

THE UNIVERSITY OF MANITOBA

EXCESS VOLUMES, VAPOUR PRESSURES AND
VAPOUR COMPOSITIONS OF THE SYSTEMS
ACETONE-CHLOROFORM AND
ACETONE-CHLOROFORM-BENZENE

A Thesis

Presented to

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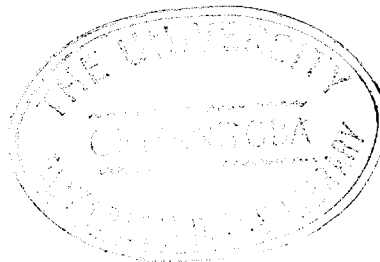
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by

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TO MY BELOVED PARENTS

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ABSTRACT

The volume changes on mixing of the three binary mixtures acetone-chloroform, benzene-chloroform and acetone-benzene and of the ternary mixture acetone-chloroform-benzene have been determined by a direct dilatometric method. In the system acetone-chloroform a volume contraction occurs till the concentration reaches about 68 mole percent acetone, where V^E changes sign and becomes positive. In the system benzene-chloroform the excess molal volume function is positive over the complete concentration range, but this does not necessarily suggest a positive deviation from ideality in terms of Raoult's law. The system acetone-benzene exhibits volume contraction of relatively smaller magnitude than the system acetone-chloroform, but the function V^E changes sign at a higher concentration of acetone in this system compared to the latter. In the ternary system there exists a region with a positive excess molar volume function and a region with a negative excess molar volume function. Two curves have been obtained in the composition triangle showing the concentrations of mixtures for which the excess molar volume is equal to zero.

The refractivities of the binary systems show that the true molecular volumes of the components are additive on mixing.

The viscosity data on the binary systems have been obtained. A general correlation with other data such as V^E , G^E , H^E and S^E has not been possible.

Studies of the vapour-liquid equilibria show that there is positive as well as negative deviation from Raoult's law in the ternary system. The binary systems acetone-chloroform and benzene-chloroform have been found to exhibit negative deviation from Raoult's law. This strengthens the idea of compound formation in the former system. The system benzene-chloroform does not seem to form a compound and the deviation from ideality is very small as evident from the partial vapour pressure curves. The system acetone-benzene shows a positive deviation from Raoult's law.

Excess Gibbs free energies of mixing have been calculated in the three binary systems and in the ternary system. The data for the binary systems have been treated together with the heats of mixing data of Campbell, Kartzmark and Friesen (2) to calculate the excess entropy of mixing.

Zero excess molar volume and zero excess Gibbs free energy in the ternary system are probably caused by the counteracting effects of acetone and of benzene molecules on chloroform molecules and on each other.

GLOSSARY OF SYMBOLS

P_i	Partial pressure of component i.
x_1	Mole fraction of component 1 in the liquid phase.
y_1	Mole fraction of component 1 in the vapour phase.
G^M	Gibbs free energy of mixing.
V^M	Volume change of mixing.
H^M	Heat of mixing.
S^M	Entropy of mixing.
μ^M	Partial molal free energy of mixing.
v^M	Partial molal volume of mixing.
\bar{R}	Partial molal refraction.
J	Arbitrary extensive property.
n	Number of moles.
G^E	Excess Gibbs free energy of mixing.
S^E	Excess entropy of mixing.
H^E	Excess enthalpy of mixing.
V^E	Excess volume of mixing.
C_p^E	Excess molal heat capacity.
\bar{v}^E	Excess partial molal volume.
P	Pressure
R	Gas Constant.
T	Absolute Temperature.
f	Fugacity
ϕ	Volume fraction
\bar{G}^{id}	Ideal partial molal free energy.
γ_i	Activity coefficient of component i.

n_D^t	Refractive index for Na-D line at $t^\circ\text{C}$.
d_4^{25}	Absolute density of liquid at 25°C .
η	Viscosity
F	Fluidity
i	As a subscript, donotes the i^{th} component of a solution.
o	As a superscript, donotes the property in the pure state.
I	Souder's viscosity-constitutional constant.
m	Souder's viscosity-density constant.
M	Molecular weight.
α	Coefficient of volume expansion.
K_T	Isothermal compressibility.
K_S	Structural part of the coefficient of compressibility.
K_g	Geometrical part of the coefficient of compressibility.

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CHAPTER I

A. GENERAL INTRODUCTION

Of all the physical properties of solutions none is more accessible to thermodynamic treatment than the vapour pressure. In the study of the colligative properties of solutions use has been made of methods involving the elevation of the boiling point, the lowering of the vapour pressure and the lowering of the freezing point of the solvent by the solute. Because of the ease and accuracy of the measurements most investigators have confined themselves to the application of the freezing point and the boiling point methods. These methods suffer from the drawback of limited application because of the fact that they can be used accurately only for a narrow temperature interval. The latter method is further handicapped because accurate specific heat data for liquids at temperatures near their boiling points are not usually available.

The study of solutions of non-electrolytes is already very old. The thermodynamic relations were developed quite early, particularly for dilute solutions. In the study of the thermodynamic properties of binary or ternary systems it is necessary to establish the observed deviations from ideal behaviour on the basis of the predictions from the theory of perfect solutions.

The nature of solutions is complex. Numerous experimental methods have been developed, and many branches of mathematical physics, such as thermodynamics, statistical mechanics, etc., have been applied to the study. A great deal has been achieved by theory, but this achievement has been by no means enough to warrant the neglect of further experimental investigation.

The system Acetone-Benzene-Chloroform has been studied extensively by Reinders and de Minjer (1) as regards boiling points, isobaric vapour-liquid equilibria and the distillation paths. Although their studies have contributed substantially to the elucidation of the complex nature of the course of the distillation paths, no attention has been given to the thermodynamics of this system or of its component binary systems. The system Acetone-Chloroform has been studied with respect to its vapour pressure at different temperatures but accurate data are not available at 25°C. In undertaking a general study of the physical properties of this system, I have turned my attention to isothermal measurements in order to be able to describe some aspects of the thermodynamics of the system. Of numerous thermodynamic data, those of most importance for isothermal studies are heats of mixing, vapour pressures, volume changes, etc. The heats of mixing for Acetone-Benzene-Chloroform system and its contiguous binary systems have been investigated by Campbell, Kartzmark and Friesen (2).

The first aim of the present research was to investigate the volume changes and the vapour-liquid equilibria. The thermodynamic implications of vapour pressure determinations are to ascertain quantitatively the non-ideality of the system. At the same time the direct measurements of volume changes on mixing yield partial molal volumes of the constituents, another measure of non-ideality.

A theory of solutions of non-electrolytes which describes adequately the thermodynamic properties on the basis of the observed data has yet to be developed. This, of course, is obvious, since the specialized application of the fundamental concepts of statistical mechanics under circumstances where influences such as intermolecular forces are predominant tends to complicate the treatment. Consequently the first step in constructing a theory requires a quantitative investigation of these effects. If this is done correctly, and if under suitable conditions the results are verified experimentally, the next step in elucidating the liquid state of matter from the observed deviations from these laws may be undertaken with some hope of success. Unfortunately, experimental work is too limited to give any evidence in support of a probable theory. Nevertheless, experimental work with the solutions of non-electrolytes is continuing in almost all the leading research laboratories, specially since it has

been realised that all deviations from ideal solution laws should not necessarily be attributed to chemical effects, association, dissociation, and solvation, as has been so often done, to the neglect of the van der Waals effects. The consideration of "van der Waals forces" is essential to an appreciation of the meaning of ideal behaviour and to the derivation of any particular form of ideal solution law.

B. THEORETICAL INTRODUCTION

CHARACTERISTICS OF IDEAL SOLUTION

(a) Raoult's law for vapour pressures.

The vapour pressure of a liquid is defined as the pressure exerted by the vapour in equilibrium with the liquid at a particular temperature. Obviously the vapour pressure is characteristic of the nature of the substance and of the temperature, and of the composition if the liquid is a mixture.

When two liquids are dissolved in each other, the vapour pressure of the mixture is due to both types of molecule that are present in the mixture (interactions). In such a case the composition of the vapour may differ from that of the liquid if the vapour pressures of the two components are different. The magnitude of partial vapour pressure is given by Dalton's law which states that at constant temperature the total pressure of a mixture is

equal to the sum of the partial pressures of the individual components of the mixture assuming the components to be ideal in gas phase. The partial vapour pressure depends on the concentration of the molecules of the species concerned in the vapour phase. This is readily evaluated from the mole fraction of the species in the vapour phase and the total vapour pressure of the mixture by the relation,

$$P_1 = y_1 P \dots\dots\dots (1)$$

In a solution each component exerts a partial pressure P_1 . An ideal liquid solution is defined as one which obeys Raoult's law over the whole range of composition at all temperatures and pressures. According to the original form of this law, the partial vapour pressure P_1 of any constituent of a liquid solution is equal to the product of its mole fraction x_1 in the solution and its vapour pressure P_1° in the pure state at the same temperature.

Expressed in symbols

$$P_1 = P_1^{\circ} x_1 \dots\dots\dots (2)$$

If a liquid has a low vapour pressure, it must have a high boiling temperature, and, in general, the boiling-point - composition curves are opposite in character to the vapour pressure - composition curves.

In an ideal liquid pair, the liquidus or vapour pressure curve must be a straight line joining the vapour pressure of the pure components (when composition is plotted as mole percentage) and the vapour curve may lie above or below this. In Figure 1, a vapour-pressure-vapour composition curve for a solution obeying Raoult's law is shown. The straight line gives the total pressure above the solution as a function of the mole-fraction of B in solution, x_B , while the curve lying below it represents the total vapour pressure as a function of the mole fraction of B in the vapour, y_B . It will be observed that the vapour is always richer in B than the solution, i.e., the vapour is richer in the more volatile component.

In a non-ideal solution, particularly if the boiling points are fairly close together, the increased or decreased volatility due to the chemical influence of the other component may be sufficient to cause a minimum or a maximum in the boiling-point curve (corresponding to a maximum or a minimum in the vapour pressure curve).

Several examples of solutions showing different characteristics noted above are reported in the literature. Comprehensive discussions of vapour-liquid equilibria in various systems are to be found in the works of Dodge (3), Robinson and Gilliland (4) and Young (5).

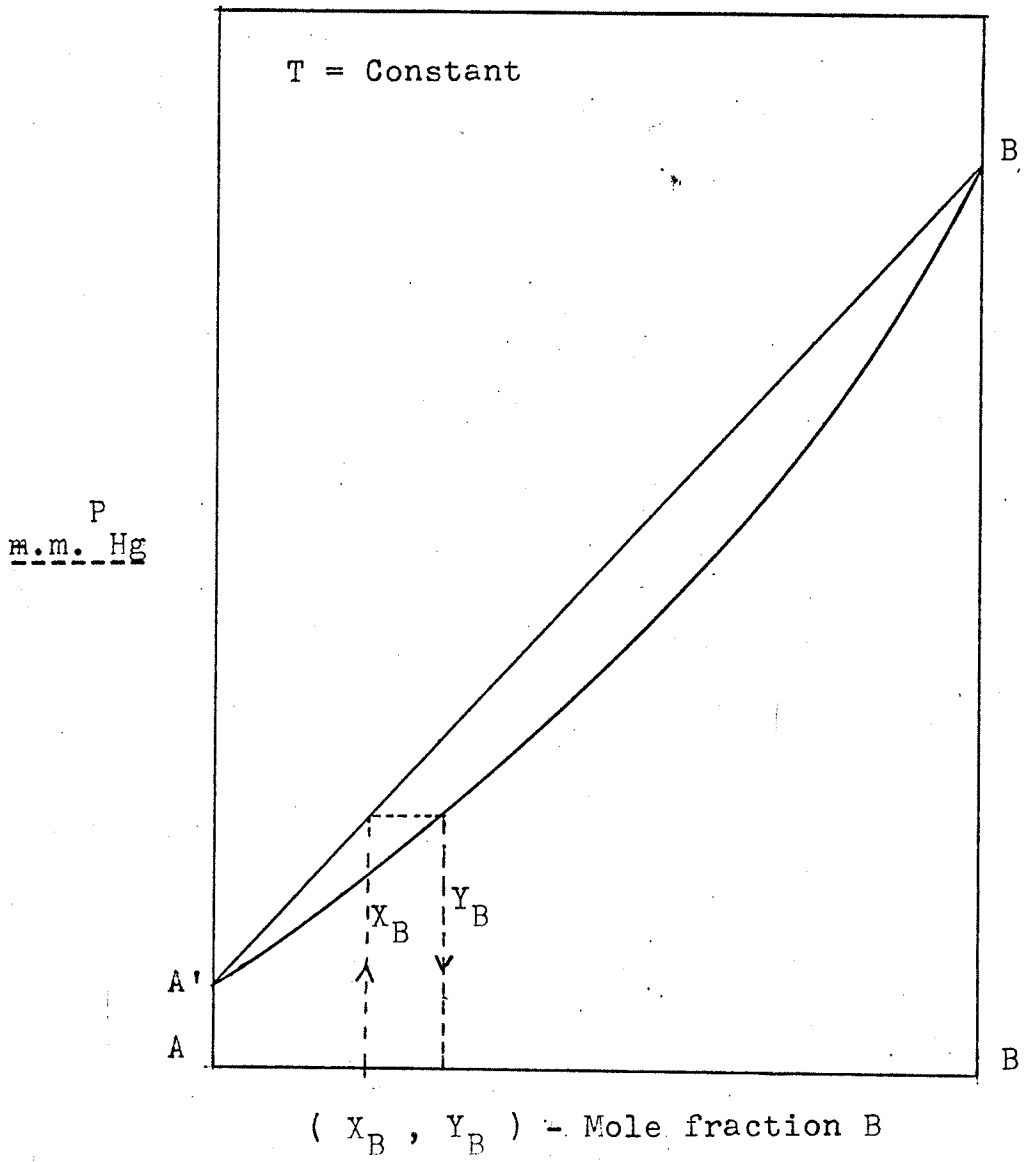


Figure I - Liquid and Vapour Composition Curves for an Ideal Solution

Attention may be called here to the restriction in connection with Raoult's law that the total (external) pressure, under which the system is in equilibrium, should remain constant as the composition is changed, at a given temperature. This has been implied in the foregoing treatment of Raoult's law. At moderate pressures, however, the vapour pressure is virtually independent of the external pressure; hence, in many of the practical applications of Raoult's law, the restriction of constant total pressure is not emphasized, although for strict accuracy it should be understood.

Theoretical considerations show that if a mixture of two liquids is to behave ideally, the two types of molecules must be similar. The environment of any molecule in the solution, and hence the force acting upon it, is then not appreciably different from that existing in the pure liquid. It is to be anticipated, therefore, that under these conditions the partial vapour pressure of each constituent, which is a measure of its tendency to escape from the solution, will be directly proportional to the number of molecules of the constituent in the liquid phase. For thermodynamic purposes it is preferable to use the idealized form of Raoult's law,

$$f_1 = x_1 f_1^0 \dots\dots\dots (3)$$

where f_1 is the fugacity of the constituent i , either in

the vapour or in the solution in equilibrium with it, since they are identical, and f_i^0 is the fugacity of the pure liquid at the same temperature and pressure. In an ideal case the fugacity is assumed to be identical with vapour pressure. In most solutions, however, there is some type of influence of one component on the other so that equation (2) does not hold. There may be a tendency for chemical action, forming a compound in solution as, for example, in a chloroform and acetone mixture. In other cases the presence of the second liquid breaks down the larger units of the first liquid and renders the first liquid more volatile (de-polymerization and dissociation).

If the constituents of a mixture differ appreciably in nature, deviations from ideal behaviour are to be expected and are, in fact, observed. These deviations are most frequently "positive" in nature, so that the actual partial vapour pressure (or fugacity) of each constituent is greater than it should be if Raoult's law were obeyed. Negative deviations from ideal behaviour are only observed in systems in which the different molecules have a very strong attraction for one another. It has been argued by Hildebrand and Scott (6) that positive deviations are favoured by differences in "internal pressure" or molecular attractive force and that negative deviations are favoured by a tendency to compound formation

between the two components or by a marked difference in size of molecules. It seems that the use of the deviations from Raoult's law for the characterization of the deviation from ideality is somewhat questionable, especially because, for instance, when there are large differences in the molar volumes of the components, the simple relations assumed in Raoult's law have to be modified. This has been discussed at some length by Guggenheim (7) and by Fredenhagen (8). According to Scatchard (9) the thermodynamic functions of mixing might be plotted usefully as a function of the volume fraction, when the differences in molar volumes are large. However, the data are generally reported as functions of mole fraction and have been so done in this thesis.

(b) Thermodynamic functions of mixing

The use of the foregoing definition of an ideal solution given by equation (2) implies certain properties of such a solution. Accordingly a solution can be termed perfect or ideal when the Gibbs free energy of mixing of two components is given by

$$G_{id}^M = RT (x_1 \ln x_1 + x_2 \ln x_2) \dots\dots\dots (5)$$

Prigogine (10) in his treatise provided definitions for the thermodynamic functions of mixing for non-electrolytes. He pointed out that all existing relations between extensive and intensive parameters in classical thermodynamics should equally hold for these functions of mixing. Taking the simplest case of binary solutions different functions can be written according to Prigogine. Thus Gibbs free energy, entropy, enthalpy and volume changes of mixing are represented by the following equations

$$G^M = G - (x_1 G_1^{\circ} + x_2 G_2^{\circ}) \dots\dots\dots (6)$$

$$S^M = S - (x_1 S_1^{\circ} + x_2 S_2^{\circ}) \dots\dots\dots (7)$$

$$H^M = H - (x_1 H_1^{\circ} + x_2 H_2^{\circ}) \dots\dots\dots (8)$$

$$V^M = V - (x_1 V_1^{\circ} + x_2 V_2^{\circ}) \dots\dots\dots (9)$$

where for example in equation (6), G = free energy of the solution, G_1° , G_2° are the free energies of the pure components and x_1, x_2 their mole fractions. The thermodynamic functions of mixing, and their deviation from ideality provide a more useful and general method for the classification of binary or ternary solutions.

PARTIAL MOLAL QUANTITIES

The quantitative study of solutions has been greatly

advanced by the introduction of the concept of partial molal quantities. A property of a solution, e.g., the molal volume of a mixture of alcohol and water, changes continuously as the composition is changed, and considerable confusion formerly existed in expressing these properties as a function of composition. In this connection the concept of partial molal properties, as developed by Lewis (11), is of great value. He defined the partial molal property of a component of a solution as follows: Let J represent any extensive property (e.g., V , G , S , H etc) of a binary solution; at constant temperature and pressure J then will be a function of the independent variables n_1 and n_2 which represent the numbers of moles of the two components present. The partial molal property of component 1 is then defined by the relation

$$\bar{J}_1 = \left(\frac{\partial J}{\partial n_1} \right)_{n_2, T, P} \dots \dots \dots (10)$$

Similarly for component 2,

$$\bar{J}_2 = \left(\frac{\partial J}{\partial n_2} \right)_{n_1, T, P} \dots \dots \dots (11)$$

This is readily extended to the i^{th} component of a multi-component system

$$\bar{J}_i = \left(\frac{\partial J}{\partial n_i} \right)_{T, P, n_{j \neq i}} \dots \dots \dots (12)$$

The usefulness of the concept of partial molal quantities lies in the fact that it may be shown mathematically that

$$J(n_1, n_2) = n_1 \bar{J}_1 + n_2 \bar{J}_2 \quad (T, P \text{ constant}) \dots\dots (13)$$

Any extensive property of the solution may be expressed in this manner in terms of partial molal properties, which themselves are functions of the concentration of the solution, the temperature and the pressure and must be evaluated by means of experimental measurements.

The partial molal free energy is identical with the function described by J. W. Gibbs, known as the chemical potential and is given by

$$\bar{G}_i = \mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq i}} \dots\dots\dots (14)$$

The chemical potential of a component of a solution can be defined in terms of thermodynamic function of mixing and in the case of the volume of the component in a solution, partial molal quantities are written as

$$\mu_1^M = \mu_1 - \mu_1^0 \dots\dots\dots (15)$$

$$\bar{V}_1^M = \bar{V}_1 - \bar{V}_1^0 \dots\dots\dots (16)$$

where $\mu_1^0 = G_1^0$ = Gibbs free energy of the pure component.

Similarly the partial molal entropy is

$$\bar{S}_1^M = \bar{S}_1 - \bar{S}_1^0 \dots\dots\dots (17)$$

The definition of an ideal solution in terms of equation (5) implies that if this equation is valid over a non-zero range of temperature and pressure, then the heat of mixing and the volume of mixing are necessarily zero. The entropy of mixing, however, is given as

$$S^M = - \frac{\partial G^M}{\partial T} = - R (x_1 \ln x_1 + x_2 \ln x_2) \dots (18)$$

and is not equal to zero.

ACTIVITY COEFFICIENTS

It is instructive to compare a few of the related functions. Lewis (12) introduced the activity coefficient $\gamma = \frac{a}{x}$, where a is the activity and is assumed to be equal to P/P^0 . The logarithm of the activity coefficient is proportional, in an isothermal system, to the difference, $\bar{G} - \bar{G}_{id}$, between the actual partial molal free energy and what it would be in an ideal solution. When the partial quantities are known, it is possible also to calculate the total free energy of mixing of a mole of solution from its pure liquid components by the relation,

$$\begin{aligned} G^M &= x_1 (\bar{G}_1 - G_1^0) + x_2 (\bar{G}_2 - G_2^0) \\ &= RT (x_1 \ln \gamma_1 x_1 + x_2 \ln \gamma_2 x_2) \dots \dots \dots (19) \end{aligned}$$

The γ - values in the above expression can be determined from vapour-pressure measurements. The functions V^M and

H^M are not necessarily zero in this case. The total heat of mixing and the total entropy of mixing are similarly related to the partial quantities and any one of these three functions can of course be calculated when the other two are known.

MEASURES OF ACTIVITY

The two commonly used measures of the activities of the components of liquid mixture are (1) vapour pressures, for completely miscible liquids, and (2) mutual solubility or critical temperature and composition for mixtures of limited solubility. Systems with two liquid phases such as Acetic acid-Water-Chloroform studied by Campbell, Kartzmark and Gieskes (13) in this laboratory offer the advantage of presenting larger deviations from ideality, and put greater strains upon any theory. Total vapour pressure is easily measured, but it is considered desirable to know the partial pressures, and it is usually difficult to measure vapour compositions accurately, especially in the region where one component is dilute. Moreover, unless the pressures are low, accurate corrections for deviations from ideal gas behaviour must be made (14,15).

If the total vapour pressure is measured over the whole composition range, one may calculate the partial pressures with the aid of the Gibbs-Duhem equation.

Barker (16) has outlined successive approximation methods for deducing excess free energies from total pressure data, and Myers and Scott (17) have refined his procedures for data processing with high speed electronic computers.

Williamson and Scott (18) have recently found that the data on the system $C_6F_{14} + C_6H_{14}$ show more consistency and a better fit if only total vapour pressures are used, and if the vapour composition data are disregarded. They urge a careful re-examination of the whole problem of deriving free energies from vapour pressure data to see whether the extra effort required to measure vapour compositions in an equilibrium still is worthwhile.

However, very few investigators have attempted to calculate partial pressures from total pressure data alone, without trying to know the vapour composition data. I have used vapour pressure and vapour composition data to calculate the free energies.

The total vapour pressure is given by Dalton's law as follows

$$P = x_1 P_1^0 + x_2 P_2^0 \dots\dots\dots (20)$$

In the ideal case P_1 as defined in equation (1) and in equation (2) are equal. In a non-ideal system, of course, they are different. Taking the difference between the actual partial vapour pressure calculated from (1) and the

ideal vapour pressure calculated from (2) it is possible to find the positive or negative deviation of any system from Raoult's law. The ratio of these two pressures has been defined earlier as activity.

EXCESS FUNCTIONS

Although it is still customary to consider the behaviour of solutions of non-electrolytes from the point of view of deviations from Raoult's law, in recent years the importance of the description of deviations from ideality by means of thermodynamic excess functions has been realized.

Various functions have been used for expressing the deviation of observed behaviour of solutions from that expected for idealized systems. Some, such as the activity coefficient, are most convenient for measurement of departures from ideality for a particular component of a solution. The most convenient measure for the solution as a whole, however, is the series of excess functions, first introduced by Scatchard (19). A thermodynamic excess function is defined by the difference between the thermodynamic function of mixing for an actual system and the thermodynamic function of mixing of a perfect system under the same conditions of temperature, pressure and composition. Thus the excess Gibbs free energy may be represented by the following expressions for a binary mixture

$$\begin{aligned}
 G^E &= G - (x_1 G_1^0 + x_2 G_2^0 + RTx_1 \ln x_1 + RTx_2 \ln x_2) \\
 &= G^M - (RTx_1 \ln x_1 + RTx_2 \ln x_2) \\
 &= RTx_1 \ln \gamma_1 + RTx_2 \ln \gamma_2 \dots\dots\dots (21)
 \end{aligned}$$

The thermodynamic excess functions differ from the thermodynamic functions of mixing only for quantities which involve the entropy. For example, the excess enthalpy H^E is identical with the enthalpy of mixing given by equation (8). Furthermore the excess volume V^E is identical with the volume of mixing given by equation (9). This is evident from the fact that the volume change on mixing and heat of mixing are equal to zero for a perfect solution, and as a consequence the volume changes and heats of mixing are by definition excess functions.

The excess entropy in terms of activity coefficients is given by

$$S^E = -Rx_1 \ln \gamma_1 - Rx_2 \ln \gamma_2 - x_1 RT \frac{\partial \ln \gamma_1}{\partial T} - x_2 RT \frac{\partial \ln \gamma_2}{\partial T} \dots\dots (22)$$

The excess free energy is deduced from the determination of the activity co-efficients which are generally obtained from vapour pressure measurements. The data for activity coefficient of a component are generally arrived at using the formula

$$\gamma_1 = \frac{P_{y1}}{P_1^0 x_1} \dots\dots\dots (23)$$

where P is the total pressure, y_1 is the vapour composition, P_1^0 the vapour pressure of the pure component at the same temperature and x_1 the liquid composition.

The excess enthalpy is the heat of mixing at constant pressure per mole of solution; it may be deduced either from direct measurements or from the temperature variation of the activity co-efficients. The excess entropy can then be calculated from

$$TS^E = H^E - G^E \dots\dots\dots (24)$$

Another important excess function is the excess volume which is derivable from the change of the activity coefficients with pressure. It may be directly obtained from density measurements of the mixture and the pure components or by using a direct dilatometric method, the method actually used in this research.

Other interesting excess functions are the excess specific heat and the change of the excess volume with pressure. The quantities of importance providing some useful information on the excess functions are the excess free energy and excess enthalpy as functions of pressure and temperature respectively. The former is the excess volume of mixing and the latter the excess heat capacity as given by the following expressions

$$v^E = \left(\frac{\partial G^E}{\partial P} \right)_T \dots\dots\dots (25)$$

$$C_P^E = \left(\frac{\partial H^E}{\partial T} \right)_P \dots \dots \dots (26)$$

Several different equations have been suggested or developed by Herington (19), Coulson, Hales and Herington (20), Redlich and Kister (21), Scatchard (22,23), Kamke and Kummerle (24) and Wilson (25) for testing the consistency of the derived excess functions. Scatchard and Raymond (15) and also Haase (26) developed a formula for the activity coefficients which included a second virial coefficient of the pure vapour as a corrective term. All the above mentioned equations represent the excess functions of nonelectrolytes with two, or sometimes three, parameters for a binary mixture and additional parameters for poly-component systems. A theoretical or semitheoretical interpretation has always been given, but unfortunately, in the systems reported in the literature sufficient P-V-T data are not available for the non-electrolytes, thereby making it difficult to apply the corrections. Another drawback is the failure to measure the second virial coefficients directly. Lambert (27) pointed out that in the case where association occurs in the vapour phase the second virial coefficient cannot be calculated from the data for corresponding states, and has to be measured. The series of publications in recent years by Scatchard and his associates gives theoretical treatment of the vapour-liquid equilibrium.

ZAWIDZKI TREATMENT

Apart from the investigation of non-ideality on the basis of deviations from Raoult's law, another interesting example is the thermodynamic behaviour of solutions with regard to the applicability of the Gibbs-Duhem equation. von Zawidzki (14) treated several binary systems by this method, after determining the vapour pressures.

