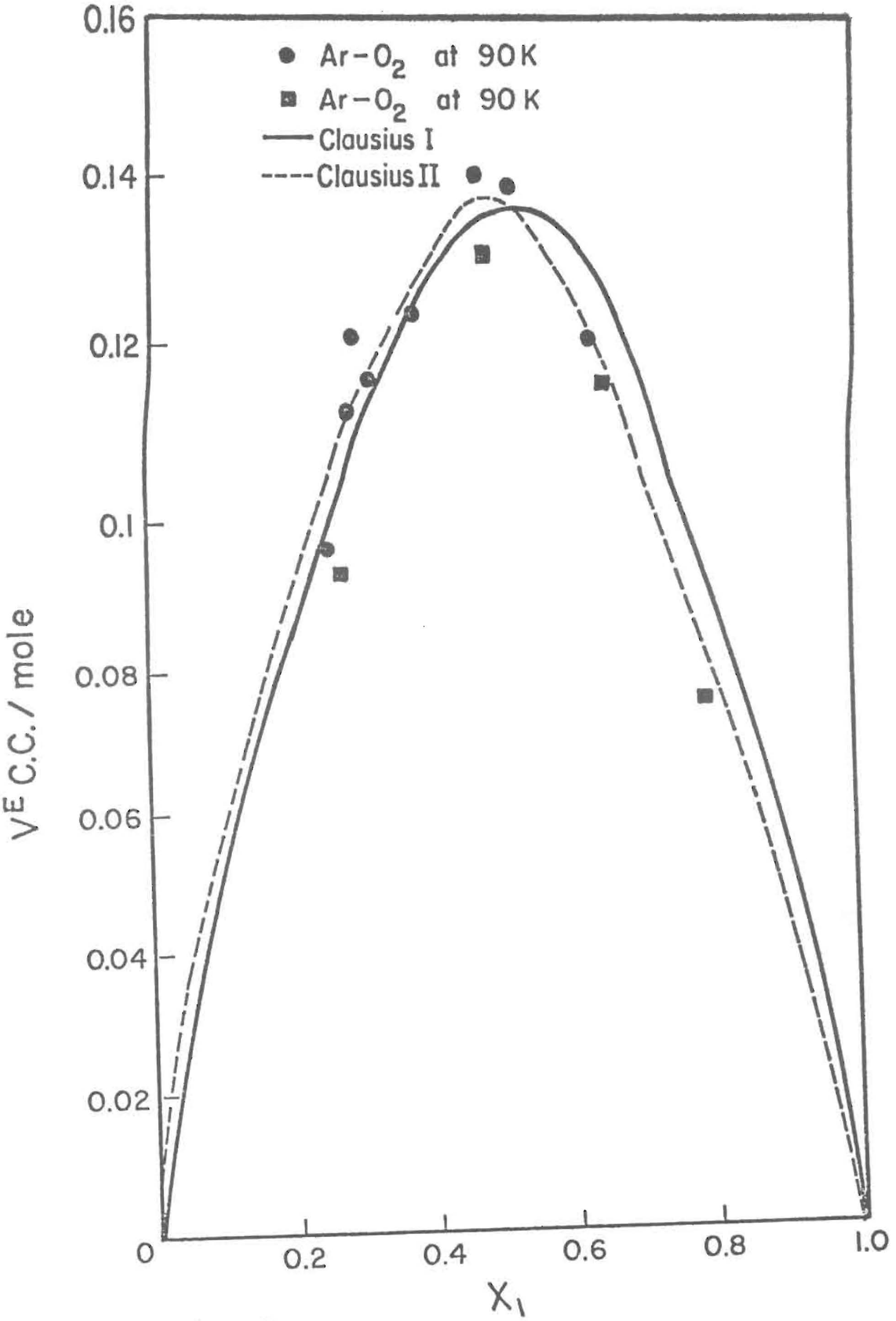

Argon - Oxygen at 83.82 K
● Pool & Stavely
Clausius I
Clausius II
0.14
0.12
0.10
0.08
0.06
0.04
0.02
V^E C.C/mole
0
0.2
0.4
0.6
0.8
1.0
X_1

Figure 2



● Ar − O_2 at 90 K
■ Ar − O_2 at 90 K
—— Clausius I
- - - - Clausius II
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
V^E C.C. / mole
0
0.2
0.4
0.6
0.8
1.0
X_1