In contrast to binary solutions, for which the Gibbs-Duhem equation requires a reduction of activity of one component when it is diluted by another component, the activity of one component of a multi-component system may either increase or decrease upon addition of another component. This may be seen by inspection of the Gibbs-Duhem equation of the general form.

$$\sum_1 x_1 d\mu_1 - VdP + SdT = 0 \dots\dots\dots (27)$$

According to von Zawidzki (14) the mole fraction in equation (27) is determined by the molecular weight of the substances concerned in the vapour phase. This is of particular interest in highly complex systems where several types of association, polymerization etc., in the liquid phase have been suggested. In such a case, however, surface energies and forces are neglected and only the work of dilution is considered.

For an isothermal equilibrium the Gibbs-Duhem-Margules equation for a two-component system can be derived as

$$\frac{d \ln P_1}{d \ln x} = \frac{d \ln P_2}{d \ln (1-x)} \dots\dots\dots (28)$$

where P_1 and P_2 are the partial pressures of the components and x is the mole-fraction of the component with the lower boiling point, in the liquid phase.

Zawidzki (14) studied a number of two-component systems and measured their vapour pressures to justify the Gibbs-Duhem-Margules equation.

Margules (28) indicated the possible solutions for the differential equation in the following way

$$P_1 = P_1^0 x^{\alpha_0} e^{\alpha_1(1-x) + \frac{\alpha_2}{2}(1-x)^2 + \frac{\alpha_3}{3}(1-x)^3}$$

$$P_2 = P_2^0 (1-x)^{\beta_0} e^{\beta_1 x + \frac{\beta_2}{2} x^2 + \frac{\beta_3}{3} x^3} \dots\dots\dots (29)$$

In the above equations α and β are constants between which the following relations exist

$$\beta_0 = \alpha_0 - \alpha_1 \qquad \beta_2 = \alpha_2 + \alpha_3$$

$$\beta_1 = -\alpha_1 \qquad \beta_3 = -\alpha_3$$

When Raoult's law is obeyed these relations become

$$\alpha_0 = \beta_0 = 1 \quad \text{and} \quad \alpha_1 = \beta_1 = 0, \quad \alpha_2 = \beta_2 = 0$$

$$\alpha_3 = \beta_3 = 0$$

In most cases, even with only two constants a satisfactory approximation may be obtained and thus Zawidzki arrived at the following equations whose validity is to be checked with the experimental results

$$\begin{aligned} P_1 &= P_1^0 x e^{\frac{\alpha_2}{2} (1-x)^2 + \frac{\alpha_3}{3} (1-x)^3} \\ P_2 &= P_2^0 (1-x) e^{\frac{\beta_2}{2} x^2 + \frac{\beta_3}{3} x^3} \end{aligned} \quad (30)$$

The constants in the above equations are derived from any of the experimental partial pressure curves. If the result is unsatisfactory this can be followed by a further approximation of the values of the constants.

KAMKE TREATMENT

Kamke (24) indicated another method of making use of the vapour-liquid equilibrium data. The Gibbs-Duhem-Margules equation as given in equation (28) can be written as

$$x \frac{d \ln P_1}{dx} + (1-x) \frac{d \ln P_2}{dx} = 0 \quad (31)$$

From equation (1) it follows

$$P_1 = y P \quad (32)$$

$$P_2 = (1-y)P \quad (33)$$

where P is the total pressure and y is the mole-fraction in vapour phase of the component with the lower boiling

point. It is then possible to write the differential equation

$$\frac{1}{P} \frac{dP}{dx} = - \frac{x-y}{y(1-y)} \frac{dy}{dx} \dots\dots\dots (34)$$

Kamke then wrote

$$\frac{x-y}{y(1-y)} = f(y)$$

and rearranging he obtained

$$x = y + y (1-y) f (y) \dots\dots\dots (35)$$

This is the equation of the equilibrium curve associated with the total pressure curve. For the total pressure it also follows

$$P (y) = P_2^0 e^{-\int_0^y f(y) dy} \dots\dots\dots (36)$$

where P_2^0 = total pressure of the higher boiling component at $y = 0$

Use is made of the plot of this function $f(y)$ to obtain the $P(x)$ curve from the $y-x$ curve by stepwise integration. Lewis and Murphee (29) and Scatchard and Raymond (15) used this function to calculate the total pressure and compared the values with the observed total pressures.

The ideal curve $f_{ideal}(y)$ is calculated according to the formula

$$f_{ideal}(y) = - \frac{1}{a-y} \dots\dots\dots (37)$$

where

$$a = \frac{P_1^0}{P_1^0 - P_2^0}$$

and $P(x)$ has a straight line relationship and also where

$$P(y) = P_2^0 e^{-\int_0^y f_{id}(y) dy}$$

$$= P_2^0 \left(\frac{a}{a-y} \right)$$

Campbell et al (13) have treated the binary system Chloroform-acetic acid according to this and have found the method satisfactory, though it has been somewhat difficult to obtain a reasonable formula for $f(y)$.

They further made use of Kamke's function, $f(y)$, to obtain information on the course of the curve of the excess free energy for the binary system. If molecular free energy of mixing is defined as equation (21) where γ_1 and γ_2 are the appropriate activity coefficients one obtains

$$\frac{G^E}{RT} = x \ln \frac{P_y}{P_1^0 x} + (1-x) \ln \frac{P(1-y)}{P_2^0 (1-x)} \dots \dots \dots (38)$$

which leads to

$$\frac{1}{RT} \frac{dG^E}{dx} = \ln \frac{P_2^0}{P_1^0} \frac{y(1-x)}{x(1-y)}$$

$$= \ln \frac{P_2^0}{P_1^0} e$$

$$= \ln \frac{\gamma_1}{\gamma_2} \dots \dots \dots (39)$$

where $\theta = \frac{y(1-x)}{x(1-y)}$ is the relative volatility and

$$\frac{1}{RT} \frac{d^2 G^E}{dx^2} = \frac{1}{y(1-y)} \left[\frac{1}{1 + (1-2y)f(y) + y(1-y)\frac{df(y)}{dy}} - \frac{1}{1 + (1-2y)f(y) + y(1-y)\{f^2(y)\}} \right] \dots\dots (40)$$

It is possible to find the sign of the curvature and the position of the maximum or minimum of the excess free energy curve from these equations. If G^E does not show a point of inflexion of curvature in the interval $0 \leq x \leq 1$ then it follows from (40) that

$$\frac{df(y)}{dy} \gg -f^2(y) \dots\dots\dots (41)$$

for all values of x .

The position of the maximum or minimum can be found with the help of the relative volatility function and equation (39), since at the maximum or minimum

$$\frac{dG^E}{dx} = 0$$

EXCESS VOLUME

It is important in the theory of liquids to know how the energy of a liquid depends on its volume, and in the theory of solutions to know how the parameters involved

in this relationship for a mixture of two liquids are related to those for the pure components. This problem involves the more fundamental one of how the intermolecular energy of a pair of molecules 1 and 2 at a given separation is related to the energies of the pairs 1-1 and 2-2 at the same separation. It has often been supposed that there is a parameter on which the relationship between the energy and volume of a liquid depends such that for a binary solution this parameter is the geometric mean of those for the pure liquids. This, according to Staveley, Tupman and Hart (30) often seems to hold surprisingly well, even though the systems on which it has been tested usually consist of polyatomic molecules for which the intermolecular forces are not isotropic and certainly do not act from the geometrical centres of the molecules.

It appears therefore that the volume change V^M on mixing at constant pressure (which is the same as the excess volume V^E) is one of the most interesting thermodynamic functions for the mixing process, yet certainly still one of the least understood.

That the simple theories of solutions apply more straightforwardly to processes with zero volume change was recognized at an early stage. Many non-ideal solutions have sufficient thermal energy virtually to overcome the tendency to segregation due to different molecular fields,

and therefore possess nearly ideal entropy of mixing due to maximum randomness, just as in an ideal solution. In other words, there would be no change in randomness and therefore of entropy in transferring one component from the solution to an ideal solution of the same composition, the total volume remaining unchanged. Such solutions have been designated as "regular" by Hildebrand (31). In 1931 Scatchard (9) derived an expression for the heat of mixing with the assumption that the change of volume on mixing is zero.

However, the volume change on mixing at constant pressure is rarely zero, yet it is the constant pressure process which we normally measure in the laboratory. To compare the experimental quantities with those predicted by most theories, it becomes necessary to convert the constant pressure numbers to "constant volume" or vice versa. Methods of making these thermodynamic corrections were first outlined by Scatchard (32), and have been extensively discussed since then by Hildebrand and Scott (33,34), Staveley, Tupman and Hart (30,35) and Scott (36). There are in fact several different processes (36) for which the total volume remains constant, but the only one of practical interest is one which starts with the two as-yet-unmixed components in volumes V_1 and V_2 , each at the same initial pressure, and each of which ends with the mixture

in volume $V_m = V_1 + V_2$ and a different final pressure. The necessary compression or expansion may be performed either on the unmixed components or on the solution; if the necessary data are available for the solution the latter equations are simpler. Accordingly the equations and arguments developed by Scott (36), it does not seem probable that the system Acetone-Chloroform will be suitable for testing the validity of a rough concept like that of the "regular solution".

The notion that positive volume changes (expansions on mixing) are associated with positive deviations from ideality (positive values of G^E) and with the absorption of heat (positive ΔH 's), and negative ΔV 's are associated with negative deviations or liberation of heat is an old one. Early in his research on solutions, Hildebrand (37) noted an empirical relation between the partial molal ΔV and $\log \gamma$. Hildebrand and Scott (38) found a reasonable relation using the data of Zawidzki (14) and Hubbard (39). The first attempt to deduce a quantitative relation between volume change and excess free energy was made by Scatchard (32) in 1937. Hildebrand and Scott (38) applied this relation to a number of systems and found only a qualitative fit. They further described the validity of this relation in case of Acetone-Chloroform as extremely poor. Hence this equation is hardly quantitative.

The change in molar volume on mixing of two liquids has been defined in equation (9). It has also been seen that

this function is the same as the excess volume function V^E . Of special interest are the partial molal volumes of liquids in solution

$$\bar{V}_1^M = \bar{V}_1^E = \bar{V}_1 - V_1^O \quad \dots\dots\dots (42)$$

In the study of systems consisting of two or more substances, i.e., solutions, and of heterogeneous systems containing two or more phases, it is necessary to consider open systems, where composition and mass may vary. In this connection partial molal properties are of importance.

Scatchard (22) has found that V^E or ΔV can usually be expressed by an equation of the form

$$V^E = x_1 x_2 [A + B (x_1 - x_2)] \quad \dots\dots\dots (43)$$

where A and B are constants. The former is about four times the value of ΔV for the equimolar solution, and the latter is zero when the ΔV -x curve is symmetrical.

MOLAR VOLUME AND OPTICAL PROPERTY

Most of our present day knowledge on the polarisability has been derived from an analysis of the refractive index of binary solutions. The molar volume of a binary solution, i.e., the volume of solution containing in all one gram-mole of substance, is defined in terms of the molar fractions, x, and the molar weights, M, of the components and the density, d, of the solution,

$$\bar{V} = \frac{x_1 M_1 + x_2 M_2}{d} = \frac{M_1 + (M_2 - M_1)x_2}{d} \dots\dots\dots (44)$$

Similarly, the molar refraction of the solution is defined by the relation

$$\begin{aligned} \bar{R} &= \frac{x_1 M_1 + x_2 M_2}{d} \frac{n^2 - 1}{n^2 + 2} \\ &= \bar{V} \left(\frac{n^2 - 1}{n^2 + 2} \right) \dots\dots\dots (45) \end{aligned}$$

This is a direct derivation from the Lorenz and Lorentz formula. The molar refraction calculated in this way is the experimental value of molar refraction. In an ideal case equation (45) should be written as

$$\bar{R} = \bar{V} \left(\frac{n^2 - 1}{n^2 + 2} \right) = R_1 x_1 + R_2 x_2 \dots\dots\dots (46)$$

where R_1 is the partial molar refraction of the first component, and R_2 the partial molar refraction of the second. In binary solutions, $x_1 + x_2$ is unity; hence

$$\bar{R} = R_1 + (R_2 - R_1) x_2 \dots\dots\dots (47)$$

For a real solution only experiment can tell us whether R_1 and R_2 are functions of the composition, or whether they are the same as the molar refractions of the pure components.

VISCOSITY

On the basis of his classical researches on the flow of liquids through capillary tubes, Poiseuille (41) deduced the law connecting the viscosity with the geometry of the tube, the driving pressure, and the efflux time. There are several corrections arising from drainage, hydrostatic head, kinetic energy, end effects, and surface tension. It is rather difficult, therefore, to measure the absolute viscosity. Ordinarily, however, relative viscosities are determined and several types of viscometers have been designed to get high degree of accuracy.

The theoretical interpretation of viscosity is one of the most difficult problems in the theory of liquids. Solvation, intermolecular forces, molecular aggregation and other quantities related to the internal structure of liquids and solutions are factors to be considered. The close relationship between viscosity and molecular constitution has rendered this one of the most important properties in the study of solutions.

Early speculators attempted to correlate viscosity with other thermodynamic properties such as specific volume. Ideas regarding the available free space in a liquid were developed from these considerations and many empirical equations were proposed on this basis. These are now of historical interest only. The only important relation

surviving, from its support from theoretical considerations, was suggested by numerous investigators (41,42) of whom Andrade (43) appears to be the first, is

$$\eta = A e^{B/RT} \dots\dots\dots (48)$$

where B is a positive constant. It is generally recognized that this equation does not apply to polar liquids. A critical analysis shows that it is also incapable of reproducing the experimental viscosities of non-polar liquids with sufficient accuracy. The same type of equation was later derived by Eyring (44) and co-workers applying Eyring's reaction rate theory

$$\eta = 1.09 \times 10^{-3} \frac{M^{1/2} T^{3/2}}{V^{2/3} \Delta H_{\text{vap}}} \cdot e^{E_{\text{vis}}/RT} \dots (49)$$

where M = molecular weight

V = molar volume

ΔH_{vap} = latent heat of vaporization

E_{vis} = activation energy of viscous flow

If Eyring's interpretation of viscosity as a rate process, involving the activation energy for viscous flow, is accepted, then this flow may be considered as a thermodynamic property which may be correlated with more familiar similar properties in particular the entropy. Mason, Kampmeyer and Robinson (45) have measured the viscosities of aqueous

solutions of a number of amino-acids at 25°C and 35°C and have interpreted their data with this correlation in mind. They pointed out that a liquid possessing a high degree of order may be expected to have a greater energy of activation for viscous flow than a liquid possessing a lower degree of order. Since entropy is related to structural order, they deduced a "differential energy of activation" which can be compared to the differential entropies of dilution. They expected that these quantities should show a parallel behaviour with changes in concentration. Their results for the amino acids are not very convincing as might be expected from the questionable applicability of Eyring's theory to solutions in an associated solvent. The treatments of Eyring equation are exceedingly complex and are not considered here in detail, especially since the derivations, and interpretations put on the results, are still very much a controversial matter. For example, Telang (46) deduced an exponential relationship from slightly modified assumptions and obtained an activation energy approximately one-third that obtained through Eyring's theory. Obviously, a theory which is in such a state for pure unassociated liquids is a long way from being applicable to solutions in general.

A number of equations (47) involving quantities such

as pressure, volume, surface tension, density, velocity of sound, refractive index, latent heat of fusion and evaporation and molecular weight have been given very recently to describe viscosity data.

In the absence of any satisfactory equation from which viscosities may be calculated, recourse must be made to equation (48). The equation suggests a rate process where B is the activation energy of viscosity, and A a constant of the system. This was thought to be independent of temperature by Andrade (48), but later on proved to be temperature dependent by Frenkel (49). Since the bonds between neighbouring molecules which must be broken in order to form a hole, are the same as those broken in the process of vapourization, it follows that the energy required to form a hole should be equal to the energy of vapourization E_{vap} . (surface energy). The free energy of activation should thus be similar to the energy of vapourization. Empirically it is found (50) that $\Delta E_{\eta} = \frac{\Delta E_{\text{vap}}}{2.5}$. This result indicates that the hole size required for molecular motion is only a fraction of the specific volume of the molecule (51).

A further relationship was proposed by Batschinski (52)

$$\eta = \frac{C}{V_S - V_0} \dots\dots\dots (50)$$

where V_S is the specific volume and V_0 and C are constants.

This requires the fluidity to be a linear function of the specific volume, over a range of temperature.

VISCOSITY OF MIXTURES

Using the average potential model of Prigogine and coworkers (10) one can predict, at least semiquantitatively, the thermodynamic functions for mixtures when one knows the properties of the pure components. With regard to a property like the viscosity of mixtures the situation is less satisfactory. The only workable theory is perhaps that of Eyring and coworkers (44) and its extension by Grunberg (53). This theory, however, contains an empirical correction term of appreciable magnitude, and it can therefore primarily be considered as a convenient way of classifying experimental results.

The difficulty in setting up a theory for viscosity of mixtures is that one does not have a good theory for viscosity of pure liquids. A more promising way of attacking the problem for the time being is therefore to make a semi-phenomeno-logical theory in which one uses the properties of the pure liquids without trying to account for them by means of corresponding states, since the fluidity of a liquid can be described using only two parameters, viz. $F = A \exp(-B/RT)$. Bak and Anderson (54) developed a method for treating the fluidity of mixtures on this basis. For a

mixture, ideal with respect to fluidity, they wrote

$$F = x_1 F_{11} + x_2 F_{22} \dots\dots\dots (51)$$

where F_{11} and F_{22} are the fluidities of the pure components, and x_1 and x_2 are the mole fractions. For a non-ideal solution they therefore set

$$F = x_1 F_1 + x_2 F_2 \dots\dots\dots (52)$$

where F_1 and F_2 are quantities calculated from the consideration of the size effect and the dipolar effect. They have not been able to give a satisfactory theoretical development along these lines for two out of three mixtures for which they measured viscosity.

Souders (55) found an equation relating viscosity and density to fit the data on several organic compounds

$$\log_{10} (\log_{10} \eta) = m d - 2.9 \dots\dots\dots (53)$$

The viscosity-density constant, m , is characteristic of each liquid and when multiplied by molecular weight, M , becomes a constitutive property, I , of each compound

$$mM = I \dots\dots\dots (54)$$

Samú and Lima (56) proposed an equation to calculate the viscosity-constitutional constant of Souders for binary mixtures as follows

$$I_{12} = x_1 I_1 + x_2 I_2 \dots\dots\dots (55)$$

or, combining equations (53) and (54),

$$I_{12} = \left[(x_1 M_1 + x_2 M_2) / d \right] \left[\log (\log \eta) + 2.9 \right] \dots\dots (56)$$

in which x_1 and x_2 are the mole fractions; I_1 and I_2 Souder's constants; M_1 and M_2 the molecular weights of components 1 and 2 respectively; d is the density of the mixture; η the viscosity of the mixture in millipoises. Thus, it is possible to calculate I_{12} for a binary mixture if the viscosities of both components are known.

A further equation was derived by Tamara and Kurata (57) that connected the viscosity coefficient of a mixture of liquids, that of its constituents, and its composition. Thus, for the liquids A and B

$$\eta = x_A \phi_A \eta_A + x_B \phi_B \eta_B + 2 (x_A x_B \phi_A \phi_B)^{1/2} \eta_{AB} \dots\dots (57)$$

where η_A and η_B are the viscosity coefficients of the corresponding liquids, η_{AB} is "mutual viscosity", x_A and x_B are mole fractions, and ϕ_A and ϕ_B are volume fractions.

In order to study the interaction between components A and B, it is often useful to investigate the properties of solutions of A and B in a solvent C. Izmailov (58) argues that this becomes imperative if either A or B is associated. Indeed, departure from additivity must be defined as the difference between the value of some property of the system

after interaction between A and B sets in and the value of that property before interaction but after mixing of A and B. This last restriction is important if A or B are associated and a study of the system A-B in a solvent C is a convenient way of removing it. This idea can be applied to all properties of the system including viscosity as shown by theoretical derivatives with the Duhem-Margules law as a starting point in Izmailov's publication (58).

Thus the theory of viscosity for simple liquids and for solutions is obviously not in a very advanced stage of development. Some results of importance to the theory of viscosity have been obtained from studies of colloidal systems, but in general, workers in this field have adopted a somewhat different method of attack, of particular applicability to solutions of large molecules, so that their deductions do not have universal significance. The lack of theoretical support, however, has not deterred investigators from making use of viscosity measurements in a wide variety of investigations and applications. The attempt to measure viscosity in this research is therefore not fruitless.

CHAPTER II

NATURE OF THE PROBLEM AND REVIEW OF THE LITERATURE

ACETONE-CHLOROFORM-BENZENE

The ternary system Acetone-Chloroform-Benzene has been extensively studied by Reinders and de Minjer (1) as regards isobaric boiling points, isobaric vapour-liquid equilibria and the distillation paths. The vapour-liquid equilibria at constant temperature for this system have not been reported in the literature. Reinders and de Minjer have discussed the course of distillation paths for several types of systems, with or without ternary miscibility gap. Haase (59) gave a detailed treatment of the vapour-liquid equilibria, distillation paths and boiling points of ternary systems. He (60) has further given a good account of the thermodynamic relationships of the various phases in multi-component systems. The study of the isothermal vapour pressures of the present system has not been done by any investigator. In this laboratory Campbell, Kartzmark and Gieskes (13) studied the vapour pressures at 25°C for the system Acetic Acid-Chloroform-Water. They also measured the volume changes on mixing for this system. Campbell and Gieskes (61) studied the boiling points at 760 mm. Hg for this system. The study of the dielectric behaviour and heats of mixing for the Acetic Acid-Chloroform-Water system

was also reported by Campbell and Gieskes (62,63). The critical temperatures for this system were earlier reported by Campbell and Kartzmark (64).

In view of the above study by Campbell et al in this laboratory and their calculations of the thermodynamic functions in a partially miscible system, it was proposed to extend it to the present system which did not show any miscibility gap and which was known to form a binary compound. Accordingly the study of Acetone-Chloroform-Benzene system was taken up to complete the thermodynamic data. A study of this system is of particular interest in relation to that carried out by Campbell, Kartzmark and Gieskes (13). In the system Acetic Acid-Chloroform-Water there appeared a curve of zero-volume of mixing in the ternary system. This curve coincided with that of zero-heat of mixing. It was proposed by the authors to call this "the line of semi-ideality". An argument was developed in which they predicted that along the curve of semi-ideality thermodynamic functions G^E and TS^E are zero. This argument, however, could not be convincingly proved.

Campbell, Kartzmark and Friesen (2) studied the heats of mixing for the system Acetone-Chloroform-Benzene at 25°C and found that there appeared a curve of zero-heat of mixing in this system. The volume changes on mixing for this ternary system were therefore determined in this research in order to find out whether the curve of zero volume of



mixing co-incided with that of zero-heat of mixing obtained by Campbell, Kartzmark and Friesen (2), as it did for the system Acetic Acid-Chloroform-Water. No data on volume changes are reported in the literature for the ternary system Acetone-Chloroform-Benzene excepting those calculated from the density data of Campbell, Kartzmark and Friesen (2). These values were very small and both positive and negative values were obtained, though attention was limited to a small region of the concentration triangle. The curve of zero-heat of mixing was of considerable interest, since it seemed to indicate a narrow region of pseudo-ideality, in a very non-ideal system.

I have also determined the isothermal vapour-liquid equilibria and the vapour pressures of the ternary system Acetone-Chloroform-Benzene, in order to complete the thermodynamic data. These permit the calculations of the excess Gibbs free energy of mixing, G^E . Then, by means of the heats of mixing data of Campbell et al (2) it is possible to evaluate TS^E from these data.

Campbell et al (2) have studied the freezing points, boiling points and dielectric constants for this system. The densities, refractive indices and the viscosities have been determined by me in this research.

ACETONE-CHLOROFORM

To study a binary system from the standpoint of its "excess function curves", it is necessary to know the excess Gibbs free energy G^E and the heat of mixing H^E at the same temperature. Usually, however, G^E , has been determined at a higher temperature than H^E , and a knowledge of C_p for the system is necessary to correct H^E to the temperature of measurement of G^E . On the other hand, it is possible to determine the vapour pressures at the same temperature at which H^E 's have been determined. Campbell *et al* (2) have reported H^E values for this binary system at 25°C. H^E values at different temperatures are given in the literature. The important excess heat content data for this system are reported by Hirobe (65) and Kearns (66) and they agree fairly well with those of Campbell and Kartzmark (67), who further studied the compound between acetone and chloroform in the liquid state and calculated the energy of the hydrogen bond, from the heats of mixing data.

The vapour pressures at different temperatures have been studied for this system by numerous investigators including Zawidzki (14), Skirrow (68), Schmidt (69), "Rock and Schröder" (70), Mueller and Kearns (71), Rabinovitch and Nikolaev (72). These authors also reported the vapour-

liquid equilibria at the temperatures of their study.

The density, refractive index, and viscosity for this system are reported in the literature (14,39,73). Hubbard (39) measured the density and refractive index, Zawidzki (14) the refractive index and Yajnik et al (73) the viscosity, of which only Hubbard's data are at 25°C. Timmermans (68) lists the density and viscosity available in the literature since 1930. Reinders and de Minjer (1) have determined the refractive index at 25°C for the helium D-line. Schmidt (69) reported the volume changes on mixing for this binary at 18°C. Hubbard (39) and Staveley et al (30) also investigated the volume changes on mixing at 25°C, 35°C and 50°C.

Isobaric studies on the system have been carried out by a number of investigators and these are listed by Timmermans (68). Tyrer (74) gave the results for boiling points, vapour compositions, latent heats at constant pressure and latent heats at constant composition for this system.

The boiling point curve at 760 m.m. as investigated by Reinders and de Minjer (1) has a maximum at 65.5°C and about 78 weight percent chloroform. The curve had already been determined by Thayer (75) at a pressure of 737 m.m. and by Tyrer (74) at 750 m.m.

Theoretical treatments for this system have been offered by many authors including Tyrer (74), Dolezalek (76), Moelwyn-Hughes (77), Kehiaian and Sosnkowska-Kehiaian

(78) and Wilson (79).

BENZENE-CHLOROFORM

No data on the vapour pressures at 25°C are reported for this system.

A list of investigations carried out on this system is given by Timmermans (68). The only vapour pressure data near 25°C are due to Kireev and Sitnikov (80). Schmidt (69) investigated the vapour pressures at 20°, 30°C and at higher temperatures. This author also reported data for V^E at 18°C and the heats of mixing at room temperature.

Isothermal vapour-liquid equilibrium data at 25°C are not known. Reinders and de Minjer (1) determined the vapour-liquid equilibria at constant pressure. An investigation of the isobaric boiling point diagram at 760 m.m. Hg by these authors showed a continuous rise of the boiling point with the benzene content. Tyrer (74) also found a similar curve, but his figures were somewhat higher, since however, he did not mention the pressure at which he had worked, it is possible, that this was higher.

Linebarger (81) determined the fluidity for this system at 25°C. The density and refractive index have been determined at 25°C by Reinders and de Minjer (1). Other investigators reporting densities at 25°C are Linebarger

(81) and Hirobe (65). Tyrer (82) determined the latent heat of vapourization and the compositions of mixed vapours which were in equilibrium with the mixed liquid of known compositions at their boiling points. He also treated this system from the point of view of solvate formation.

The freezing point diagram has been studied by Wrocinski and Guye (83), Wyatt (84) and Campbell and Kartzmark (67).

ACETONE-BENZENE

Vapour pressures have been determined at several temperatures and the complete literature is presented by Timmermans (68). Reinders and de Minjer (1) determined the isobaric boiling point diagram. There was a rise in boiling point with increasing benzene content a result similar to that found by Soday and Bennett (85) at slightly lower pressure.

An isothermal vapour pressure study at 25°C was made by Lumbuhob (86). Reinders and de Minjer (1) determined the compositions of condensed vapour which was in equilibrium with the boiling solution. These authors reported the densities and refractive indices at 25°C. Refractive index data at 16°C are given by Drude (87). Fluidity for this system was determined by Fischler (88).

Campbell and Kartzmark (67) determined the freezing point diagram for this system.

The densities have been determined by Ebersole (89) at 25°C, Barr and Bircumshaw (90) at 25°C, Bingham and Brown (91) at 25°C, McCombie, Roberts and Scarborough (92) at 15°C, Harms (93) at 6°C, Howard and Pike (94) at 25°C, and Brown and Smith (95) at 25°C also.

The excess volume of mixing for this system has been calculated by Brown and Smith (95) from their density data. The values calculated from the density determinations of Howard and Pike (94) showed good agreement with their values. The volume changes calculated from the density data of Reinders and de Minjer (1) suggested a positive value near pure chloroform, quite contrary to the results obtained in this research by a direct method. The complete range of concentration has not been covered by any investigator.

The heats of mixing have been determined by Campbell, Kartzmark and Friesen (2).

CHAPTER III

EXPERIMENTAL PROCEDURE AND APPARATUS

A. PURIFICATION OF THE MATERIALS

ACETONE

Spectranalyzed Acetone (A.C.S.) from the Fisher Scientific Company was dried by calcium chloride and then subjected to distillation after adding potassium permanganate to remove any non-aqueous impurities. The distillate collected was again dried by means of calcium chloride and distilled once again without adding potassium permanganate. Care was taken to avoid unnecessary exposure to air and freshly distilled acetone was used for each measurement. The physical properties observed for purified acetone are compared with the literature values in the following table.

Relevant investigations	Density 25°/4	Refractive index, D/25	Viscosity, 25° centipoises
1) This research	0.7842	1.3563	0.302
2) Perkin (96)	0.7844	-	-
3) Hubbard (39,97)	0.78492	1.35621	-
4) Timmermans (98)	0.7844	-	-
5) Schwerts (99)	0.78799	-	-
6) Baker (100)	-	-	0.316
7) Reinders and de Min- jer (1)	0.7849	1.3563	-
8) Sears, Wilhoit and Dawson (101)	0.7845	-	0.302
9) Brown and Smith (95)	0.78422	-	-

CHLOROFORM

Chloroform (A.C.S.) from the Fisher Scientific Company was purified to remove ethanol. Repeated extraction by concentrated sulfuric acid and final washing with distilled water removed ethanol completely. Chloroform was dried over anhydrous calcium chloride and then finally distilled from anhydrous phosphorous pentoxide, twice, in air. The purified reagent was stored in the dark. The sample purified in this manner could not be kept for more than a week. Fresh treatments were made every week. The physical properties of the purified material are listed in the table below along with the literature values.

Relevant Investigations	Density, 25°/4°	Refractive index, D/25	Viscosity 25° in centipoises
1) This research	1.4805	1.4433	0.542
2) Hubbard (39,97)	1.47993	1.44309	-
3) Schulze (102)	1.4785	-	-
4) Dolezalek and Schulze (103)	1.4785	-	-
5) Lewis (103a)	-	-	0.542
6) Reinders and de Minjer (1)	1.4789	1.4431	-
7) Campbell <u>et al</u> (13)	1.4806	1.4433	-

BENZENE

Thiophene-free Benzene (A.C.S.) from the Fisher Scientific Company was frequently shaken with concentrated sulphuric acid until the yellow colour in the acid layer

disappeared. It was then washed with a solution of sodium bicarbonate and water, and the product then dried with anhydrous sodium sulfate and sodium. Finally it was distilled twice from sodium. The physical constants found for pure benzene are tabulated with the literature values.

Relevant investigations	Density 25°/4°	Refractive index, D/25°	Viscosity 25° in centipoises
1) This research	0.8734	1.4979	0.602
2) Linebarger (104)	0.8742	-	-
3) Dunstan and Stubbs (105)	0.8736	-	0.6145
4) Hubbard (39,97)	-	1.49794	-
5) Gibson and Kincaid (106)	0.8736	1.4983	-
	0.8737	1.49807	-
	0.8738	1.49815	-
	-	1.49825	-
6) Reinders and de Minjer (1)	0.8738	1.4980	-
7) Gilkerson and Stamm (107)	0.8734	-	0.610
8) Brown and Smith (95)	0.87365	-	-

B. METHOD OF ANALYSIS

Vapour-liquid equilibrium data on the ternary system Acetone-Chloroform-Benzene and the component binary systems were determined from measurements of refractive index and density.

Generally the analysis of the compositions of the liquid mixtures are made from physical properties. The determining factors for the suitability of a certain

physical property for analytical purposes are: 1) the accuracy and reproducibility of the measurement, 2) the degree of variance of the property with concentration and 3) the requirement of small amount of the sample in order to finish the measurement. In case of binary mixture the slope of the straight-line curve or the steepness of the curvature of a non-linear calibration curve are important.

The ternary is dealt in a special way. Two physical properties are chosen. When these properties are plotted on an equilateral triangle superimposing on the corresponding concentrations it is possible to construct lines in the triangle linking the concentrations for which the value of a certain physical property is constant. These lines of isometric values serve to determine the composition of unknown liquid mixtures.

Properties of the mixtures are chosen in such a way as to allow the lines of equal magnitude to intersect each other at as large an angle as possible. The point of intersection of two measured physical properties, then enables one to determine the exact composition of the ternary mixture.

DENSITY DETERMINATION

The density was determined with an Ostwald-Sprengel pycnometer as described by Daniels et al (108). The capa-

city of these pycnometers was about 20 mls. and they were calibrated by means of distilled water in a thermostat controlled at $25.00^{\circ}\text{C} \pm 0.005$.

REFRACTIVE INDEX

The refractive index measurements were made using an Abbe Refractometer with prism thermostated at $25.00^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$ and monochromatic light of a sodium lamp (5893\AA). The accuracy of this instrument made by Officine Galileo of Italy, is ± 0.0001 unit of refractive index.

An uncertainty of ± 0.0001 in density and refractive index means an uncertainty of 0.001 in the values of mole-fraction.

ANALYSIS OF BINARY MIXTURE

The binary mixtures were analyzed by a calibration chart of physical properties vs. compositions made from known mixtures. The compositions of binary systems determined by measurements of refractive index and density agreed to 0.001 mole fraction.

ANALYSIS OF TERNARY MIXTURE

The ternary calibration mixtures were prepared by making three sets of sections through the ternary diagram. The first one was obtained by adding benzene in increasing amounts to a mixture of acetone and chloroform of composition A (Figure 2a). The physical properties of the resulting pseudo-binary mixtures A', A'', A''' etc., were determined. The chloroform content in such a mixture 'A' varied by

FIGURE 2a. The Pseudo-Binary Sections for the
Ternary Calibration Graph.

CHCl₃

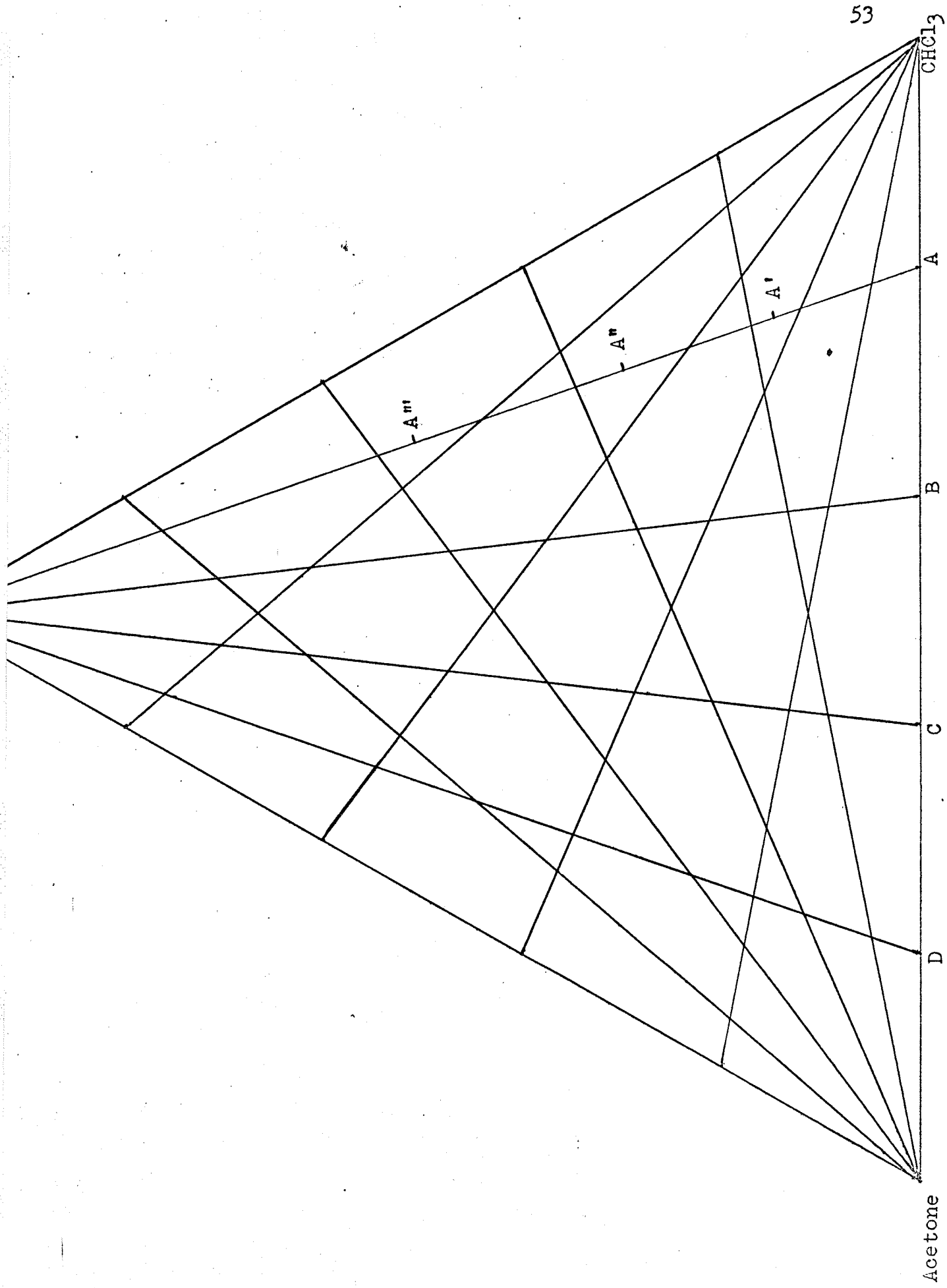
A

B

C

D

Acetone



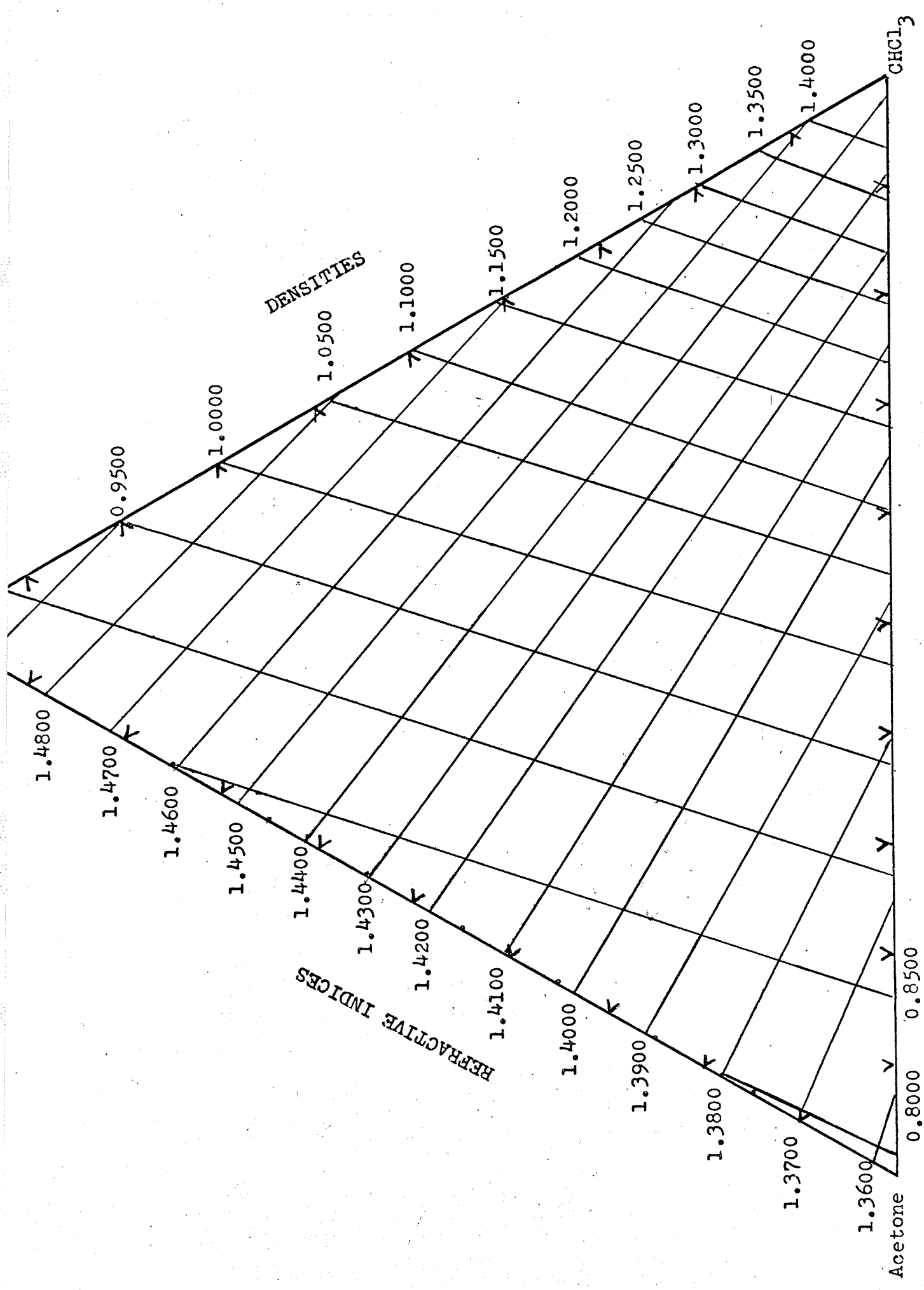
20% in successive sections B, C, D etc. The second set was made similarly by adding acetone to benzene-chloroform mixtures differing in chloroform concentration by 20% from one another and the third by adding chloroform in increasing amounts to acetone-benzene mixtures differing in benzene content by 20% from one another.

For every section the values found were represented graphically as a function of the percentage of the third component added, and curves were obtained, from which the composition of various mixtures, having all the same density or the same refractive index, could be read. The points, representing these compositions, were set out in the triangle and so it was possible to construct the desired lines of equal density and equal refractive index. Figure 2b shows this diagram on a reduced scale.

From this diagram it is obvious, that the curves of equal density are a set of parallel and nearly straight lines. For the same difference in density they lie closer together in the region near chloroform than in that near acetone.

The lines for equal refraction are also nearly straight. The distance between these lines for equal differences in refractive index is approximately constant in all parts of the triangle. They intersect those of equal density at an angle of about 60° .

FIGURE 2b. Lines of Constant Density and Refractive
Index for the Ternary System.



By means of this diagram the composition of a mixture could be deduced from the values of the density and the refractive index with an accuracy of about 0.2%.

Very similar results were obtained by Reinders and de Minjer (1) and the method followed here is due to them. Their density and refractive index measurements for the binary systems agreed with my values but no numerical data were listed in their publication (1) for the ternary system. The vapour and liquid compositions could not be read from the reduced triangular diagram of equal densities and refractive indices appearing in their publication (1). It was therefore decided to repeat the measurements for the ternary system in this laboratory and to plot the values on a much larger triangular diagram so that the compositions could be read with the accuracy claimed by them (1).

DETERMINATION OF VOLUME CHANGES ON MIXING

Attempts were made to calculate excess volumes from density measurements on the ternary and binary systems. The density data could be used to calculate the molar volume in a ternary system, thus:

$$v_{\text{exp}} = \frac{x_1 M_1 + x_2 M_2 + x_3 M_3}{d} \dots\dots\dots (58)$$

The ideal molar volume is

$$V_{id} = x_1 \frac{M_1}{d_1} + x_2 \frac{M_2}{d_2} + x_3 \frac{M_3}{d_3} \dots\dots\dots (59)$$

v^E or ΔV is then given by

$$v^E = v_{exp.} - v_{ideal}$$

The order of the magnitude of these volume changes was, however, rather small and required great accuracy in the density determinations. Though excellent agreement with the recent literature values, was obtained for densities of pure liquids, the mixtures could not be reproduced to the same degree, presumably due to unequal loss of the components by evaporation. Hence, it was decided to use a direct method of determination of volume change on mixing.

A survey of the literature showed that very few investigators attempted a direct measurement. Apparatus for the direct measurement of V^M has been described by Keyes and Hildebrand (109), Staveley and Spice (110), Desmyter and van der Waals (111) and Brown and Smith (112). The apparatus used by me in this investigation is based on the principles of Keyes and Hildebrand (109) and essentially the same in construction as that of Brown and

Smith (112).

The mixing cell used for the measurements had a total capacity of 15 ml. It is shown in Figure 3. The only difference from the cell used by Brown and Smith consisted in having a 2 m.m. bore stop-cock at the filling-end of the apparatus instead of the ground stopper used by them. It differed from the cell of Keyes and Hildebrand in not having two capillaries. The capillary used in my apparatus varied in its internal diameter from 1.55 - 1.56 m.m. in different regions of its length. The capillary was calibrated using pure re-distilled mercury in the following way.

Before the mixing cell was blown to its final shape shown in Figure 3, the capillary was sealed to a pyrex bulb of 10 ml. capacity. The capillary had several circular marks etched at about 10 m.m. distance apart. These marks were made on the stem to facilitate accurate measurement of the liquid level inside the capillary.

The capillary with the bulb was cleaned with hot chromic acid, thoroughly rinsed with distilled water, dried and weighed. Mercury was then introduced by means of a long drawn-out capillary tube extending to the bottom of the bulb, taking care to avoid the entrapment of air bubbles. The capillary was fixed in position inside the thermostat at

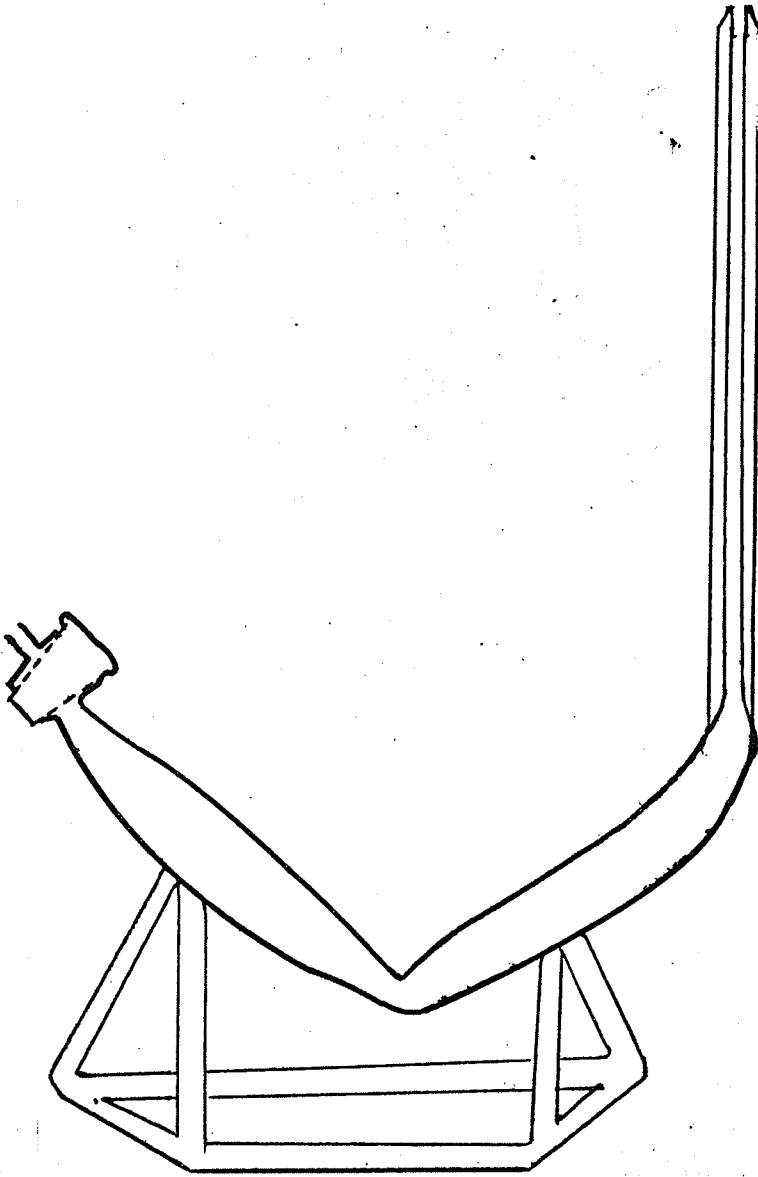


Figure 3 - The Mixing Cell

25.00°C ± 0.005 with its top protruding out of the water level in the bath. The meniscus level of the mercury column inside the capillary was adjusted to coincide with one of the ten marks on the stem, by using a long hypodermic needle and a syringe. The capillary with the bulb was removed from the thermostat, its outside cleaned thoroughly, dried and weighed. Using the density of mercury as given in Lange's handbook (13.5340), the volume corresponding to one of the ten marks on the stem was calculated. This procedure was repeated for each of the marks and the volume per unit length in each region at 25°C was calculated. Thus the non-uniformity of the capillary bore, if any, was taken into account. Next, the bulb was detached and the capillary was sealed to the bottom part of the mixing cell, i.e., to the two mixing compartments. The lowest mark on the capillary was never used for volume determinations, since it was apprehended that the calibration in this region might have changed during the heat applied for fusing the glass.

This cell required only one set of liquid level measurements and no significant errors resulted from keeping only the stop-cock out of the thermostat liquid. In their measurements Brown and Smith (112) allowed the ground-joint to immerse in the water of the thermostat and observed

no errors. The ground-joint could not be used in this investigation and the difficulty of using several of these mixing cells to cover the whole composition range as was done by them, was circumvented by having a stop-cock and using different amounts of mercury to separate the compartments. Thus with only one mixing cell the whole composition range was covered in the binary system. The experimental technique as described by Brown and Smith (112) is as follows.

Mercury was first placed in the cell to separate the liquids and the first component was added to the stop-cock side, with the help of a hypodermic syringe, and the cell reweighed. The second component was then added to the other chamber using a long hypodermic needle. The full cell was mounted on four legs on a metallic support inside the thermostat. The legs also facilitated the weighings. After filling the cell it was thermostated to reach temperature equilibrium. The level was adjusted to a suitable position relative to one of the reference marks on the capillary, such that this liquid level was not very far away from the liquid level of the thermostat itself. The upper walls of the capillary were dried by means of a small current of dry nitrogen through a hypodermic needle. The level was read off by means of a cathetometer. The cell contents were then thoroughly mixed

by repeated rocking of the cell about a horizontal axis through about 90° . The change in liquid level in the capillary, read to 0.1 m.m., gave the volume change on mixing and the final weighing of the cell gave the amount of the second component. Using different amounts of mercury, so as to allow of varying proportions of the two components in the chambers, direct measurements could be made of mixtures for the complete range of mole-fractions.

Brown and Smith (112) used degassed components for direct measurement. Organic liquids are known to have good solubility for gases and therefore this precaution seemed justified. In this investigation, however, all the samples used were freshly distilled and were not allowed to come into contact with air. Thus the precaution suggested by Brown and Smith (112) was not necessary for the measurements. The accuracy of the method was about ± 0.003 ml/mole.

The ternary system was treated in a special way. Stock solutions were made up containing fixed mole fractions of benzene, e.g.,



These were mixed in varying proportions and the volume changes measured, corrections being applied for the volume change that

had occurred in the original mixing of the quantities of stock solution used. This procedure was repeated for each 1/10th mole fraction benzene and the results interpolated on a triangular graph paper.

The volume change on mixing was calculated as follows

$$\Delta V = \Delta V_1 + \Delta V_2 + \Delta V_3$$

in which

ΔV = volume change due to the mixing of the three components

ΔV_1 = volume change that had occurred due to mixing in one of the binaries (obtained from the binary graph)

ΔV_2 = volume change that had occurred due to binary mixing in the second binary (obtained from the binary graph)

ΔV_3 = experimental volume change due to the mixing of the two binaries (that is, the ternary effect).

The direct measurement of volume change on mixing is both quicker and more accurate than its determination from density measurements on the mixture and on pure components. The direct method requires fewer and less accurate weighings and errors due to evaporation are far smaller than those found using the density method, particularly at

higher temperatures.

DETERMINATION OF VAPOUR PRESSURES AND VAPOUR COMPOSITIONS

(a) Development of experimental technique

Four general methods have been employed for measuring the vapour pressures. They are:

- (1) Static
- (2) Indirect
- (3) Differential
- (4) Dynamic

The static method had been used by Raoult (113) and Wüllner (114), but the defect of their method due to the presence of small traces of air was later shown by Tammann (115) and thus led to the neglect of their procedures.

The indirect method of Ramsay and Young (116) consisted in observing the temperatures at which solutions boiled under various pressures. This method was unsuitable for isothermal work.

The differential method involved the comparison of the vapour pressures of two solutions, or of one solution and the pure solvent, by means of a manometer and did not give any knowledge of the absolute value of the vapour pressure over either liquid phase.

The most widely used method for the measurement of vapour pressures has been the dynamic method, which makes use of the isothermal distillation of the liquid by means of displacement by air of the vapour in equilibrium with the liquid.

An excellent review of the experimental techniques and their development is given by Everett (117). The dynamic, or air-saturation method of measuring vapour pressures, is based upon Dalton's law of partial pressures. The essential features of the method as commonly used are: (1) a measured volume of air is saturated with vapour by passing it over the surface of, or bubbling it through the liquid contained in the saturator, (2) the weight of the liquid evaporated is determined by the loss in weight of the saturator, or by the gain in weight of an absorber which removes the liquid from the effluent air and (3) the total pressure exerted by the gaseous mixture in contact with the liquid is obtained from barometer and manometer readings. From the data thus obtained the vapour pressure of the liquid may be calculated.

A survey of the vapour pressure data obtained by the dynamic method shows not only a wide variation in the values reported by different investigators for a single liquid, but also very frequently a considerable variation in the data

given by a single investigator. The chief reasons for these deviations are few, but they have been difficult to overcome. One of the main sources of error is due to the inability to measure accurately and at the same time conveniently, the large volume of air required for a single determination. The error thus introduced will be greater or less depending upon the magnitude of the vapour pressure of the liquid studied. Forms of apparatus involving the bubbling of air through the liquid are obviously compact, but they introduce errors for the reason that while a bubble may be saturated with the vapour in the depth of the liquid, it will expand on rising and may become unsaturated, eventually leaving the apparatus without becoming entirely saturated. Again, the mathematical formulae which have been used, have been complicated; slight errors of observation are highly magnified in calculating vapour pressures.

In view of the above difficulties, in the present investigation, following Parks and Chaffee (118) the vapour pressures were measured with a manometer (static method) and the vapour compositions by means of isothermal distillation using the air displacement method. Thus the necessity of measuring the volume of air was obviated. This decision was the outcome of excellent results obtained by Campbell et al (13) in this laboratory for Acetic Acid-Chloroform-Water

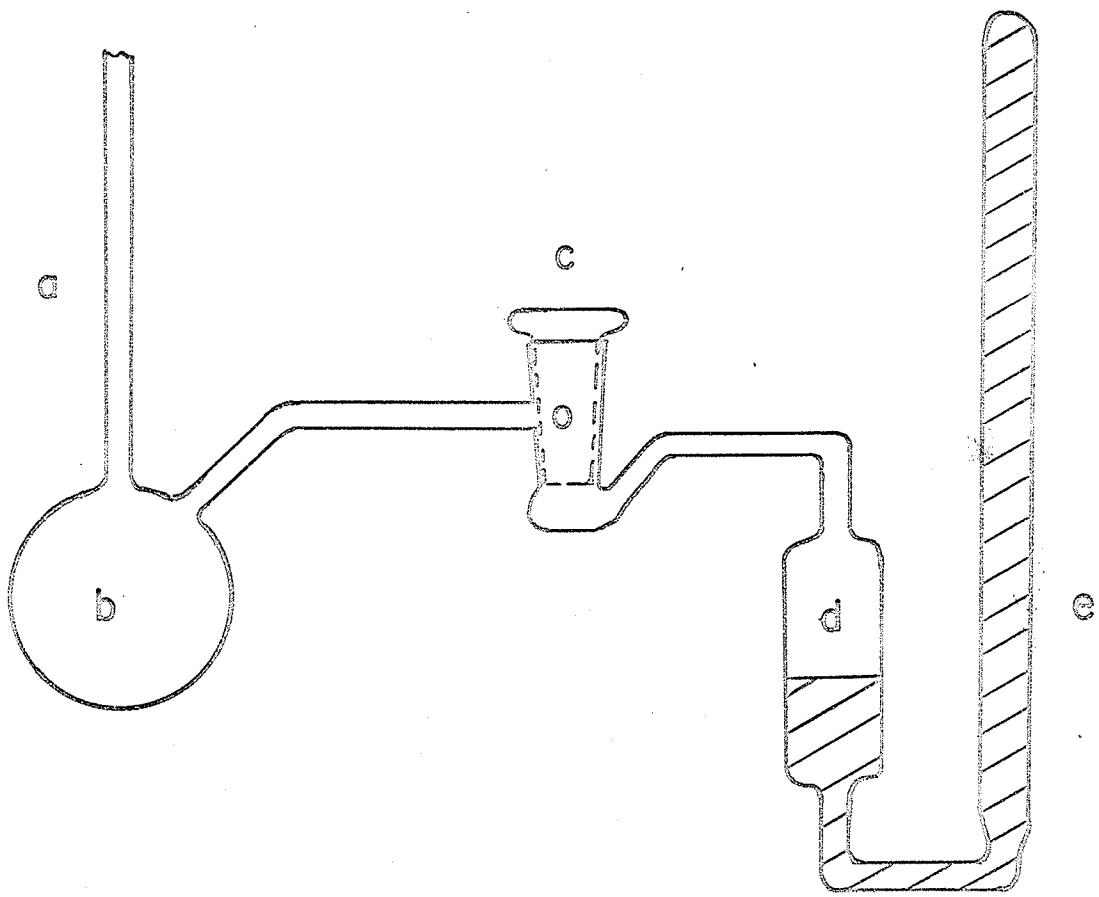
system investigated by this method.