Figure 3

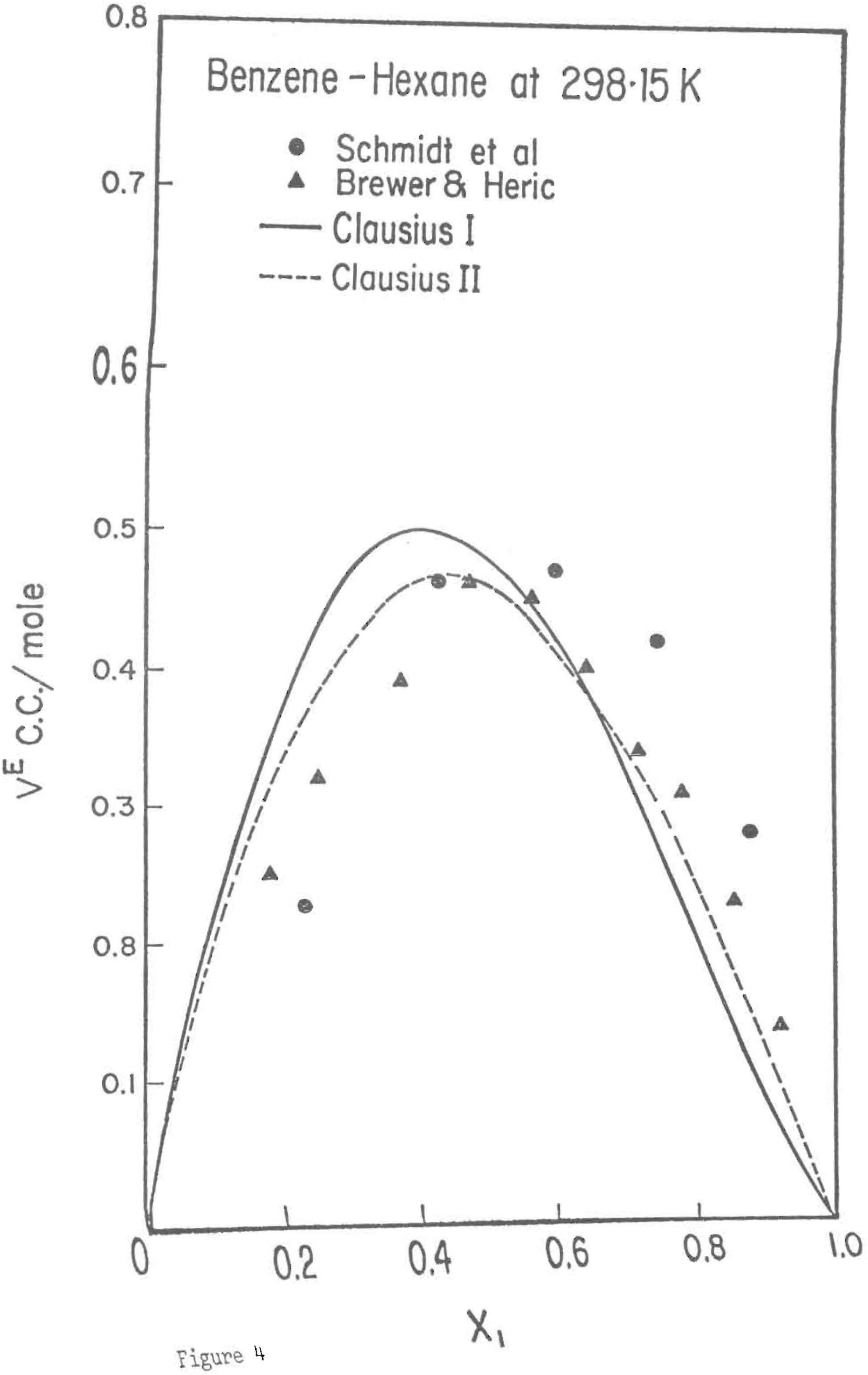

Benzene - Hexane at 298·15 K
● Schmidt et al
▲ Brewer & Heric
—— Clausius I
---- Clausius II
0.8
0.7
0.6
0.5
0.4
0.3
0.8
0.1
V^E C.C./mole
0
0.2
0.4
0.6
0.8
1.0
X_1