(b) Vapour pressures at 25°C

The vapour pressures at 25°C for the pure components of the Acetone-Chloroform-Benzene system, for the component binary systems and for the ternary system were measured using a manometer as shown in Figure 4. The apparatus consisted of a bulb "b" of about 50 ml. capacity which could be filled through the tube "a", and the manometer arm "e" having a diameter greater than 10 m.m., connected to the bulb "b" through a stop-cock "c". Even with the tube of diameter greater than 10 m.m., there still could be a depression of 0.2 m.m., but this error was obviated by the use of comparative techniques. The cathetometer used for reading the height of the mercury column in the manometer arms was standardized against CHCl_3 at 25°C or acetone at 25°C. All measurements were referred back to this standardization.

The method employed for measurements was as follows. In each case a 25 ml. sample of the liquid under consideration was introduced into the small bulb "b", while stop-cock "c" was opened, so that "d" was in connection with "b". The closed-end manometer had been earlier filled with pure mercury and the occluded air had been boiled out by inverting the U-shaped manometer, connecting to a vacuum

FIGURE 4. The Manometer.



pump, and heating gently and cautiously with a moving flame, throughout the length of mercury to remove any trapped air between the mercury and the wall. Such a manometer was then subjected to evacuation to remove the air in and above the experimental liquid, which was kept frozen during the evacuation by immersing the bulb "b" in a flask containing liquid nitrogen or acetone-dry ice mixture. The vacuum pump was connected to the tube "a" through a trap immersed in liquid nitrogen contained in a Dewar flask. The mercury in the arms "d" and "e" stood at equal level after complete evacuation, and stopcock "c" was then closed. The bulb "b" was brought to room temperature and the process of freezing and pumping-out was repeated several times to ensure the complete expulsion of dissolved air. Finally the bulb and manometer system were sealed off from the outside atmosphere in vacuo while the experimental liquid was still frozen thus protecting it from vapourizing out. This was achieved by sealing the tube "a" under continuous suction. The bulb and contents were then brought to the room temperature and then immersed completely in a thermostat of 20 litres capacity maintained at $25.00^{\circ}\text{C} \pm 0.005$. When the manometer has reached the temperature of the thermostat, the stopcock "c" was opened slowly and after an equilibration period of half an hour, the difference in the mercury levels in the manometer arms was measured by means of a cathetometer. All readings were reduced to Hg at 0°C .

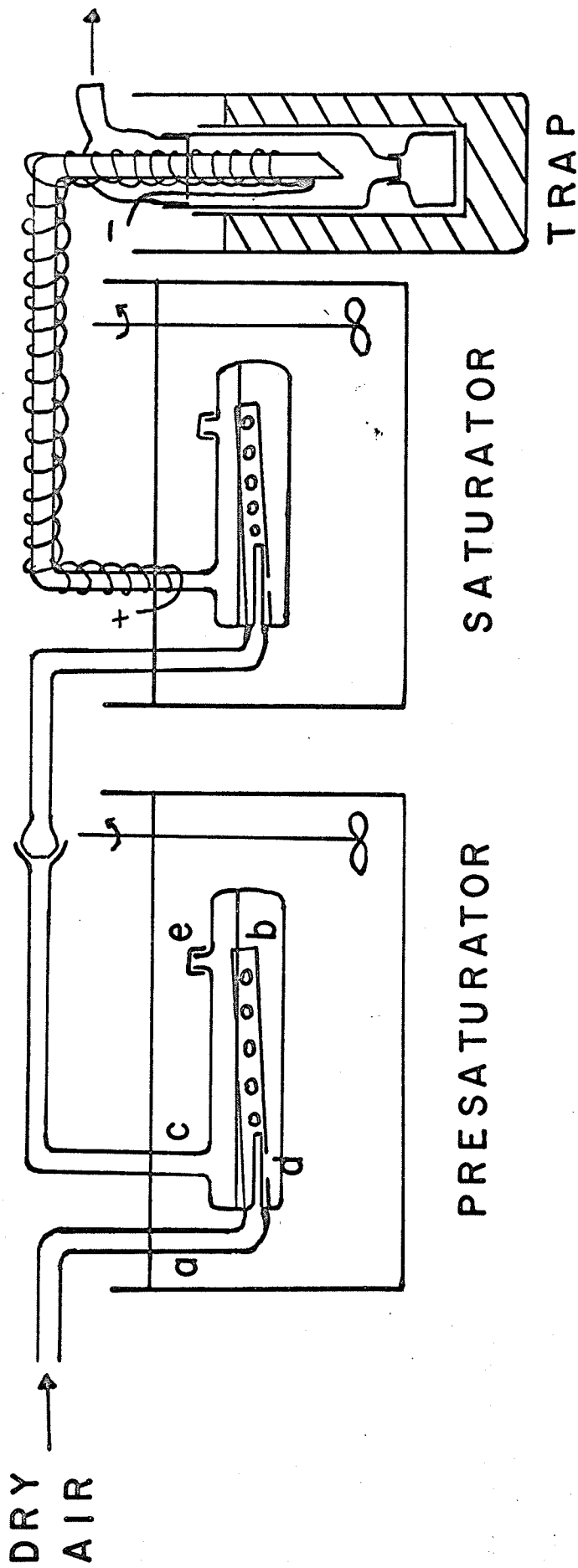
(c) Isothermal distillation apparatus

The apparatus shown in Figure 5 was used for determining the compositions of mixed vapours which were in equilibrium with the mixed liquid of known compositions at 25.00°C.

Pearce and Snow (119) used the saturators of the type originally used by Bichowsky and Storch (120). Campbell et al (13) found this to be satisfactory in their work in this laboratory with slight modifications.

The saturators consisted of a series of eight units in the saturator part and four units in the presaturator part of the apparatus. Each unit was fabricated as follows. The air entered the unit through a short central tube "a" tapered down to a 2 m.m. capillary. At the tip of the capillary the stream of air broke into bubbles which passed up a slightly inclined 5 m.m. tube 80 m.m. long and then broke at the end of the tube. An opening "d" was blown through the lower side of this inclined tube just back of the tip of the capillary. Through this opening liquid was drawn from the bottom of the saturator and carried by the air-bubbles up the slanting tube to the surface of the liquid, thereby maintaining a practically uniform vapour concentration. The gas liberated from the bubbles as they burst then passed back over the surface of the liquid to the tube "c" leading either to a second saturator, or,

FIGURE 5. The Isothermal Distillation Apparatus.



finally to the absorber in the trap. Each tube in a saturator was provided with a vertical tube "e" for filling and emptying. This had a water-tight ground glass joint thereby preventing water to mix with the liquid when the saturators were immersed in the thermostat. The capacity of each container was 35 ml. when filled.

This type of saturator has the advantage that the bubbles only have a short vertical movement in the liquid, whereas the contact with the liquid is comparatively long. This enables the air-bubbles to remain saturated when they leave the liquid surface. The saturation is further facilitated because the bubbles again pass over the liquid surface, thereby having opportunity to come into equilibrium with the latter, before finally entering the absorber.

The compressed air was purified from CO_2 by passing it through a concentrated potassium hydroxide solution and dried by passing it through concentrated sulphuric acid and anhydrous calcium chloride tube. The air was then allowed to enter the presaturator part which consisted of a series of four units, as described earlier. This presaturator was kept immersed in a 30 litres capacity thermostat, filled with water. The temperature of the bath was maintained at $30.00^\circ\text{C} \pm 0.05$.

After having passed through the presaturator the air was allowed to go to the saturator through a tube outside

the baths. The saturator consisting of eight units was kept immersed in a thermostated water-bath of 30 litres capacity at $25.00^{\circ}\text{C} \pm 0.005^{\circ}\text{C}$.

The air, after leaving the last unit of the saturators, was led to the trap through a tube. In order to avoid the condensation of the vapour on the walls of the tube a Ni-chrome resistance wire was coiled around this tube right up to the end dipped in the trap. The current from a six volts copper oxide rectifier was passed into the resistance wire thereby heating the tube to about 50 to 60°C .

The absorber consisted of a glass tube 160 m.m. in length and 30 m.m. in diameter, which could be removed from the tube that was attached to the saturator, by means of a ground glass joint. The tube coming from the saturator went down to 10 m.m. from the bottom in this wide tube. The bottom end of the trap was connected to a ground-joint bottle of 15 ml. capacity. The trap was surrounded by a glass tube and put into an acetone-dry ice mixture in a Dewar flask, giving a temperature of -80°C . After allowing the distillation to continue for sufficiently long time so as to get about 10 ml of the condensate in the ground-joint bottle, the liquid was subjected to analysis.

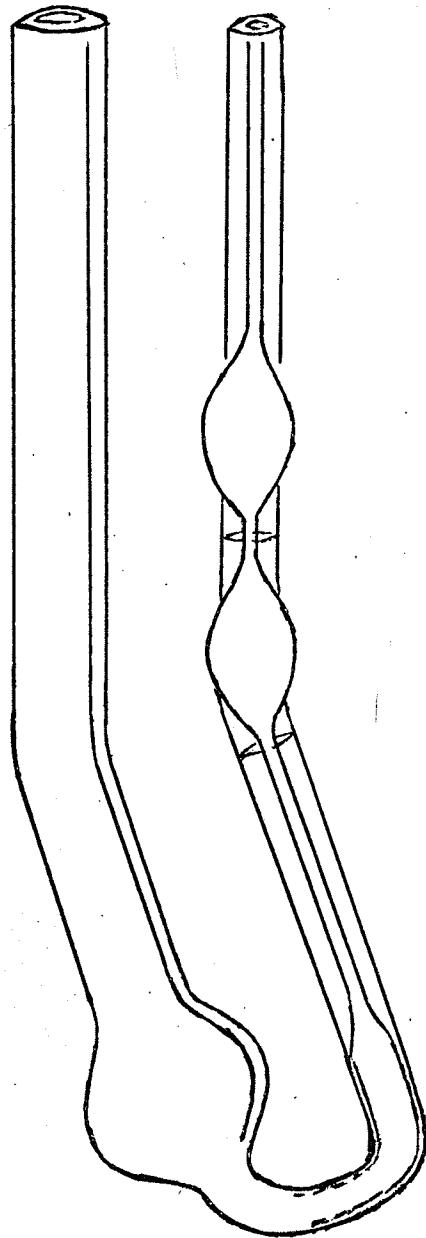
Campbell et al (13) state that air speeds up to ten litres per hour give satisfactory saturation of the air. Nevertheless, they used a speed not exceeding two litres

per hour. They further state that the results obtained for speeds varying between 0.5 and 2.0 litres per hour showed no larger deviation than the experimental error, which was less than 1% by weight. The results reported by me are based on distillations at the rate of 1-2 litres per hour of air.

The Viscosity Determinations

The choice of viscometer is vital in the determinations of accurate viscosity for non-electrolytes. An Ostwald viscometer has often been used for its simplicity in operation. The literature survey shows many publications indicating the design of viscometers, important among which is Willingham, McCliver, Fenske and McGrew (121). After taking the viscous properties of the solutions, in the present investigation, into account it was decided to use a viscometer of the Cannon and Feske type (122), where the drainage and kinetic energy corrections were considered negligible in view of the rather narrow capillary diameter used in its construction.

The bend in the viscometer (Figure 6) caused it to be much less sensitive to the angle of tilt from the vertical and permitted the viscometer to be supported in the bath by means of an ordinary clamp, separate from the thermostat and fixtures. The viscometer was calibrated



VISCOMETER (CANNON AND FENSKE TYPE)

FIGURE 6

with conductance water. Efflux times were reproducible to $\pm 0.05\%$.

Usually loading errors arise from the fact that the driving fluid head is dependent upon the amount of liquid in the instrument. The viscometer was loaded at room temperature by holding it in an inverted vertical position with capillary side submerged in the liquid under test. Suction was then applied to the other arm of the instrument and both small bulbs on the capillary arm were filled with the liquid. The liquid was brought into the working capillary to the etched mark; hence, the total charging volume was that held by the two bulbs plus that held by the capillary extending to the open end of the instrument. After filling, the viscometer was revolved to its normal vertical position and placed in the thermostat. The liquid drained into the lower reservoir during the time required for it to attain the bath temperature. When finally this temperature was reached, the efflux time was obtained by drawing the liquid up to the mark between the bulbs and measuring the time required for the meniscus to pass from the mark between the bulbs to the mark below the lower bulb on the capillary. A stop-watch reading up to tenths of a second was used to record the time.

CHAPTER IV

EXPERIMENTAL RESULTS

A. EXCESS VOLUME

THE SYSTEM ACETONE-CHLOROFORM

The results obtained for excess molal volumes by the direct method are presented in Table I. The compositions of the solutions are given in mole-fractions.

The partial molal volumes for each component were calculated from the smoothed data of excess volumes and the densities of the pure components. These data are given in Table 2. Molal volumes of solutions were obtained from calculated ideal volumes and smoothed excess volumes, from which, by the method of intercepts, the partial molal volumes, were found. Partial molal excess volumes were then calculated. Columns 8 and 9 constitute of these values for acetone and chloroform.

The excess molal volumes are plotted against mole-fraction acetone in Figure 7. The partial molal excess volumes are represented in Figure 8, as a function of the concentration of chloroform expressed in mole fraction.

THE SYSTEM BENZENE-CHLOROFORM

Table 3 gives the excess volumes for this system for

different concentrations which are expressed in mole-fractions of the components. These values are plotted in Figure 9 as a function of the concentration of chloroform expressed in mole-fraction.

Table 4 gives the partial molal excess volumes of the components in this system. These values have been calculated from smoothed excess volume data and ideal volume calculated from densities of pure components.

Figure 10 represents the partial molal excess volumes as function of the concentration of chloroform expressed in mole fractions.

THE SYSTEM ACETONE-BENZENE

The data for the excess molal volumes of this system are presented in Table 5. The concentrations are given in mole-fractions. These data are plotted against mole-fraction acetone in Figure 11.

The partial molal excess volumes, as calculated from the partial molal volumes are presented in Table 6. These data are plotted as function of mole fraction acetone in Figure 12.

THE SYSTEM ACETONE-CHLOROFORM-BENZENE

In Table 7, the excess molal volume data are reported

with the corresponding concentrations of the three components. The excess volumes of acetone-chloroform mixtures with fixed benzene content are thus reported in several series of solutions. The mole fractions of such mixtures are also reported in absence of benzene.

These excess volumes of the pseudo-binary systems were plotted as a function of mole-fraction chloroform, the latter being calculated on a benzene-free basis, at the same time making use of the binary data. It was possible from such a plot to obtain the loci of solutions having zero excess volumes. The loci thus obtained have been plotted in Figure 13.

TABLE I

EXCESS VOLUME DATA FOR SYSTEM $C_3H_6O-CHCl_3$

AT 25°C.

No.	Mole fractions		V^E (ml/mole)
	C_3H_6O	$CHCl_3$	
1.	0.0671	0.9329	-0.058
2.	0.1097	0.8902	-0.084
3.	0.1444	0.8556	-0.104
4.	0.2174	0.7826	-0.133
5.	0.2806	0.7194	-0.149
6.	0.3980	0.6020	-0.141
7.	0.4792	0.5208	-0.110
8.	0.5156	0.4844	-0.088
9.	0.5755	0.4245	-0.058
10.	0.6160	0.3840	-0.042
11.	0.6661	0.3339	-0.010
12.	0.6795	0.3205	+0.003
13.	0.7311	0.2689	+0.027
14.	0.8102	0.1898	+0.046
15.	0.8226	0.1774	+0.049
16.	0.8860	0.1140	+0.048
17.	0.9319	0.0681	+0.037
18.	0.9549	0.0451	+0.029

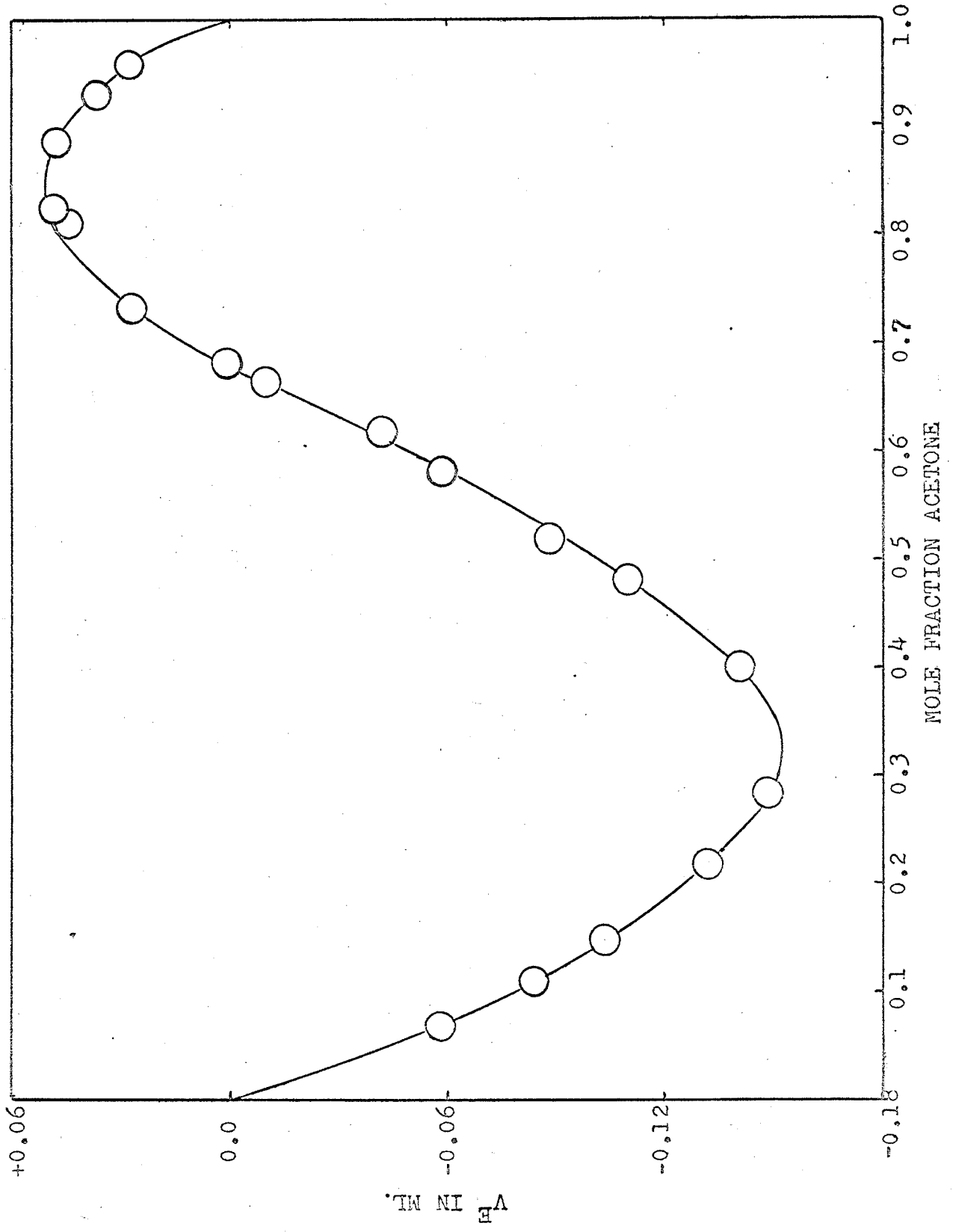


TABLE 2
 PARTIAL MOLAL VOLUMES IN THE
 SYSTEM ACETONE-CHLOROFORM AT 25°C.

Mole Fraction Acetone	Mole Fraction CHCl ₃	Ideal Volume (ml/mole)	Excess Volume (ml/mole)	Actual Volume (ml/mole)	\bar{V}_{Acetone} (ml/mole)	\bar{V}_{CHCl_3} (ml/mole)	$(\bar{V}-V)^*$ Acetone	$(\bar{V}-V)^{**}$ CHCl ₃
1.0	0.0	74.063	0.000	74.063	74.063	81.210	0.000	+0.570
0.9	0.1	74.721	+0.045	74.766	74.062	81.070	+0.001	+0.430
0.8	0.2	75.380	+0.046	75.426	74.180	80.600	+0.120	-0.040
0.7	0.3	76.037	+0.011	76.048	74.280	80.260	+0.220	-0.380
0.6	0.4	76.695	-0.049	76.646	74.320	80.150	+0.260	-0.490
0.5	0.5	77.354	-0.120	77.234	74.340	80.130	+0.280	-0.510
0.4	0.6	78.012	-0.140	77.872	74.180	80.300	+0.120	-0.340
0.3	0.7	78.670	-0.150	78.520	73.940	80.440	-0.120	-0.200
0.2	0.8	79.328	-0.128	79.200	73.700	80.560	-0.360	-0.080
0.1	0.9	79.986	-0.078	79.908	73.190	80.630	-0.870	-0.010
0.0	1.0	80.644	0.000	80.644	72.700	80.640	-1.360	0.000

* Partial Molal Excess Volume of Acetone in ml/mole.
 ** Partial Molal Excess Volume of CHCl₃ in ml/mole.

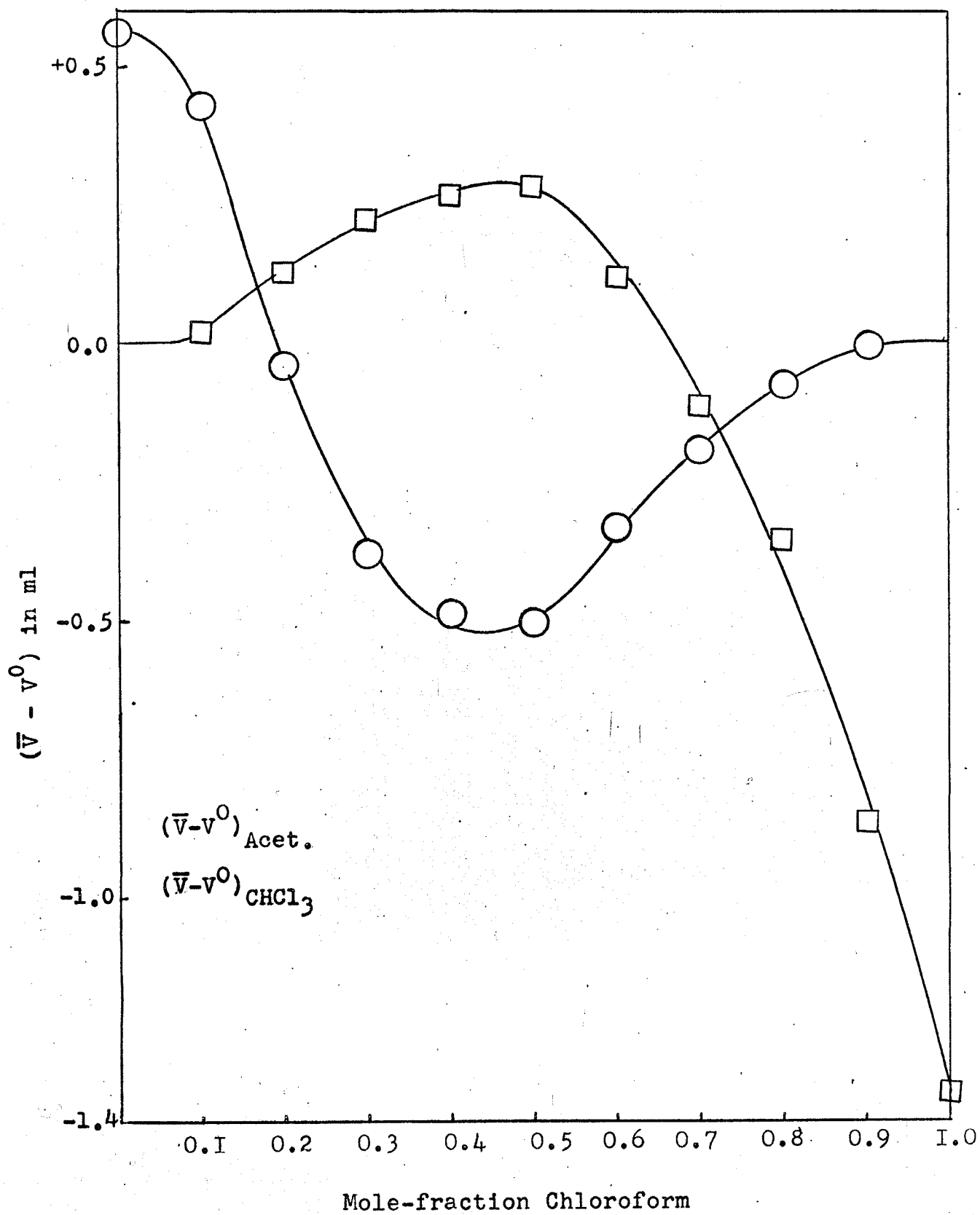


TABLE 3

EXCESS VOLUME DATA FOR SYSTEM $C_6H_6-CHCl_3$ AT $25^\circ C$.

No.	Mole fractions		V^E (ml/mole)
	C_6H_6	$CHCl_3$	
1.	0.9621	0.0379	+ 0.030
2.	0.9280	0.0720	+ 0.058
3.	0.9089	0.0911	+ 0.076
4.	0.8319	0.1681	+ 0.105
5.	0.8300	0.1700	+ 0.107
6.	0.8245	0.1755	+ 0.108
7.	0.8031	0.1969	+ 0.115
8.	0.7796	0.2204	+ 0.123
9.	0.7777	0.2223	+ 0.124
10.	0.7269	0.2731	+ 0.142
11.	0.6227	0.3773	+ 0.150
12.	0.5534	0.4466	+ 0.151
13.	0.5150	0.4850	+ 0.150
14.	0.4623	0.5377	+ 0.147
15.	0.3782	0.6218	+ 0.129
16.	0.2954	0.7046	+ 0.115
17.	0.2227	0.7773	+ 0.096
18.	0.1879	0.8121	+ 0.076
19.	0.1648	0.8352	+ 0.067
20.	0.0750	0.9250	+ 0.033

FIGURE 9. The Excess Volume Function for the
System "Benzene-Chloroform", at
25°.

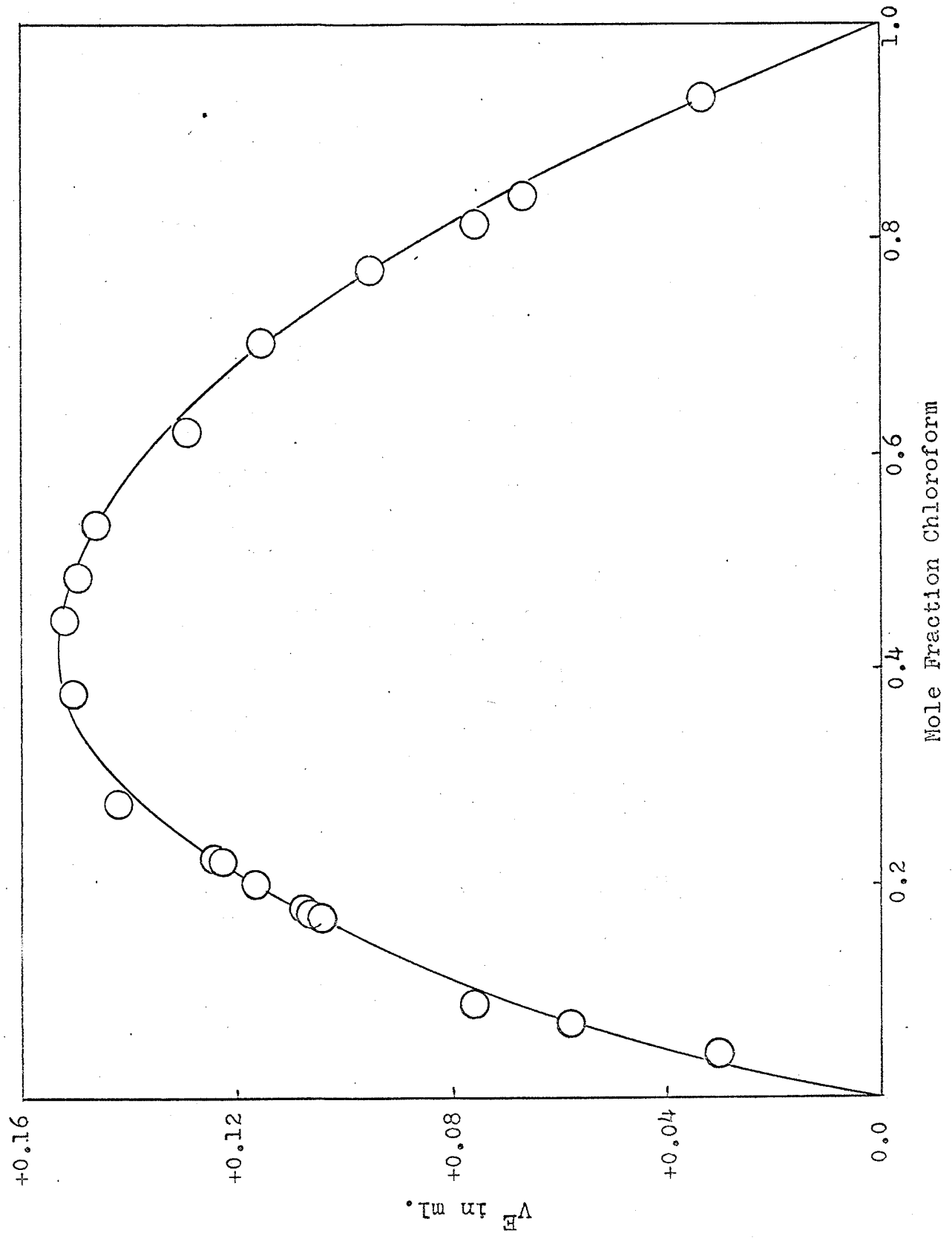


FIGURE 10. The Partial Molal Excess Volumes
in the System Benzene-Chloroform
at 25°C.

TABLE 4.

 PARTIAL MOLAL VOLUMES IN THE SYSTEM
 BENZENE-CHLOROFORM AT 25°C

Mole fractions		Ideal Volume (ml/mole)	Excess Volume (ml/mole)	Actual Volume (ml/mole)	\bar{V}_{benzene} (ml/mole)	\bar{V}_{CHCl_3} (ml/mole)	$(\bar{V}-V)_{\text{C}_6\text{H}_6}^*$	$(\bar{V}-V)_{\text{CHCl}_3}^{**}$
C ₆ H ₆	CHCl ₃							
1.0	0.0	89.432	+0.000	89.432	89.43	81.60	0.00	0.96
0.9	0.1	88.553	+0.076	88.629	89.45	81.34	0.02	0.70
0.8	0.2	87.667	+0.118	87.785	89.48	81.14	0.05	0.50
0.7	0.3	86.796	+0.142	86.938	89.52	80.96	0.09	0.32
0.6	0.4	85.917	+0.151	86.068	89.57	80.81	0.14	0.17
0.5	0.5	85.038	+0.150	85.188	89.61	80.74	0.18	0.10
0.4	0.6	84.159	+0.137	84.296	89.66	80.71	0.23	0.07
0.3	0.7	83.281	+0.114	83.395	89.71	80.68	0.28	0.04
0.2	0.8	82.402	+0.083	82.485	89.78	80.67	0.35	0.03
0.1	0.9	81.524	+0.042	81.566	89.93	80.65	0.50	0.01
0.0	1.0	80.644	+0.000	80.644	90.30	80.64	0.87	0.00

* Partial Molal Excess Volume of Benzene in ml/mole.

** Partial Molal Excess Volume of Chloroform in ml/mole.

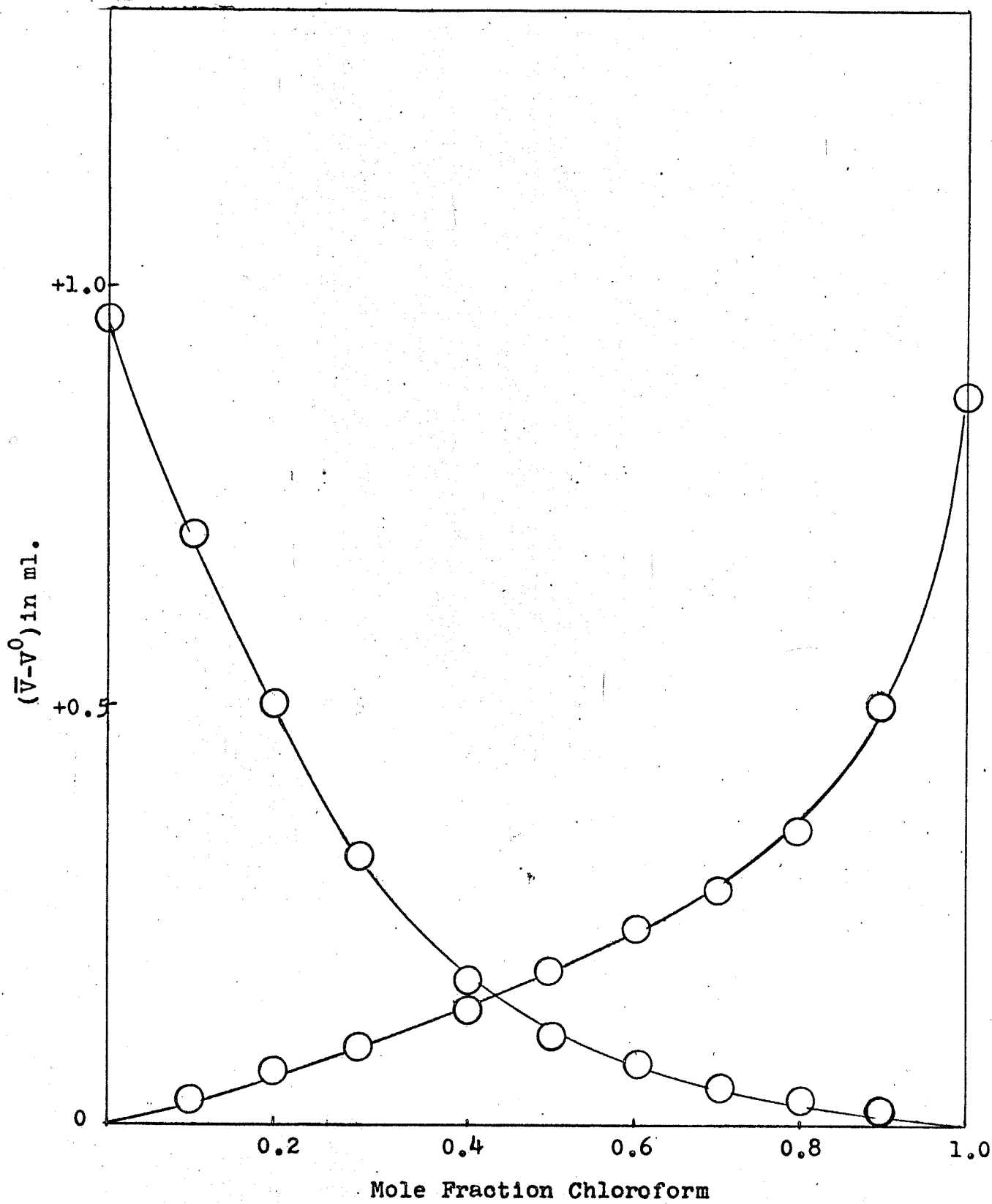


FIGURE 11. The Excess Molal Volume for the
System Acetone-Benzene at 25°C.

TABLE 5
 EXCESS VOLUME DATA FOR SYSTEM C_6H_6 ACETONE
 AT 25°C.

No.	Mole Fraction		V^E (ml/mole)
	C_3H_6O	C_6H_6	
1.	0.0455	0.9545	-0.010
2.	0.1069	0.8931	-0.021
3.	0.2003	0.7997	-0.040
4.	0.2440	0.7560	-0.049
5.	0.2966	0.7034	-0.059
6.	0.3679	0.6321	-0.067
7.	0.4517	0.5483	-0.071
8.	0.4707	0.5293	-0.069
9.	0.5312	0.4688	-0.070
10.	0.5994	0.4006	-0.066
11.	0.7079	0.2921	-0.048
12.	0.7356	0.2644	-0.036
13.	0.7796	0.2204	-0.035
14.	0.8029	0.1971	-0.023
15.	0.8463	0.1537	-0.010
16.	0.8708	0.1292	+0.002
17.	0.8950	0.1050	+0.012
18.	0.9563	0.0437	+0.033
19.	0.9586	0.0414	+0.030
20.	0.9724	0.0276	+0.019

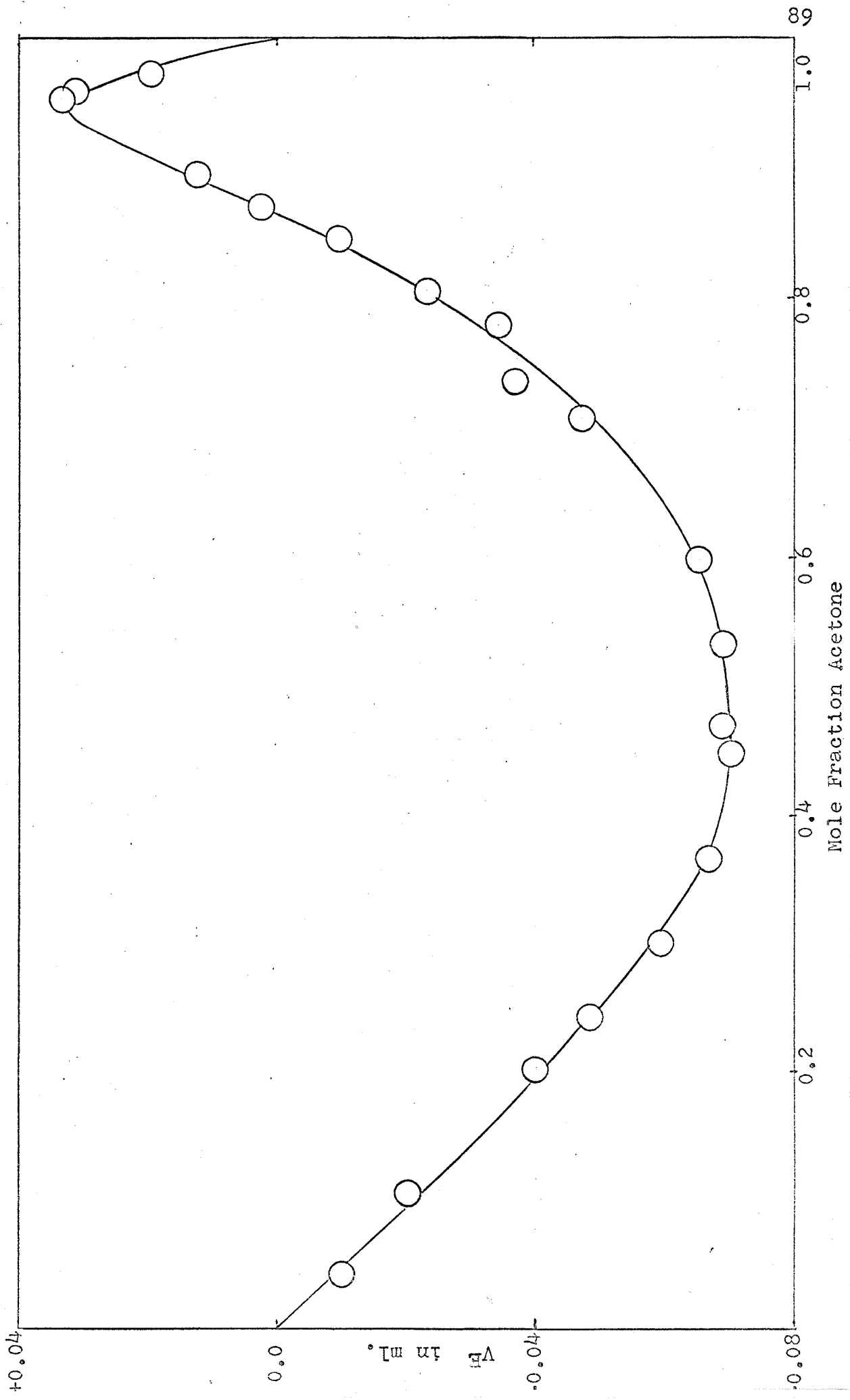


TABLE 6
 PARTIAL MOLAL VOLUMES IN THE SYSTEM
 ACETONE-BENZENE AT 25°C.

Mole fractions C_6H_6	Acetone	Ideal Volume (ml/mole)	Excess Volume (ml/mole)	Actual Volume (ml/mole)	$\bar{V}_{C_6H_6}$ (ml/mole)	$\bar{V}_{Acetone}$ (ml/mole)	$(\bar{V}-V^0)^*$		$(\bar{V}-V^0)^{**}$	
							Benzene	Acetone	Benzene	Acetone
1.0	0.0	89.432	0.000	89.432	89.43	73.50	0.00	0.00	-0.56	
0.9	0.1	87.895	-0.022	87.873	89.41	73.57	-0.02	-0.02	-0.49	
0.8	0.2	86.358	-0.042	86.316	89.40	73.66	-0.03	-0.03	-0.40	
0.7	0.3	84.821	-0.059	84.762	89.35	73.77	-0.08	-0.08	-0.29	
0.6	0.4	83.284	-0.069	83.215	89.25	73.96	-0.18	-0.18	-0.10	
0.5	0.5	81.748	-0.070	81.678	89.13	74.07	-0.30	-0.30	+0.01	
0.4	0.6	80.210	-0.065	80.145	89.05	74.15	-0.38	-0.38	+0.09	
0.3	0.7	78.674	-0.051	78.623	89.03	74.16	-0.40	-0.40	+0.10	
0.2	0.8	77.137	-0.025	77.112	89.05	74.15	-0.38	-0.38	+0.09	
0.1	0.9	75.600	+0.015	75.615	89.18	74.12	-0.25	-0.25	+0.06	
0.05	0.95	74.831	+0.033	74.864	89.32	74.08	-0.11	-0.11	+0.02	
0.0	1.0	74.063	0.000	74.063	89.88	74.06	+0.45	+0.45	0.00	

* Partial molal excess volume of benzene in ml/mole.

** Partial molal excess volume of acetone in ml/mole.

FIGURE 12. Partial Molal Excess Volumes in
the System Acetone-Benzene at
25°C.

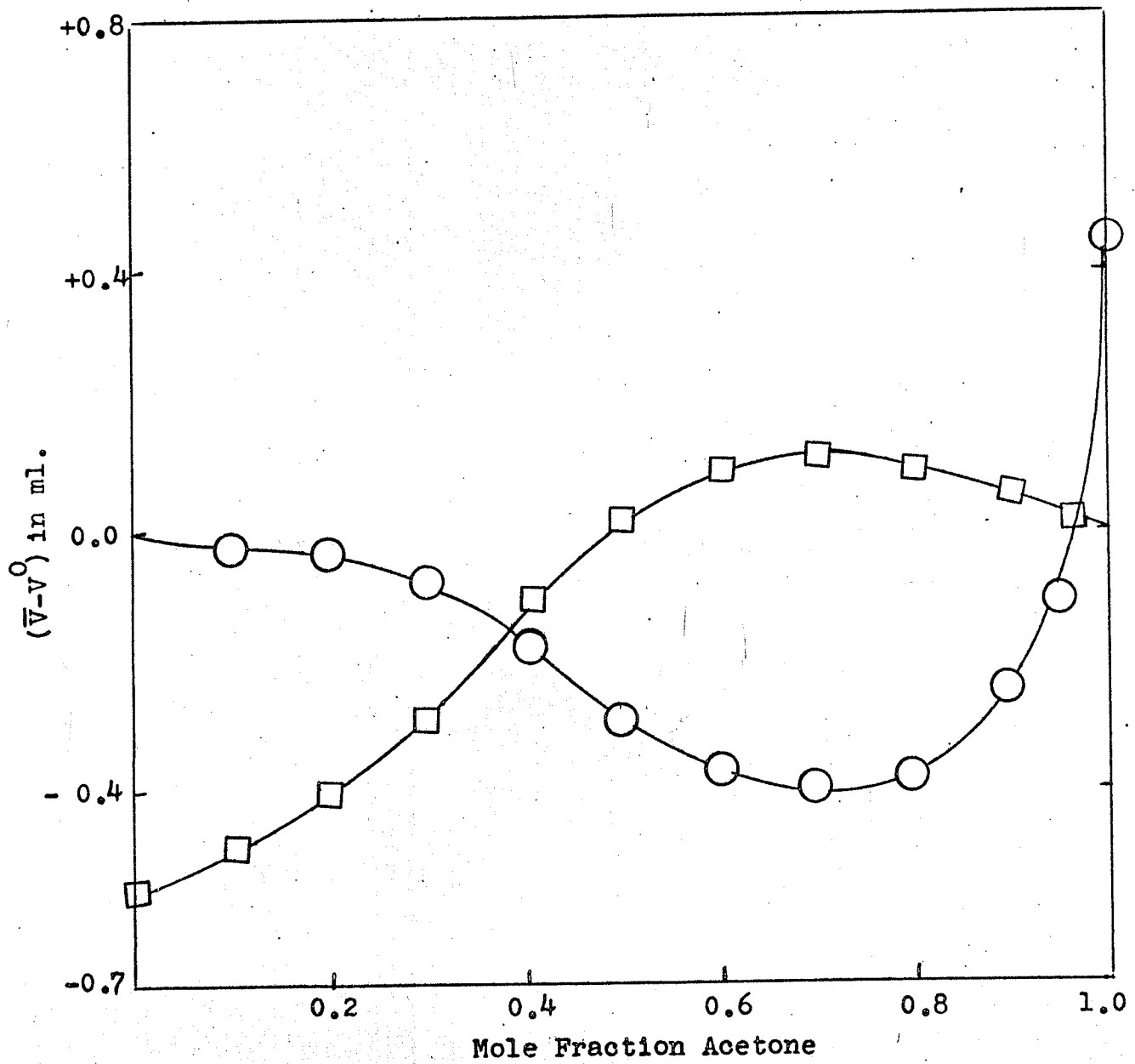


TABLE 7

EXCESS VOLUME DATA FOR THE SYSTEM
ACETONE-CHLOROFORM-BENZENE AT 25°C.

Mole fractions in mixtures		Mole fractions in absence of benzene		V^E (ml/mole)*
Acetone	Chloroform	Acetone	Chloroform	
<u>Series i.</u> 0.1 mole fraction benzene present in all solutions.				
0.0000	0.9000	0.0000	1.000	+0.042
0.1578	0.7422	0.1753	0.8247	-0.059
0.2054	0.6946	0.2282	0.7718	-0.078
0.3785	0.5215	0.4205	0.5795	-0.065
0.4236	0.4764	0.4707	0.5293	-0.051
0.5611	0.3389	0.6234	0.3766	-0.006
0.7000	0.2000	0.7777	0.2223	+0.043
0.8198	0.0802	0.9110	0.0890	+0.046
0.9000	0.0000	1.000	0.0000	+0.015
<u>Series ii.</u> 0.20 mole fraction benzene present in all solutions.				
0.1524	0.6476	0.1904	0.8096	-0.012
0.2234	0.5766	0.2793	0.7207	-0.028
0.3586	0.4414	0.4483	0.5517	-0.018
0.4893	0.3107	0.6116	0.3884	-0.001
0.6351	0.1649	0.7939	0.2061	+0.022
0.6652	0.1348	0.8316	0.1684	+0.013
0.6944	0.1056	0.8680	0.1320	+0.005
<u>Series iii.</u> 0.25 mole fraction benzene present in all solutions.				
0.1450	0.6050	0.1934	0.8066	+0.023
0.2991	0.4509	0.3988	0.6012	-0.003
0.3401	0.4099	0.4534	0.5466	-0.001
0.4371	0.3130	0.5827	0.4173	+0.008
0.5924	0.1576	0.7898	0.2102	+0.009

continued

TABLE 7 CONTINUED

Mole fractions in mixtures		Mole fractions in absence of benzene		V^E (ml/mole)*
Acetone	Chloroform	Acetone	Chloroform	
<u>Series iv.</u> 0.30 mole fraction benzene present in all solutions				
0.1389	0.5611	0.1985	0.8015	+0.046
0.2048	0.4952	0.2925	0.7075	+0.016
0.2667	0.4333	0.3811	0.6189	+0.013
0.3072	0.3928	0.4388	0.5612	+0.009
0.4024	0.2976	0.5749	0.4251	+0.011
0.4595	0.2405	0.6564	0.3436	+0.009
0.5320	0.1680	0.7601	0.2399	+0.001
0.6173	0.0827	0.8819	0.1181	-0.007
<u>Series v.</u> 0.40 mole fraction benzene present in all solutions				
0.1510	0.4490	0.2517	0.7483	+0.068
0.2242	0.3758	0.3736	0.6264	+0.044
0.2800	0.3200	0.4666	0.5334	+0.031
0.3393	0.2607	0.5655	0.4345	+0.021
0.4326	0.1674	0.7211	0.2789	-0.004
<u>Series vi.</u> 0.50 mole fraction benzene present in all solutions				
0.1145	0.3855	0.2290	0.7710	+0.096
0.1913	0.3087	0.3827	0.6173	+0.057
0.2352	0.2648	0.4705	0.5295	+0.047
0.2858	0.2142	0.5716	0.4284	+0.034
0.3193	0.1807	0.6385	0.3615	+0.014
0.4063	0.0937	0.8126	0.1874	-0.021

continued

TABLE 7 CONTINUED

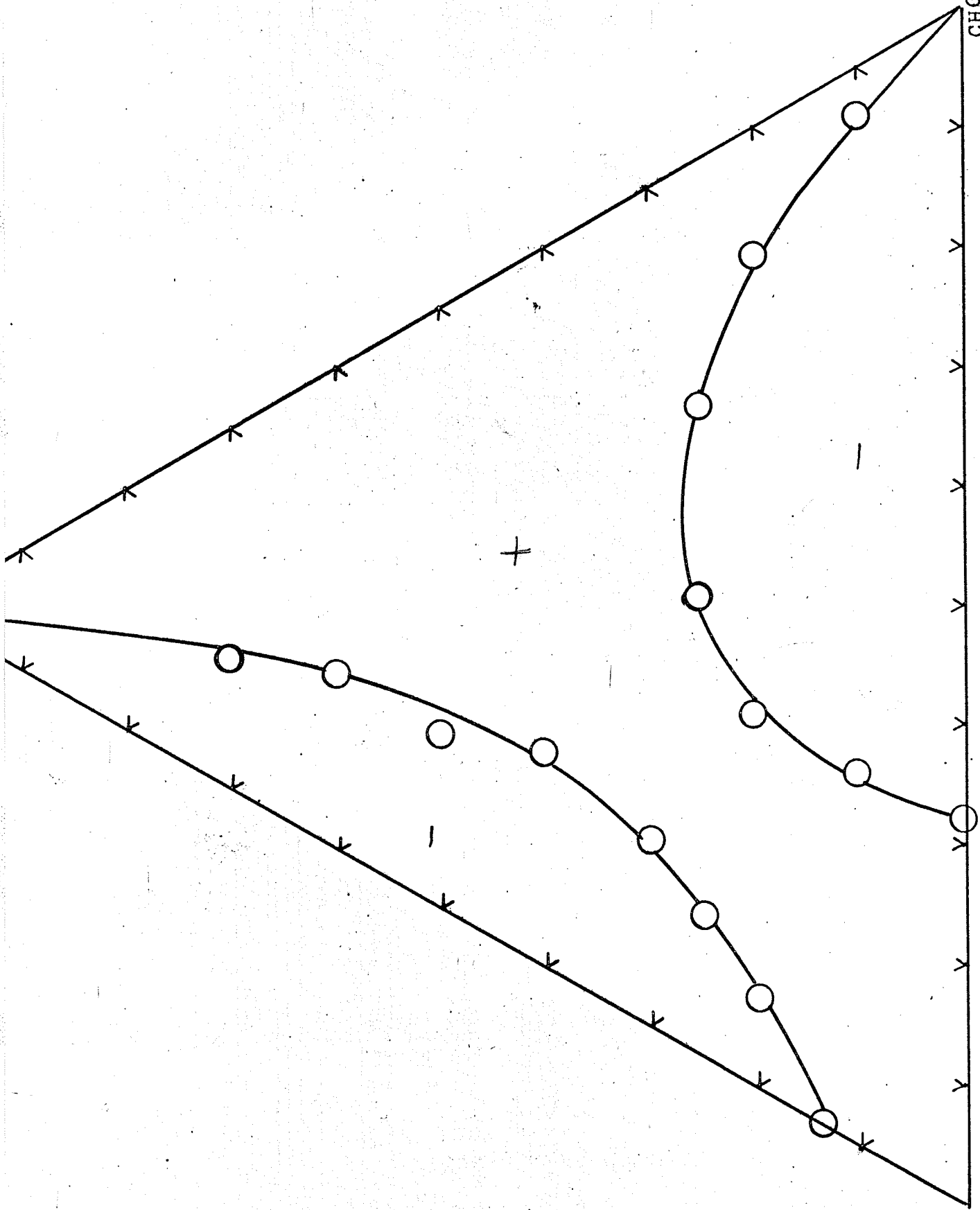
<u>Mole fractions in mixtures</u>		<u>Mole fractions in absence of benzene</u>		V^E (ml/mole)*
Acetone	Chloroform	Acetone	Chloroform	
<u>Series vii.</u> 0.60 mole fraction benzene present in all solutions.				
0.0973	0.3027	0.2433	0.7567	+0.097
0.1556	0.2444	0.3891	0.6109	+0.065
0.1823	0.2177	0.4556	0.5444	+0.058
0.2221	0.1779	0.5553	0.4447	+0.036
0.3397	0.0603	0.8492	0.1508	-0.017
<u>Series viii.</u> 0.70 mole fraction benzene present in all solutions.				
0.1150	0.1850	0.3834	0.6166	+0.065
0.1430	0.1570	0.4766	0.5234	+0.052
0.1675	0.1325	0.5584	0.4416	+0.037
0.2531	0.0469	0.8435	0.1565	-0.0141

* These figures include the volume changes on mixing of the benzene with the acetone and with the chloroform.

FIGURE 13. Zero Excess Volume Curves in the
System Acetone-Chloroform-Benzene
at 25°C.

CHCl₃

Acetone



B. DENSITY AND REFRACTOMETRIC RESULTS

THE SYSTEM ACETONE-CHLOROFORM

The densities of different mixtures are reported in Table 8. The concentrations are given in weight and mole fractions. This calibration chart was used to find out the unknown compositions of mixtures reported under vapour-liquid equilibria.

The refractive indices of several mixtures are presented in Table 9. Molar refractions are also reported in this table. These are plotted as function of mole-fraction acetone in Figure 14.

THE SYSTEM BENZENE-CHLOROFORM

Table 10 gives the densities and refractive indices of several mixtures whose concentrations are given in weight and mole fractions. This was used as a calibration chart referred to in the vapour composition determination. Molar refractions are plotted as function of mole fraction benzene in Figure 15.

THE SYSTEM ACETONE-BENZENE

Table 11 gives the densities and refractive indices as functions of concentration expressed in weight and mole-fractions. As in the other binary systems, these data were

used as a calibration chart for determining the concentrations of unknown mixtures.

THE SYSTEM ACETONE-CHLOROFORM-BENZENE

In Table 12, the densities and refractive indices are reported for 55 ternary mixtures. These were plotted on a triangular diagram as shown in Figure 26. This provided a means for the determination of concentrations in ternary systems. The concentrations were represented in weight fractions on the equilateral triangle.