Figure 4

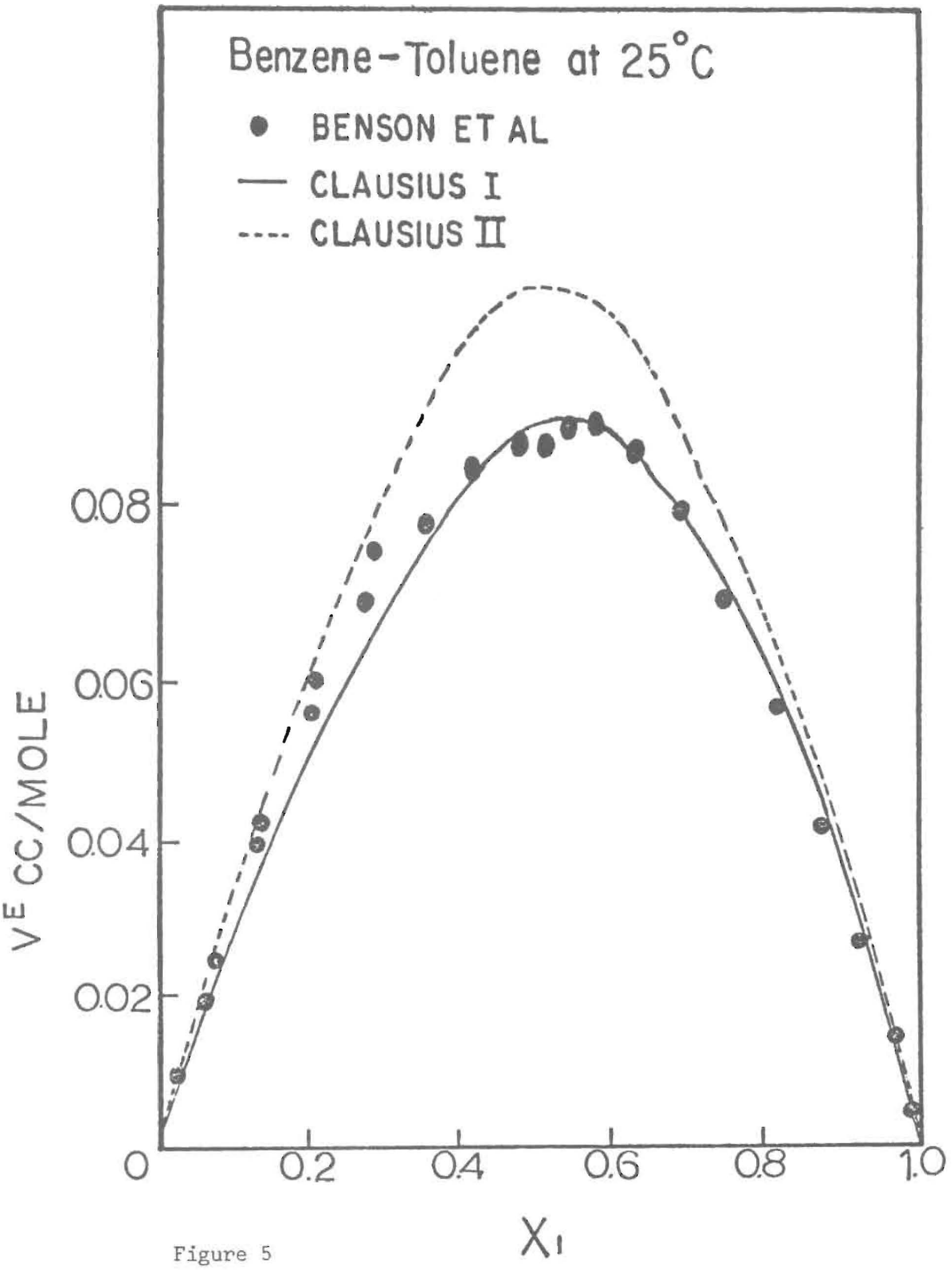

Benzene-Toluene at 25°C
● BENSON ET AL
— CLAUSIUS I
---- CLAUSIUS II
V^E CC/MOLE
0.08
0.06
0.04
0.02
0
0.2
0.4
0.6
0.8
1.0
X1

Figure 5