TABLE 8

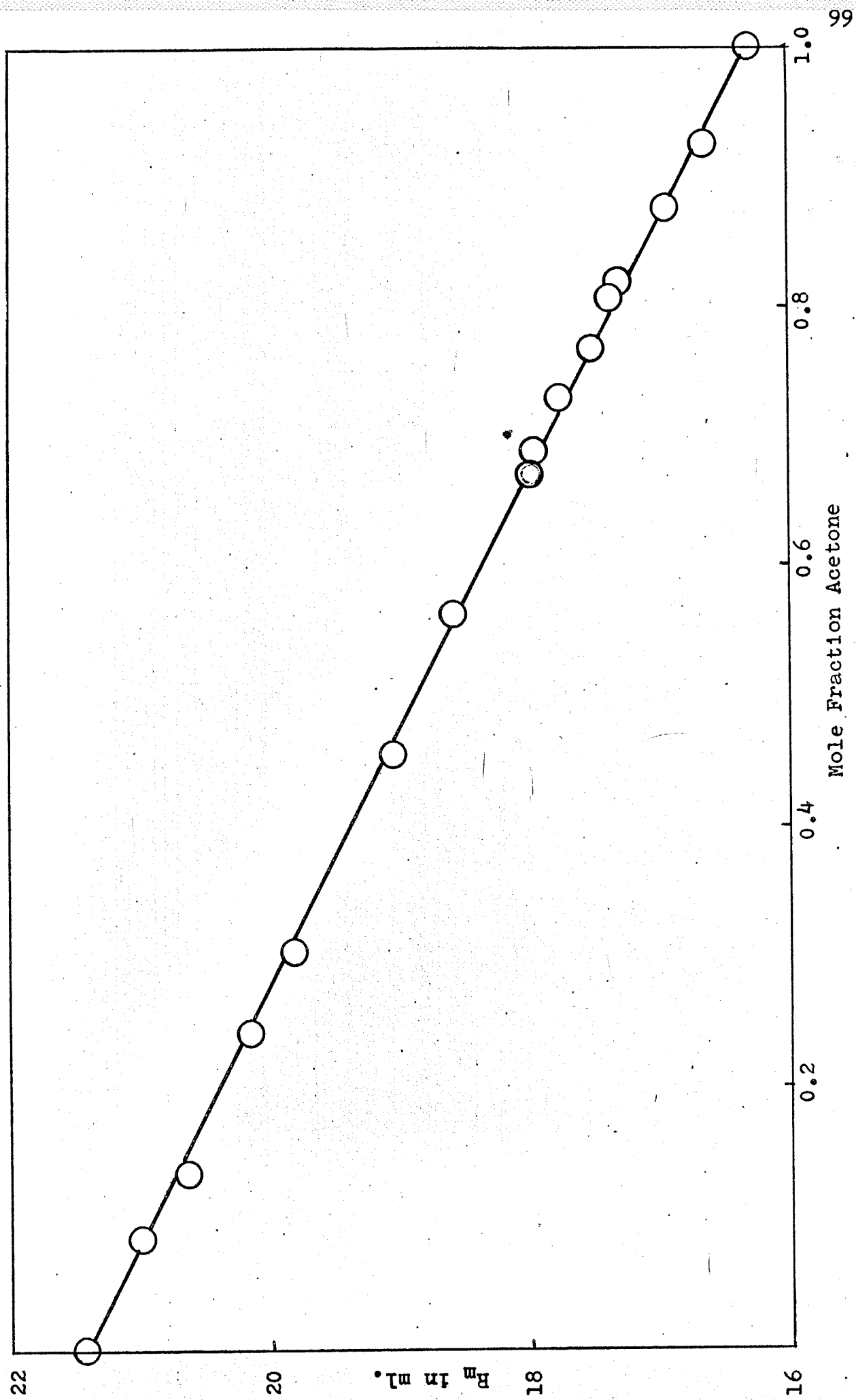
DENSITY DATA FOR ACETONE-CHLOROFORM AT 25°C.

<u>Wt. Fractions</u>		<u>Mole Fractions</u>		Density d_4^{25}
Acetone	CHCl ₃	Acetone	CHCl ₃	
0.8451	0.1549	0.9182	0.0818	0.8453
0.7742	0.2258	0.8757	0.1243	0.8772
0.6996	0.3004	0.8272	0.1728	0.9130
0.6700	0.3300	0.8067	0.1933	0.9284
0.6164	0.3836	0.7676	0.2324	0.9568
0.5683	0.4317	0.7302	0.2698	0.9842
0.5182	0.4818	0.6886	0.3114	1.0143
0.3909	0.6091	0.5688	0.4312	1.1004
0.2918	0.7082	0.4585	0.5415	1.1774
0.1741	0.8259	0.3023	0.6977	1.2842
0.1355	0.8645	0.2437	0.7563	1.3235
0.0712	0.9288	0.1361	0.8639	1.3939
0.0504	0.9496	0.0984	0.9016	1.4180
0.0434	0.9566	0.0853	0.9147	1.4262

TABLE 9
REFRACTIVE PROPERTIES OF THE SYSTEM
ACETONE-CHLOROFORM AT 25°C.

Wt. fractions		Mole fractions		n_D^{25}	R_m (in ml.)
Acetone	CHCl ₃	Acetone	CHCl ₃		
0.0000	1.000	0.0000	1.000	1.4433	21.3917
0.0434	0.9566	0.0853	0.9147	1.4359	20.9224
0.0712	0.9288	0.1361	0.8639	1.4320	20.6617
0.1355	0.8645	0.2437	0.7563	1.4239	20.1503
0.1741	0.8259	0.3023	0.6977	1.4190	19.8343
0.2918	0.7082	0.4585	0.5415	1.4063	19.0567
0.3909	0.6091	0.5688	0.4312	1.3973	18.5092
0.4993	0.5007	0.6721	0.3279	1.3879	17.9802
0.5182	0.4818	0.6886	0.3114	1.3876	17.9368
0.5680	0.4320	0.7299	0.2701	1.3834	17.7139
0.6164	0.3836	0.7676	0.2324	1.3796	17.4930
0.6700	0.3300	0.8067	0.1933	1.3764	17.3065
0.6791	0.3209	0.8130	0.1870	1.3759	17.2813
0.7742	0.2258	0.8757	0.1243	1.3693	16.9143
0.8451	0.1549	0.9182	0.0818	1.3643	16.6497
1.0000	0.0000	1.0000	0.0000	1.3563	16.1946

FIGURE 14. Molar Refraction as Function of Mole-Fraction Acetone in the System Acetone-Chloroform at 25°C.



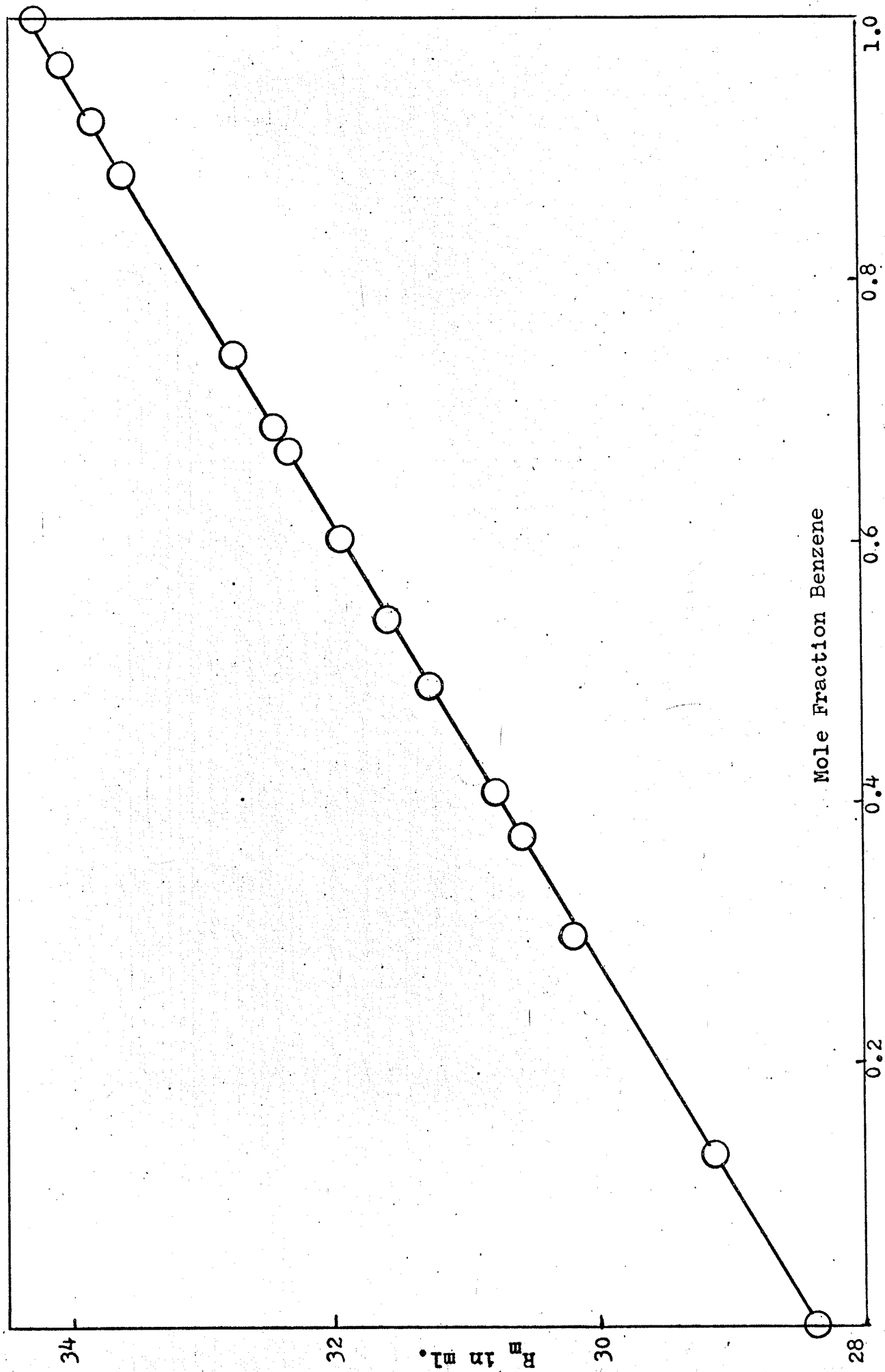
Mole Fraction Acetone

P_m in ml.

TABLE 10
 DENSITY AND REFRACTIVE INDEX DATA FOR THE
 SYSTEM BENZENE-CHLOROFORM
 AT 25°C.

Wt. fractions		Mole fractions		Density d_4^{25}	n_D^{25}	R_m (in ml.)
Benzene	CHCl ₃	Benzene	CHCl ₃			
1.000	0.0000	1.0000	0.0000	0.8734	1.4979	34.302
0.9421	0.0579	0.9613	0.0387	0.8942	1.4960	34.077
0.8847	0.1153	0.9214	0.0786	0.9161	1.4936	33.832
0.8277	0.1723	0.8801	0.1199	0.9387	1.4916	33.607
0.6523	0.3477	0.7414	0.2586	1.0171	1.4842	32.783
0.5886	0.4114	0.6862	0.3138	1.0482	1.4810	32.469
0.5713	0.4287	0.6707	0.3293	1.0577	1.4800	32.351
0.4978	0.5022	0.6023	0.3977	1.0975	1.4769	31.978
0.4339	0.5661	0.5395	0.4605	1.1347	1.4735	31.609
0.3113	0.6887	0.4086	0.5914	1.2147	1.4659	30.794
0.2796	0.7204	0.3724	0.6276	1.2374	1.4642	30.583
0.2176	0.7824	0.2983	0.7017	1.2837	1.4607	30.176
0.0888	0.9112	0.1297	0.8707	1.3935	1.4505	29.105
0.0000	1.0000	0.0000	1.0000	1.4805	1.4433	28.323

FIGURE 15. Molar Refraction as Function of
Mole-fraction Benzene in the System
Benzene-Chloroform at 25°C.



Mole Fraction Benzene

R_m in ml.

TABLE 11
 DENSITY AND REFRACTIVE INDEX DATA FOR THE
 SYSTEM ACETONE-BENZENE
 AT 25°C.

Wt. fractions		Mole fractions		Density d_4^{25}	n_D^{25}
Benzene	Acetone	Benzene	Acetone		
0.0000	1.0000	0.0000	1.0000	0.7842	1.3563
0.1368	0.8632	0.1054	0.8946	0.7956	1.3745
0.2422	0.7578	0.1920	0.8080	0.8046	1.3883
0.2877	0.7123	0.2309	0.7691	0.8084	1.3954
0.3364	0.6636	0.2738	0.7262	0.8127	1.4014
0.4062	0.5938	0.3371	0.6629	0.8188	1.4105
0.5130	0.4870	0.4392	0.5608	0.8283	1.4264
0.5187	0.4813	0.4448	0.5552	0.8288	1.4279
0.5832	0.4168	0.5100	0.4900	0.8346	1.4364
0.6034	0.3966	0.5308	0.4692	0.8365	1.4397
0.6616	0.3384	0.5924	0.4076	0.8417	1.4484
0.7301	0.2699	0.6679	0.3321	0.8481	1.4584
0.7595	0.2405	0.7014	0.2986	0.8506	1.4624
0.8129	0.1871	0.7636	0.2364	0.8557	1.4704
0.8520	0.1480	0.8105	0.1895	0.8592	1.4764
0.9299	0.0701	0.9080	0.0920	0.8663	1.4879
1.0000	0.0000	1.0000	0.0000	0.8734	1.4979

TABLE 12

DENSITY AND REFRACTIVE INDEX DATA FOR THE
SYSTEM ACETONE-CHLOROFORM-BENZENE AT 25°C

No.	Acetone		Chloroform		Benzene		Density d_4^{25}	Ref. Index n_D^{25}
	Wt. %	Mole %	Wt. %	Mole %	Wt. %	Mole %		
1.	17.52	27.96	62.98	48.90	19.50	23.14	1.1472	1.4354
2.	12.77	19.40	45.90	33.91	41.33	46.69	1.0562	1.4560
3.	10.46	15.53	37.60	27.15	51.94	57.32	1.0173	1.4649
4.	8.38	12.18	30.11	21.30	61.51	66.52	0.9847	1.4726
5.	5.65	8.02	20.32	14.00	74.03	77.98	0.9452	1.4817
6.	7.28	12.68	72.94	61.74	19.78	25.58	1.2309	1.4486
7.	5.89	9.69	58.93	47.22	35.18	43.09	1.1402	1.4608
8.	4.47	6.98	44.74	34.01	50.79	59.01	1.0611	1.4714
9.	3.81	5.81	38.11	28.29	58.08	65.90	1.0281	1.4760
10.	2.27	3.29	22.73	16.00	75.00	80.71	0.9590	1.4860
11.	32.24	46.52	51.81	36.37	15.95	17.11	1.0612	1.4169
12.	25.64	36.44	41.20	28.50	33.16	35.06	1.0154	1.4361
13.	17.52	24.47	28.16	19.13	54.32	56.40	0.9654	1.4580
14.	13.88	19.24	22.31	15.03	63.81	65.73	0.9446	1.4671
15.	8.52	11.66	13.69	9.12	77.79	79.22	-	1.4797
16.	49.65	62.74	30.94	19.02	19.41	18.24	0.9401	1.4034
17.	39.67	50.75	24.72	15.39	35.61	33.86	0.9260	1.4238
18.	26.64	34.64	16.60	10.50	56.76	54.86	0.9079	1.4494
19.	22.21	29.03	13.84	8.80	63.95	62.17	0.9021	1.4583

continued

TABLE 12 CONTINUED

No.	Acetone		Chloroform		Benzene		Density d_4^{25}	Ref. Index n_D^{25}
	Wt. %	Mole %	Wt. %	Mole %	Wt. %	Mole %		
20.	11.76	15.58	7.33	4.72	80.91	79.70	0.8884	1.4780
21.	15.76	21.41	18.55	12.25	65.69	66.34	0.9274	1.4666
22.	12.23	17.97	36.81	26.32	50.96	55.71	1.0117	1.4620
23.	8.44	13.61	56.38	44.22	35.18	42.17	1.1216	1.4578
24.	4.15	7.51	78.54	69.19	17.31	23.30	1.2790	1.4513
25.	2.37	4.53	87.74	81.45	9.89	14.02	1.3583	1.4478
26.	37.89	46.61	10.77	6.44	51.34	46.95	0.8753	1.4356
27.	29.25	39.60	31.12	20.50	39.63	39.90	0.9653	1.4372
28.	19.90	30.24	53.13	39.28	26.97	30.47	1.0860	1.4391
29.	11.83	20.10	72.15	59.65	16.02	20.25	1.2177	1.4402
30.	5.25	9.88	87.63	80.17	7.12	9.95	1.3509	1.4420
31.	52.20	61.32	10.20	5.83	37.60	32.85	0.8594	1.4140
32.	37.43	50.04	35.61	23.16	26.96	26.80	0.9752	1.4198
33.	25.03	37.85	56.94	41.88	18.03	20.27	1.1002	1.4247
34.	13.08	22.63	77.50	65.25	9.42	12.12	1.2551	1.4339
35.	4.30	8.32	92.60	87.22	3.10	4.46	1.3974	1.4401
36.	65.27	75.77	19.28	10.89	15.45	13.34	0.8790	1.3890
37.	45.19	60.57	44.12	28.77	10.69	10.66	1.0048	1.4012
38.	26.89	41.96	66.74	50.65	6.37	7.39	1.1537	1.4139
39.	14.00	24.69	82.69	70.97	3.31	4.34	1.2920	1.4260

continued

TABLE 12 CONTINUED

No.	Acetone		Chloroform		Benzene		Density d_4^{25}	Ref. Index n_D^{25}
	Wt. %	Mole %	Wt. %	Mole %	Wt. %	Mole %		
40.	8.07	15.14	90.02	82.19	1.91	2.67	1.3656	1.4330
41.	6.26	9.09	27.47	19.39	66.27	71.52	0.9751	1.4770
42.	21.94	29.60	22.87	15.02	55.19	55.38	0.9378	1.4541
43.	42.03	52.04	16.99	10.23	40.98	37.73	0.8933	1.4252
44.	58.76	68.07	12.08	6.81	29.16	25.12	0.8591	1.4039
45.	81.93	87.15	5.29	2.74	12.78	10.11	0.8205	1.3767
46.	6.98	10.88	46.68	35.41	46.34	53.71	1.0678	1.4664
47.	17.74	25.98	41.28	29.41	40.98	44.61	1.0254	1.4496
48.	34.21	45.83	33.02	21.52	32.77	32.65	0.9665	1.4266
49.	55.29	66.80	22.44	13.19	22.27	20.01	0.8994	1.4017
50.	10.72	17.54	62.14	49.45	27.14	33.01	1.1522	1.4485
51.	40.72	54.88	41.26	27.06	18.02	18.06	0.9955	1.4100
52.	75.26	84.34	17.22	9.39	7.52	6.27	0.8614	1.3764
53.	22.02	19.45	67.06	64.50	10.92	16.05	1.1644	1.4236
54.	54.84	69.91	38.84	24.09	6.32	6.00	0.9669	1.3897
55.	67.49	79.89	27.96	16.10	4.55	4.01	0.9083	1.3787

C. VISCOSITY DATATHE SYSTEM ACETONE-CHLOROFORM

Table 13 gives the viscosity values for this system. Fluidity data are included in column 4. Viscosity values have been plotted as function of mole-fraction chloroform in Figure 16.

Considering the viscosity-composition curve to run smoothly between the viscosities of the pure components in a perfect solution (which might not be strictly true as elaborated in the discussions) it was possible to evaluate the excess viscosity from the smoothed values of viscosity-composition curve for solutions of Acetone-Chloroform. The data are presented in Table 14, and are plotted in Figure 17.

THE SYSTEM BENZENE-CHLOROFORM

Table 15 gives the viscosity and fluidity data for this system. These are plotted in Figure 18.

The differences of actual viscosity and fluidity from the corresponding ideal values are also given in Table 15. Excess viscosity values are plotted in Figure 19, and excess fluidities are plotted in Figure 20, both as functions of mole-fraction chloroform.

THE SYSTEM ACETONE-BENZENE

In Table 16, the viscosity and fluidity values are

listed. These have been plotted as functions of mole-fraction acetone in Figure 21.

The differences of actual viscosity from the corresponding ideal values are also given in Table 16. The excess viscosities are plotted in Figure 22, as function of mole-fraction acetone.

TABLE 13
 VISCOSITY AND FLUIDITY DATA FOR THE
 SYSTEM ACETONE-CHLOROFORM
 AT 25°C

Mole fractions		Viscosity Cpoise	Fluidity F, Cp ⁻¹
Acetone	CHCl ₃		
1.000	0.000	0.3020	3.312
0.9182	0.0818	0.3261	3.067
0.8757	0.1243	0.3425	2.920
0.8067	0.1933	0.3628	2.757
0.7676	0.2324	0.3817	2.620
0.7302	0.2698	0.3926	2.547
0.6886	0.3114	0.4042	2.474
0.6721	0.3279	0.4110	2.433
0.5688	0.4312	0.4495	2.225
0.4585	0.5415	0.4864	2.056
0.3023	0.6977	0.5258	1.902
0.2437	0.7563	0.5360	1.866
0.1361	0.8639	0.5423	1.844
0.0853	0.9147	0.5415	1.847
0.0000	1.0000	0.542	1.845

FIGURE 16. Viscosity as Function of Mole-Fraction
Chloroform in Acetone-Chloroform System
at 25°C.

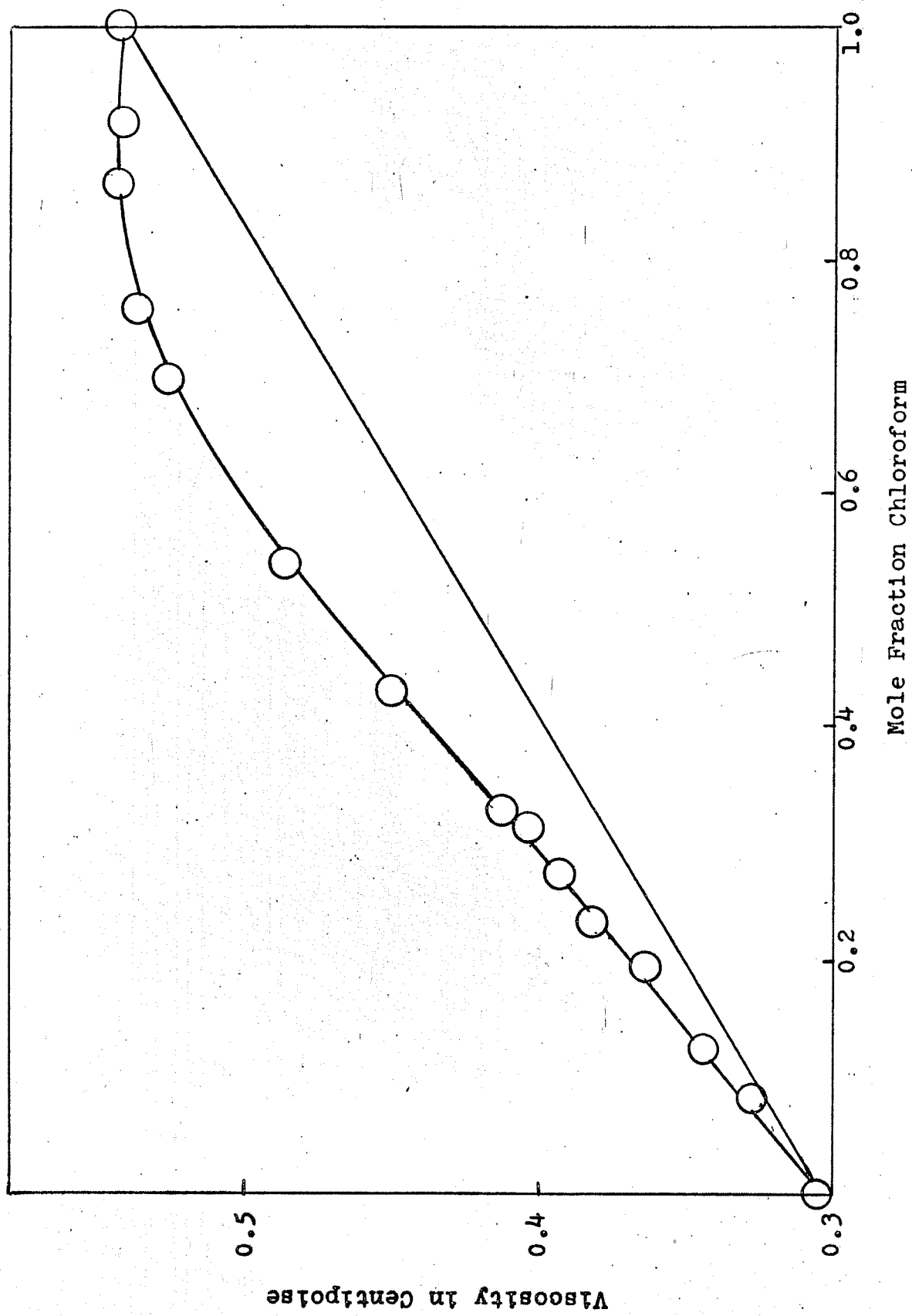


TABLE 14
SMOOTHED DATA FOR EXCESS VISCOSITY IN
ACETONE-CHLOROFORM SYSTEM AT 25°C

Mole fraction CHCl ₃	Excess viscosity, in C _p
0.1	+ 0.008
0.2	+ 0.018
0.3	+ 0.027
0.4	+ 0.038
0.5	+ 0.049
0.6	+ 0.057
0.7	+ 0.055
0.8	+ 0.044
0.9	+ 0.026

FIGURE 17. Excess Viscosity as Function of Mole-
fraction Chloroform in Acetone-
Chloroform System at 25°C.

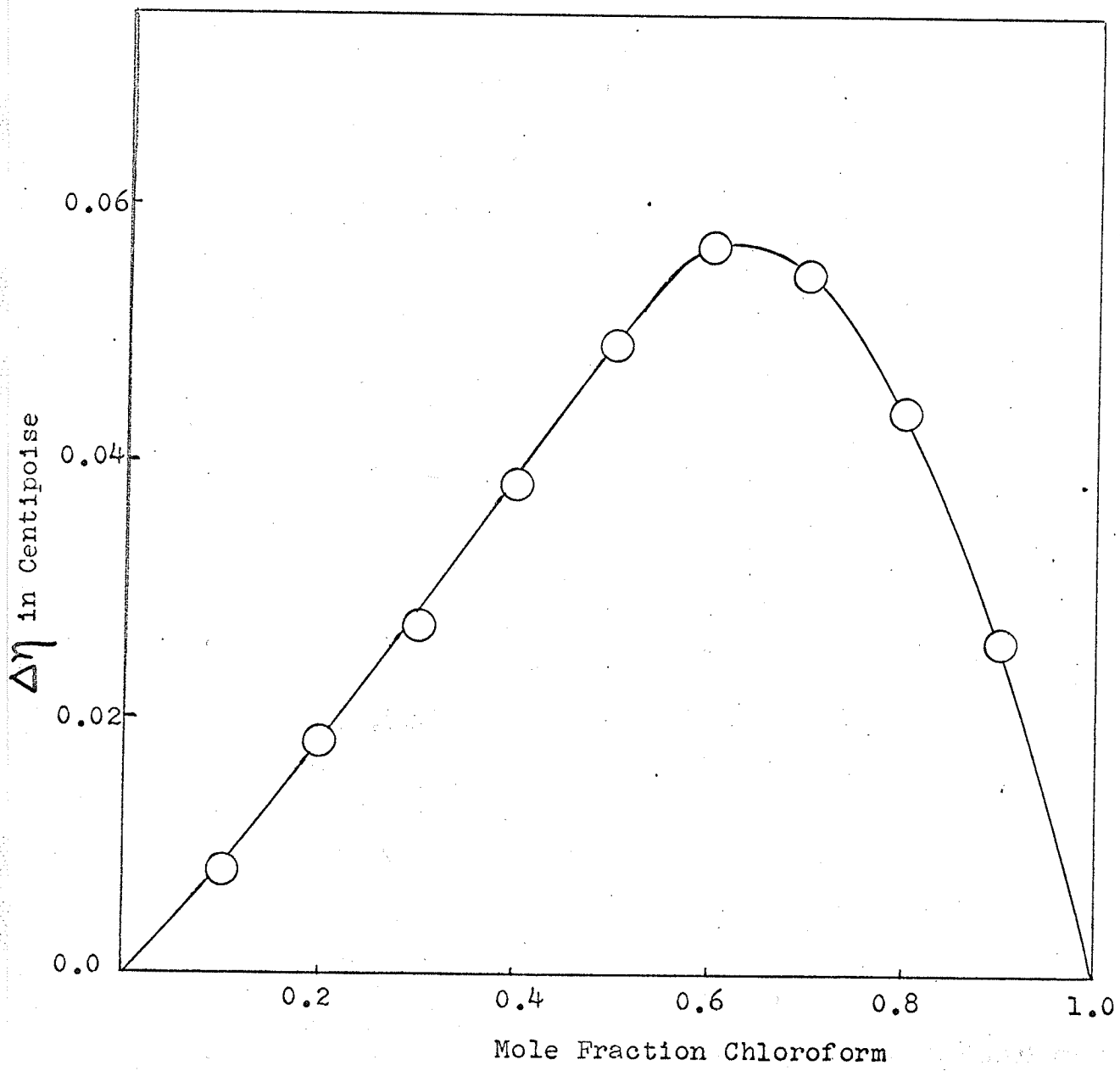
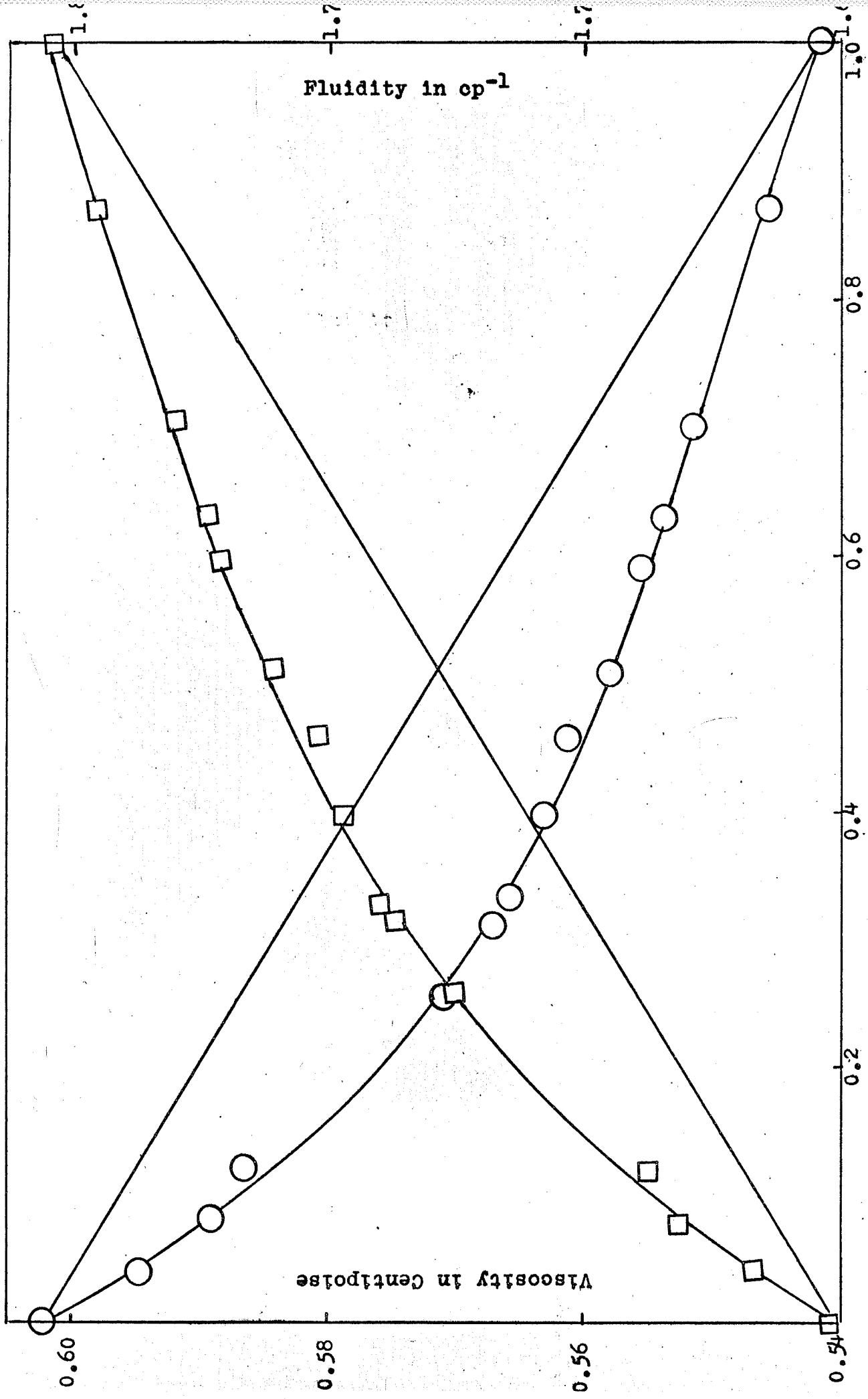


TABLE 15
 VISCOSITY AND FLUIDITY DATA FOR THE SYSTEM
 BENZENE-CHLOROFORM AT 25°C

Mole fractions		Viscosity in Cp	Fluidity F in Cp ⁻¹	$\Delta\eta$ (Negative)	ΔF (Positive)
Benzene	CHCl ₃				
0.0000	1.0000	0.5420	1.8453	0.0000	0.0000
0.1297	0.8703	0.5454	1.8335	0.0042	0.0120
0.2983	0.7017	0.5512	1.8143	0.0085	0.0250
0.3724	0.6276	0.5535	1.8065	0.0105	0.0302
0.4086	0.5914	0.5544	1.8038	0.0116	0.0330
0.4900	0.5100	0.5580	1.7922	0.0135	0.0372
0.5395	0.4605	0.5613	1.7816	0.0147	0.0400
0.6023	0.3977	0.5633	1.7753	0.0158	0.0424
0.6707	0.3293	0.5656	1.7680	0.0162	0.0429
0.6862	0.3138	0.5668	1.7643	0.0162	0.0431
0.7414	0.2586	0.5709	1.7516	0.0155	0.0412
0.8801	0.1199	0.5866	1.7047	0.0104	0.0260
0.9214	0.0786	0.5890	1.6979	0.0079	0.0195
0.9620	0.0380	0.5949	1.6810	0.0045	0.0116
1.0000	0.0000	0.6020	1.6610	0.0000	0.0000

FIGURE 18. Viscosity and Fluidity as Functions
of Mole-fraction CHCl_3 in the System
Benzene-Chloroform at 25°C .



Fluidity in cp^{-1}

Viscosity in Centipoise

Mole Fraction Chloroform

FIGURE 19. Excess Viscosity vs. Mole-fraction
CHCl₃ in the System Benzene-Chloroform
at 25°C.

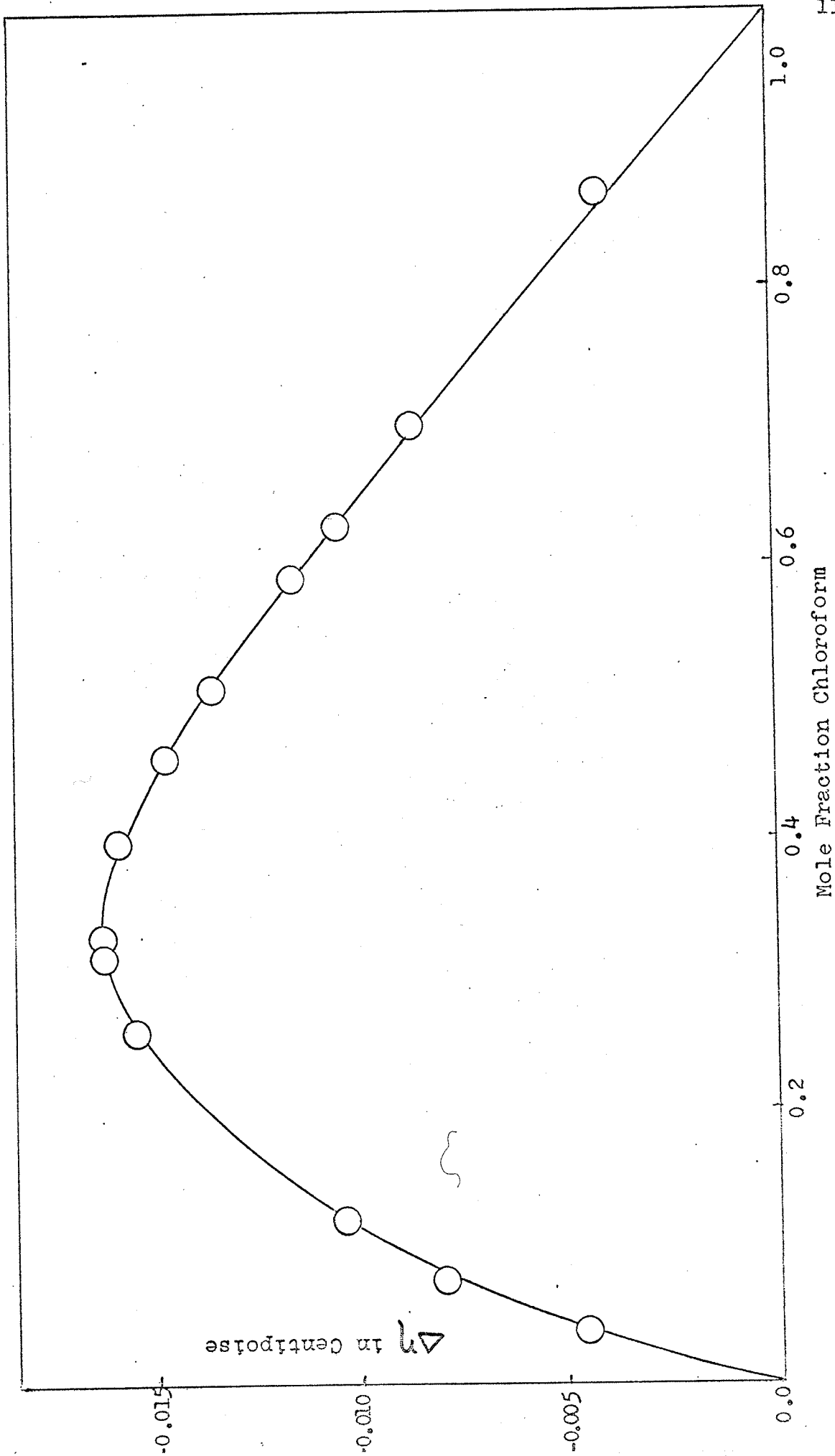


FIGURE 20. Excess Fluidity vs. Mole-fraction
Chloroform in the System Benzene-
Chloroform at 25°C.

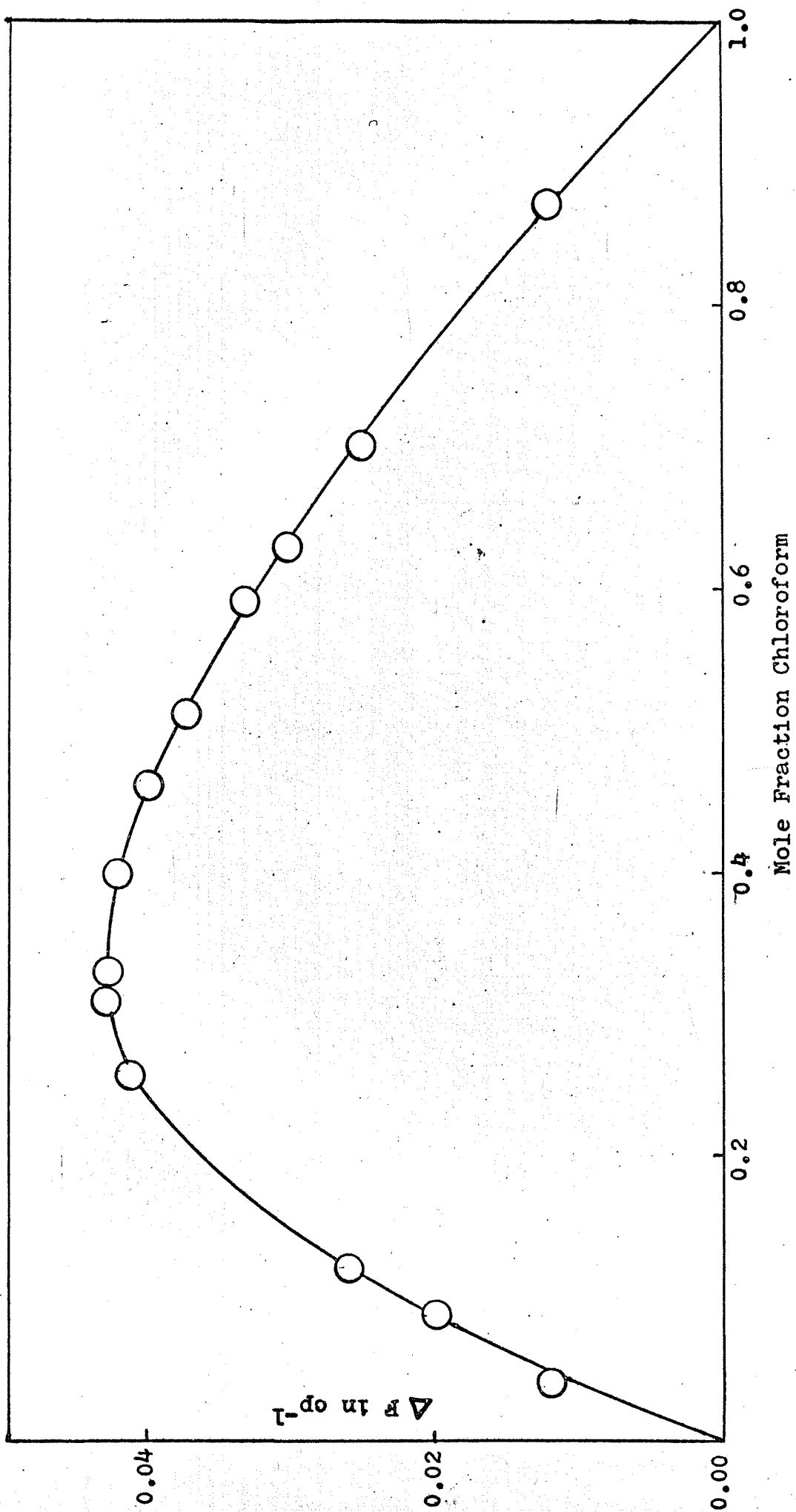


TABLE 16
 VISCOSITY AND FLUIDITY DATA FOR THE SYSTEM
 ACETONE-BENZENE AT 25°C

Mole fractions		Viscosity in Cp	Fluidity F in Cp ⁻¹	$\Delta\eta$ (Negative)
Benzene	Acetone			
0.0000	1.0000	0.3020	3.3124	0.0000
0.1054	0.8946	0.3203	3.1220	0.0138
0.1920	0.8080	0.3384	2.9555	0.0230
0.2309	0.7691	0.3451	2.8980	0.0273
0.2738	0.7262	0.3546	2.8199	0.0305
0.3371	0.6629	0.3692	2.7086	0.0345
0.4392	0.5608	0.3975	2.5160	0.0400
0.4448	0.5552	0.3985	2.5097	0.0400
0.5100	0.4900	0.4158	2.4049	0.0416
0.5308	0.4692	0.4188	2.3884	0.0423
0.5924	0.4076	0.4368	2.2894	0.0429
0.6679	0.3321	0.4654	2.1488	0.0394
0.7014	0.2986	0.4766	2.0982	0.0375
0.7636	0.2364	0.4968	2.0130	0.0334
0.8105	0.1895	0.5185	1.9287	0.0278
0.9080	0.0920	0.5569	1.7958	0.0176
1.0000	0.0000	0.6020	1.6610	0.0000

FIGURE 21. Viscosity and Fluidity as Functions
of Mole-fraction Acetone in the
System Acetone-Benzene at 25°C.

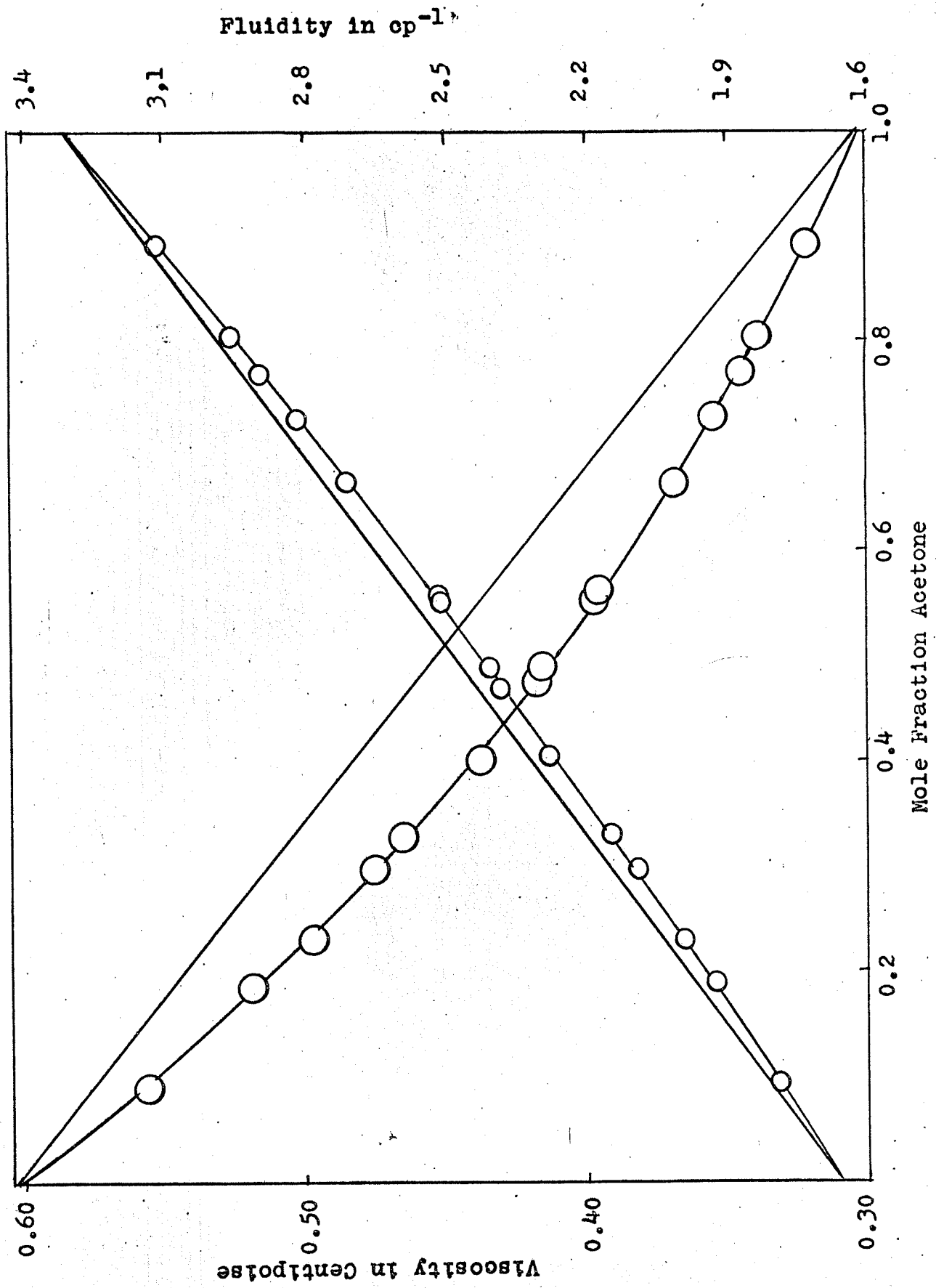
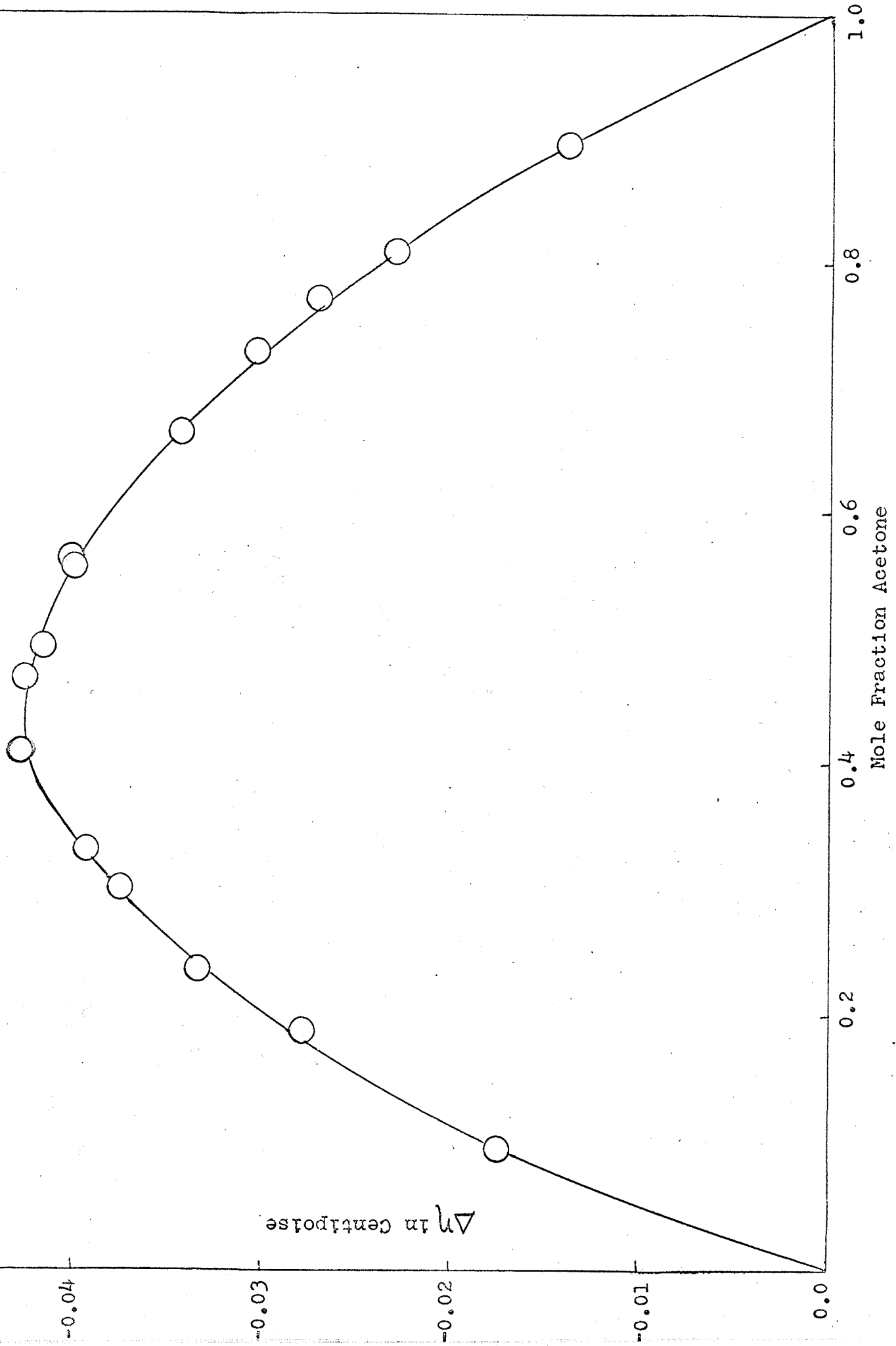


FIGURE 22. Excess Viscosity as Function of
Mole-fraction Acetone in the
System Acetone-Benzene at 25°C.



D. VAPOUR-LIQUID EQUILIBRIATHE SYSTEM ACETONE-CHLOROFORM

The total pressure as function of concentrations in weight and mole percentages is given in Table 17.

In Table 18, the results of the isothermal distillation are reported, giving the equilibrium liquid and vapour compositions expressed in weight percentages of the components. The results are plotted in Figure 23.

The data of Table 17 have been treated in order to find the partial pressures. In Table 19, the results of partial pressures are represented. This table gives respectively, the composition of the liquid in weight percentage and in mole percentage, the composition of the co-existing vapour, the total vapour pressure, and the partial vapour pressures of chloroform and acetone. The results of partial pressures and the total pressure are plotted in Figure 24, versus the mole-fraction chloroform.

Table 20 gives the values of activity, activity coefficient and partial molal excess Gibbs free energy for Acetone and for Chloroform, and the total excess Gibbs free energy of the system. The following formulae were used for this treatment

$$\mu_{\text{Acetone}}^E = RT \ln \frac{P_{\text{Acetone}}}{x_{\text{Acet.}} P_{\text{Acet.}}^0}$$

TABLE 17
 TOTAL VAPOUR PRESSURES IN THE SYSTEM
 ACETONE-CHLOROFORM AT 25°C.

Weight Percent		Mole Percent		Total Pressure mm.Hg.
CHCl ₃	Acetone	CHCl ₃	Acetone	
0.00	100.00	0.00	100.00	226.5
16.82	83.18	8.95	91.05	217.5
30.51	69.49	17.61	82.39	205.8
48.77	51.23	31.66	68.34	185.0
57.81	42.19	40.00	60.00	175.0
69.44	30.56	52.50	47.50	165.0
79.25	20.75	65.01	34.99	162.5
84.66	15.34	72.86	27.14	167.5
94.12	5.88	88.62	11.38	182.5
100.00	0.00	100.00	0.00	197.2

TABLE 18

VAPOUR-LIQUID EQUILIBRIUM COMPOSITIONS OF
THE SYSTEM ACETONE-CHLOROFORM AT 25°C.

WEIGHT PERCENT			
Liquid Composition		Vapour Composition	
CHCl ₃	Acetone	CHCl ₃	Acetone
12.54	87.46	7.00	93.00
26.63	73.37	16.95	83.05
41.91	58.09	29.00	71.00
49.95	50.05	37.50	62.50
60.03	39.97	51.50	48.50
69.56	30.44	65.60	34.40
77.93	22.07	78.00	22.00
87.48	12.52	90.00	10.00

FIGURE 23. Liquid-Vapour Composition Equilibrium
Curve for the System Acetone-Chloroform
at 25°C.

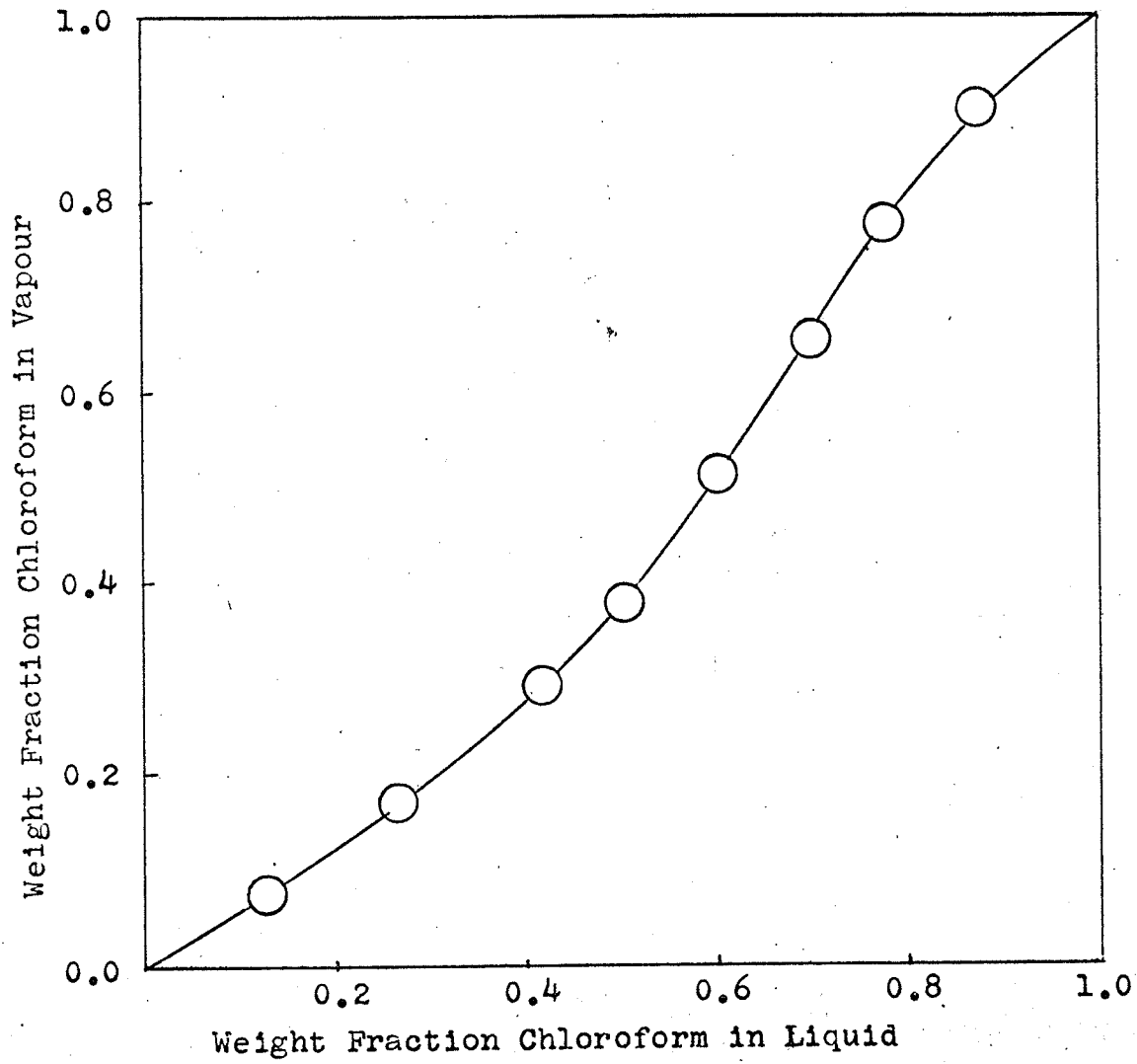


TABLE 19
 PARTIAL VAPOUR PRESSURES IN THE SYSTEM
 ACETONE-CHLOROFORM AT 25°C.

LIQUID		VAPOUR		Total Pressure (mm.Hg.)	Partial Pressures (mm.Hg.)	
Wt. % CHCl ₃	Mole % CHCl ₃	Wt. % CHCl ₃	Mole % CHCl ₃		CHCl ₃	Acetone
0.00	0.00	0.00	0.00	226.5	0.0	226.5
16.82	8.95	9.7	4.96	217.5	10.8	206.7
30.51	17.61	20.20	10.96	205.8	22.6	183.2
48.77	31.66	35.75	21.30	185.0	39.4	145.6
57.81	40.00	48.20	31.16	175.0	54.5	120.5
69.44	52.50	65.50	48.01	165.0	79.2	85.8
79.25	65.01	80.50	66.76	162.5	108.5	54.0
84.66	72.86	87.50	77.30	167.5	129.5	38.0
94.12	88.62	96.55	93.16	182.5	170.0	12.5
100.00	100.00	100.00	100.00	197.2	197.2	0.0

FIGURE 24. Total and Partial Vapour Pressure Curves
for the System Acetone-Chloroform at
25°C.

- CD Total pressure curves*
- BC Partial pressures of Acetone
- AD Partial pressures of Chloroform

*The straight lines are the
"ideal" curves.

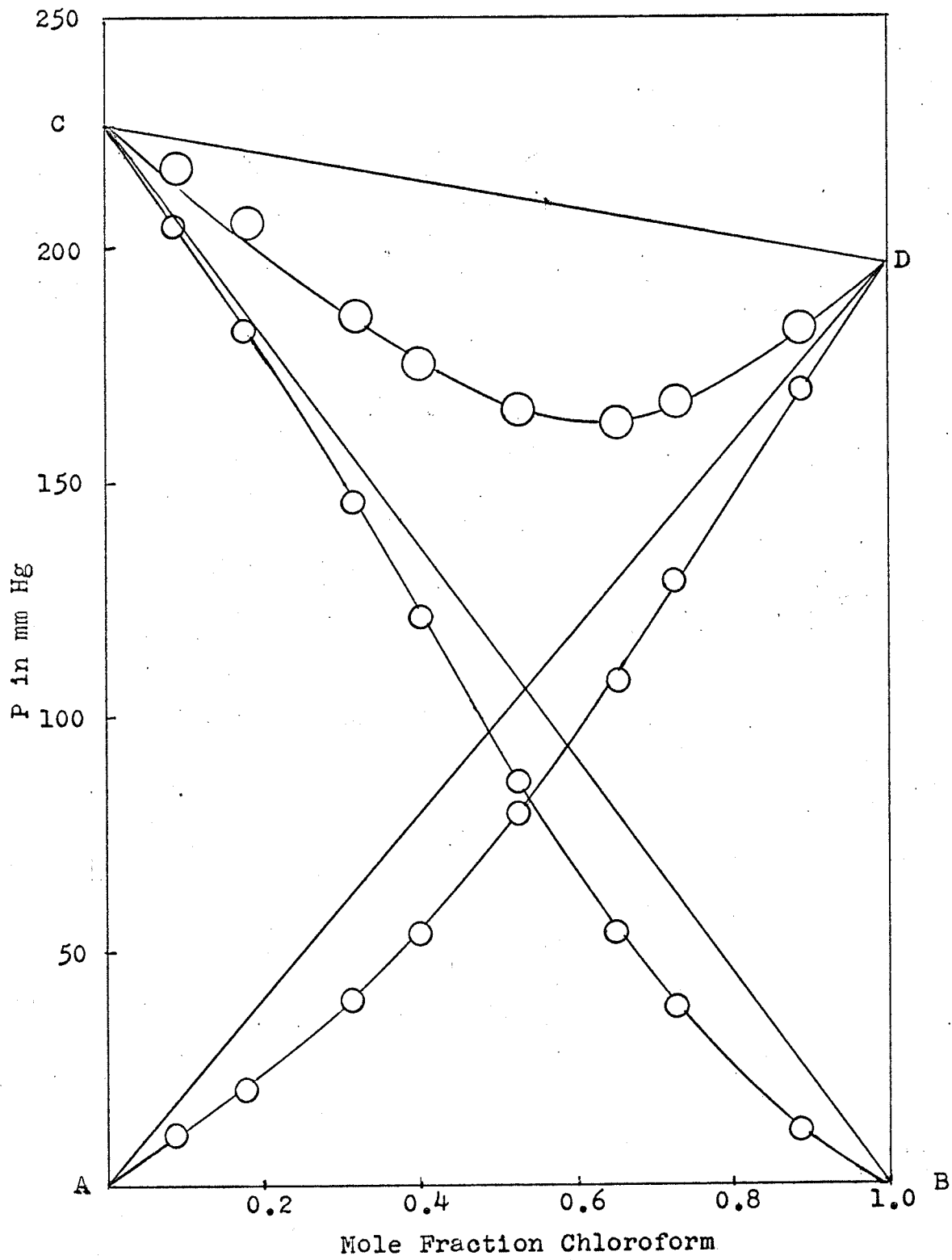


TABLE 20

EXCESS GIBBS FREE ENERGY FOR THE SYSTEM

ACETONE-CHLOROFORM AT 25°C.

Mole % CHCl ₃ in liquid	Acetone		Chloroform		G ^E (Cal/Mole)
	α	γ	α	γ	
0.00	1.000	1.000	-	-	0.0
8.95	0.9126	1.0023	+1.2	0.0548	-25.0
17.61	0.8088	0.9817	-10.9	0.1146	-53.80
31.66	0.6428	0.9406	-36.3	0.2000	-111.2
40.00	0.5320	0.8867	-71.3	0.2764	-130.4
52.50	0.3788	0.7975	-134.1	0.4016	-147.0
65.01	0.2384	0.6813	-227.4	0.5502	-142.5
72.86	0.1678	0.6183	-284.9	0.6567	-122.2
88.62	0.0550	0.4833	-430.9	0.8621	-63.4
100.0	-	-	1.000	1.000	0.0

$$\mu_{\text{CHCl}_3}^E = RT \ln \frac{P_{\text{CHCl}_3}}{x_{\text{CHCl}_3} P_{\text{CHCl}_3}^0}$$

and

$$G^E = x_{\text{Acet.}} \mu_{\text{Acet.}}^E + x_{\text{CHCl}_3} \mu_{\text{CHCl}_3}^E$$

The results of G^E have been plotted in Figure 25. From the data of Campbell and Kartzmark (67) H^E values were plotted, and from the values of H^E and G^E , the value of TS^E was calculated by means of relation (24). The results of these calculations are reported in Table 21 and in Figure 26.

The data as reported in Table 19 have been treated according to the formulas (30) proposed by von Zawidzki. For the calculation of the constants α, β , use was made of the smoothed total pressure data and approximations were applied till the values satisfied the experimental results. The constants found for chloroform are $\alpha_2 = -1.22$ and $\beta_3 = +0.49$, so that it follows for acetone $\beta_2 = -0.48$ and $\beta_3 = -0.49$. The final results showing the partial pressures as measured against the partial pressures as calculated are shown in Table 22.

THE SYSTEM BENZENE-CHLOROFORM

Table 23 shows the result of isothermal distillation giving the equilibrium liquid and vapour compositions. The

FIGURE 25. Excess Gibbs Free Energy of
Mixing of System Acetone-Chloroform
at 25°C.

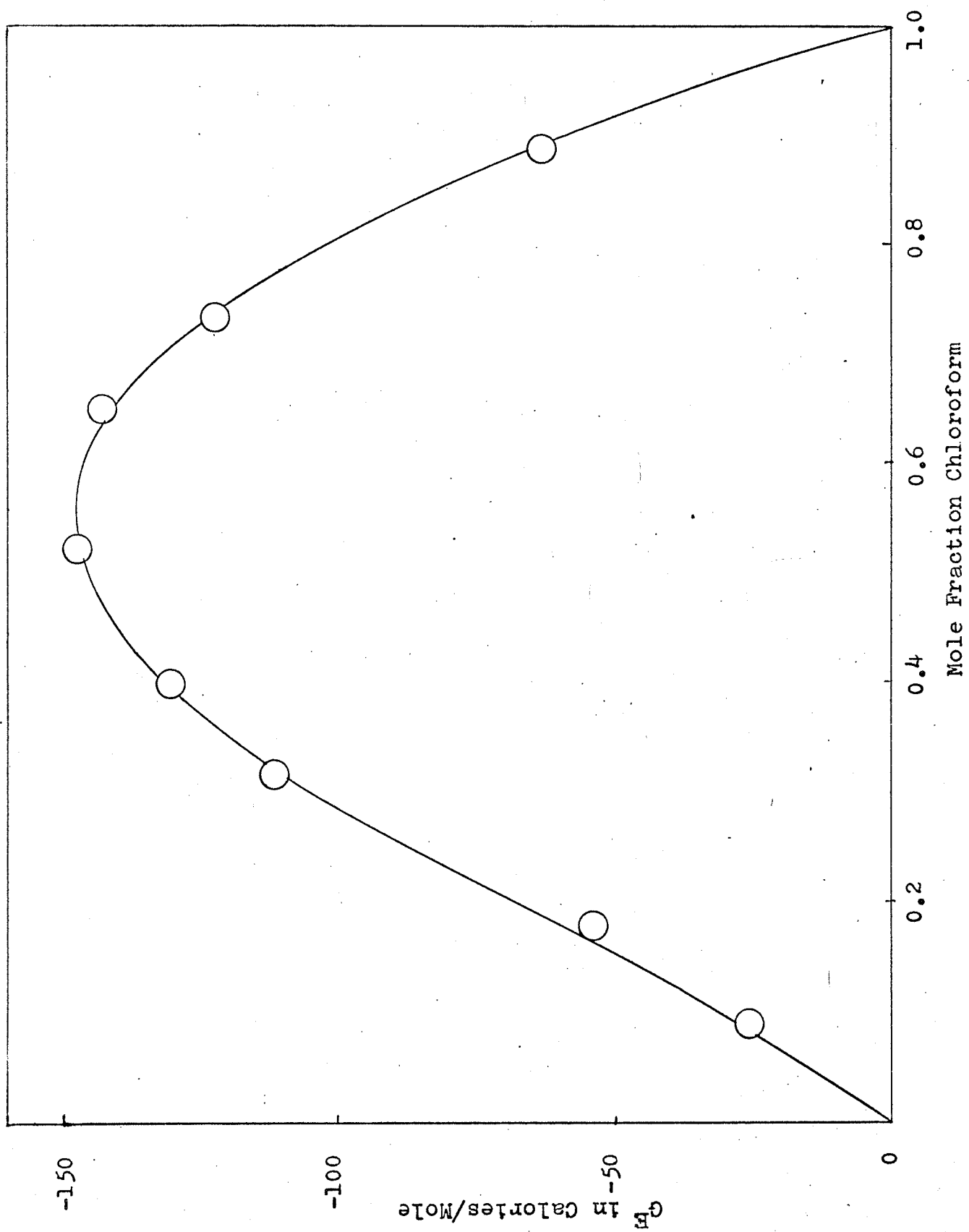


TABLE 21
EXCESS FUNCTIONS FOR THE SYSTEM ACETONE-
CHLOROFORM AT 25°C.

X_{CHCl_3}	G^E (Cal/mole)	H^E (Cal/mole)	TS^E (Cal/mole)
0.0895	-25.0	-103.8	-78.8
0.1761	-53.8	-194.0	-140.2
0.3166	-111.2	-336.8	-225.6
0.4000	-130.4	-395.2	-264.8
0.5250	-147.0	-451.2	-304.2
0.6501	-142.5	-464.0	-321.5
0.7286	-122.2	-422.7	-300.5
0.8862	-63.4	-212.8	-149.4

FIGURE 26. Excess Functions of Mixing of
System Acetone-Chloroform at
25°C.

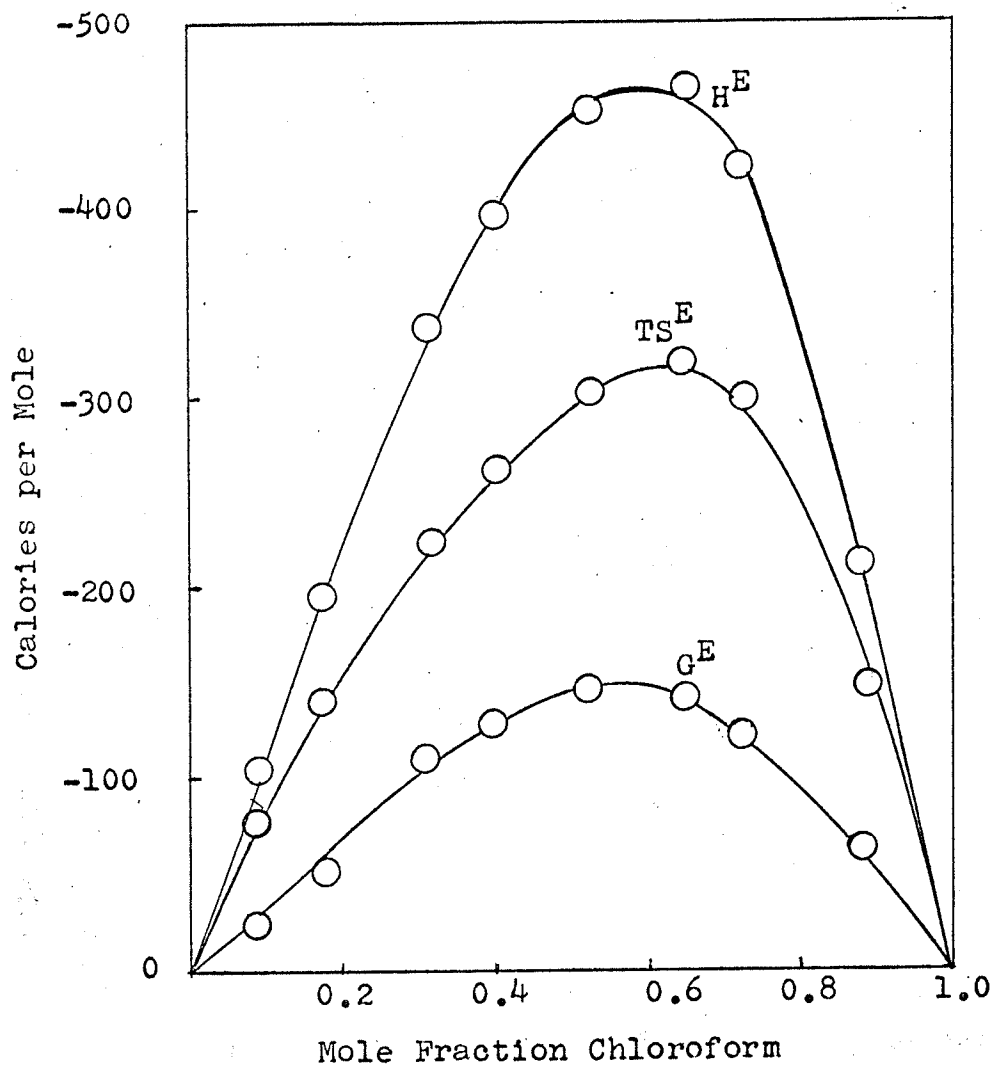


TABLE 22
 PARTIAL PRESSURES OBTAINED WITH
 VON ZAWIDZKI TREATMENT IN THE SYSTEM
 ACETONE-CHLOROFORM AT 25°C.

X_{CHCl_3}	Chloroform		Acetone	
	$P_{\text{meas.}}$	$P_{\text{calc.}}$	$P_{\text{meas.}}$	$P_{\text{calc.}}$
0.0895	10.8	9.4	206.7	205.6
0.1761	22.6	20.1	183.2	179.1
0.3166	39.4	41.4	145.6	145.2
0.4000	54.5	56.6	120.5	122.0
0.5250	79.2	82.7	85.8	88.0
0.6501	108.5	112.7	54.0	56.6
0.7286	129.5	132.7	38.0	39.5
0.8862	170.0	172.2	12.5	12.6

TABLE 23

VAPOUR-LIQUID EQUILIBRIA AND THE VAPOUR PRESSURES
OF THE SYSTEM BENZENE-CHLOROFORM AT 25°C

LIQUID Wt. % C ₆ H ₆	Mole % C ₆ H ₆		VAPOUR		Total Pressure (mm. HG.)	Partial Pressures (mm. HG.)	
	LIQUID	Wt. % C ₆ H ₆	Wt. % C ₆ H ₆	Mole % C ₆ H ₆		C ₆ H ₆	CHCl ₃
0.00	0.00	0.00	0.00	0.00	197.2	0.00	197.2
14.00	19.93	7.50	11.03	11.03	176.0	19.4	156.6
30.50	40.15	17.00	23.84	23.84	152.0	36.2	115.8
44.50	55.07	27.50	36.70	36.70	134.0	49.2	84.8
56.75	66.73	40.00	50.47	50.47	121.5	61.3	60.2
67.25	75.84	52.50	62.81	62.81	111.5	70.0	41.5
76.75	83.46	65.00	73.95	73.95	105.8	78.2	27.6
85.50	90.01	77.50	84.03	84.03	101.9	85.6	16.3
92.50	94.96	88.00	91.81	91.81	97.5	89.5	8.0
100.00	100.00	100.00	100.00	100.00	95.0	95.0	0.0

results are shown in Figure 27. The total pressure for such mixtures are also listed in this table. The partial pressures calculated from vapour-liquid equilibria are listed in the last two columns of Table 23. The total pressure and the partial pressures are plotted against mole-fraction benzene in Figure 28.

Table 24 gives the values of activity, activity coefficient, and partial molal excess Gibbs free energy for benzene and for chloroform, and the total excess Gibbs free energy of the system. From the data of Campbell et al (2) H^E values were plotted and from these H^E values and my own G^E values, the function TS^E was calculated by means of relation (24). The results of these calculations are reported in Table 25 and Figure 29.

THE SYSTEM ACETONE-BENZENE

Table 26 shows the results of isothermal distillation giving the equilibrium liquid and vapour compositions. This table also shows the total pressure for such mixtures and the partial pressures calculated from vapour-liquid equilibria. The results of vapour-liquid equilibrium are plotted in Figure 30, and those of total and partial pressures in Figure 31.

Table 27 gives the values of activity, activity coefficient and partial molal excess Gibbs free energy

FIGURE 27. Liquid-Vapour Composition Equilibrium
Curve for the System Benzene-Chloro-
form at 25°C.

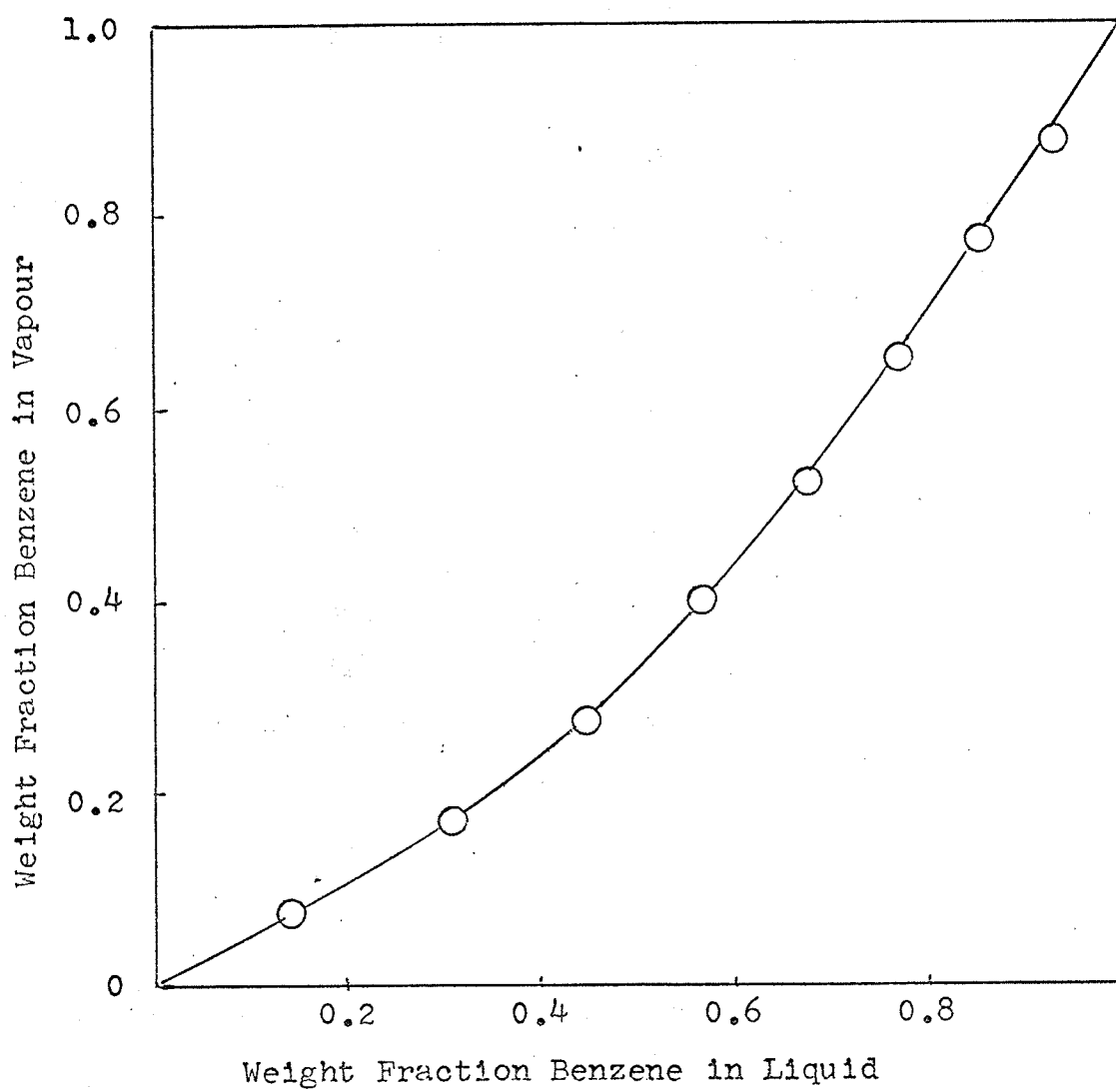


FIGURE 28. Total and Partial Vapour Pressure
Curves for the System Benzene-
Chloroform at 25°C.

CD Total pressure curve*

AD Partial pressures of Benzene

CD Partial pressures of Chloroform

*The straight lines are the "ideal"
curves.

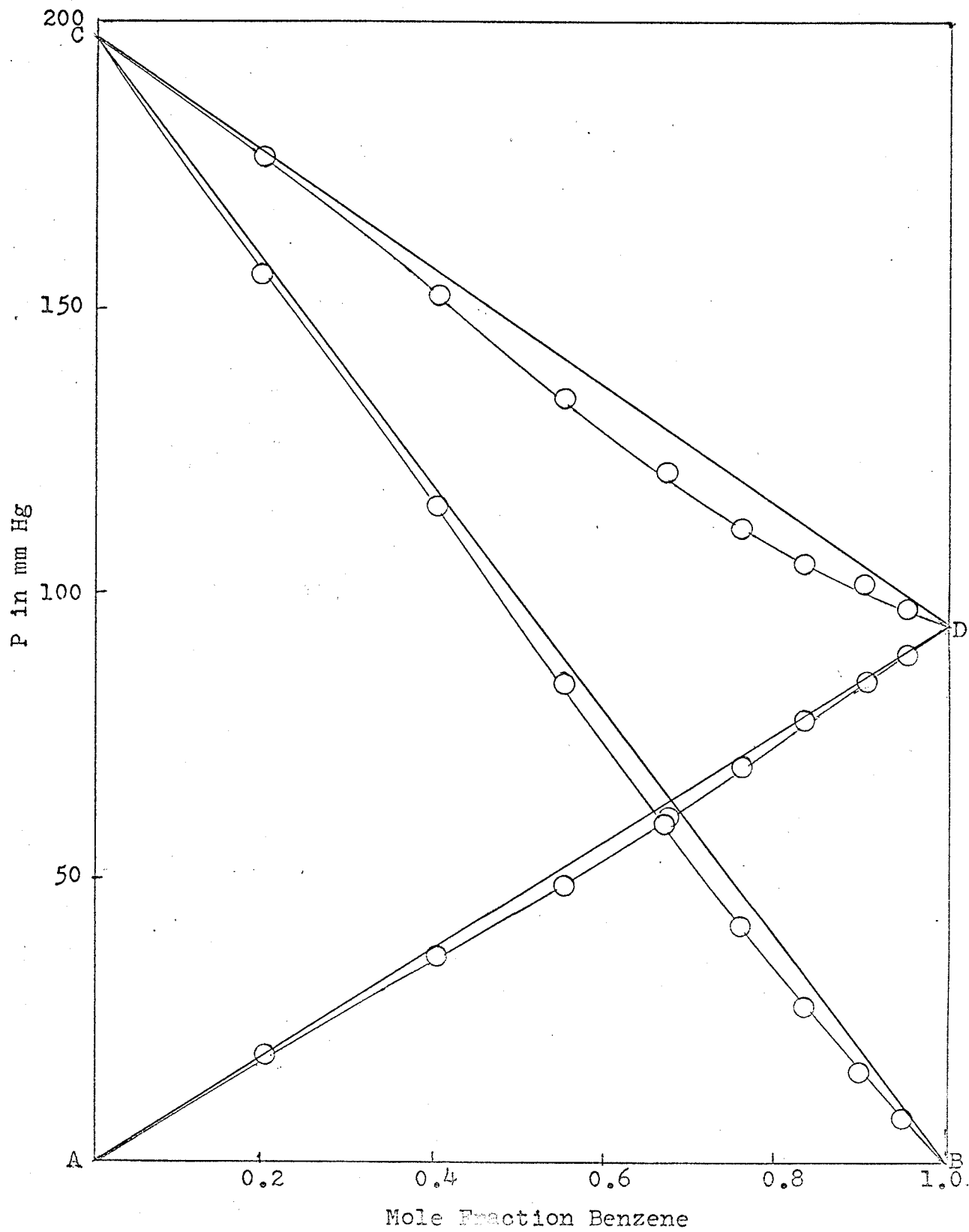


TABLE 24

EXCESS GIBBS FREE ENERGY FOR THE SYSTEM

BENZENE-CHLOROFORM AT 25°C

$x_{C_6H_6}$	BENZENE			CHLOROFORM			G^E (Cal/mole)
	α	γ	μ^E (Cal/mole)	α	γ	μ^E (Cal/mole)	
0.000	-	-	-	1.000	1.000	-	0.0
0.1993	0.2042	1.0246	+14.4	0.7941	0.9916	- 5.0	-1.1
0.4015	0.3811	0.9489	-31.1	0.5872	0.9811	-11.3	-19.3
0.5507	0.5179	0.9404	-36.4	0.4300	0.9570	-26.0	-31.7
0.6673	0.6453	0.9670	-19.9	0.3053	0.9176	-51.0	-30.3
0.7584	0.7369	0.9717	-17.0	0.2104	0.8709	-81.9	-32.7
0.8346	0.8232	0.9863	- 8.2	0.1400	0.8464	-98.8	-23.1
0.9001	0.9011	1.0011	+ 0.64	0.0827	0.8278	-112.0	-10.6
0.9496	0.9422	0.9922	- 4.6	0.0406	0.8048	-128.7	-10.9
1.000	1.000	1.000	-	-	-	-	0.0

TABLE 25
 EXCESS FUNCTIONS OF MIXING FOR THE
 SYSTEM BENZENE-CHLOROFORM AT 25°C

$X_{C_6H_6}$	G^E (Cal/mole)	H^E (Cal/mole)	TS^E (Cal/mole)
0.1993	- 1.1	-71.0	-69.9
0.4015	-19.3	-102.5	-83.2
0.5507	-31.7	-106.0	-74.3
0.6673	-30.3	- 86.0	-55.7
0.7584	-32.7	- 65.8	-33.1
0.8346	-23.1	- 46.7	-23.6
0.9001	-10.6	- 29.0	-18.4
0.9496	-10.9	- 14.0	- 3.1

FIGURE 29. Excess Functions of Mixing for the
System Benzene-Chloroform at 25°C.

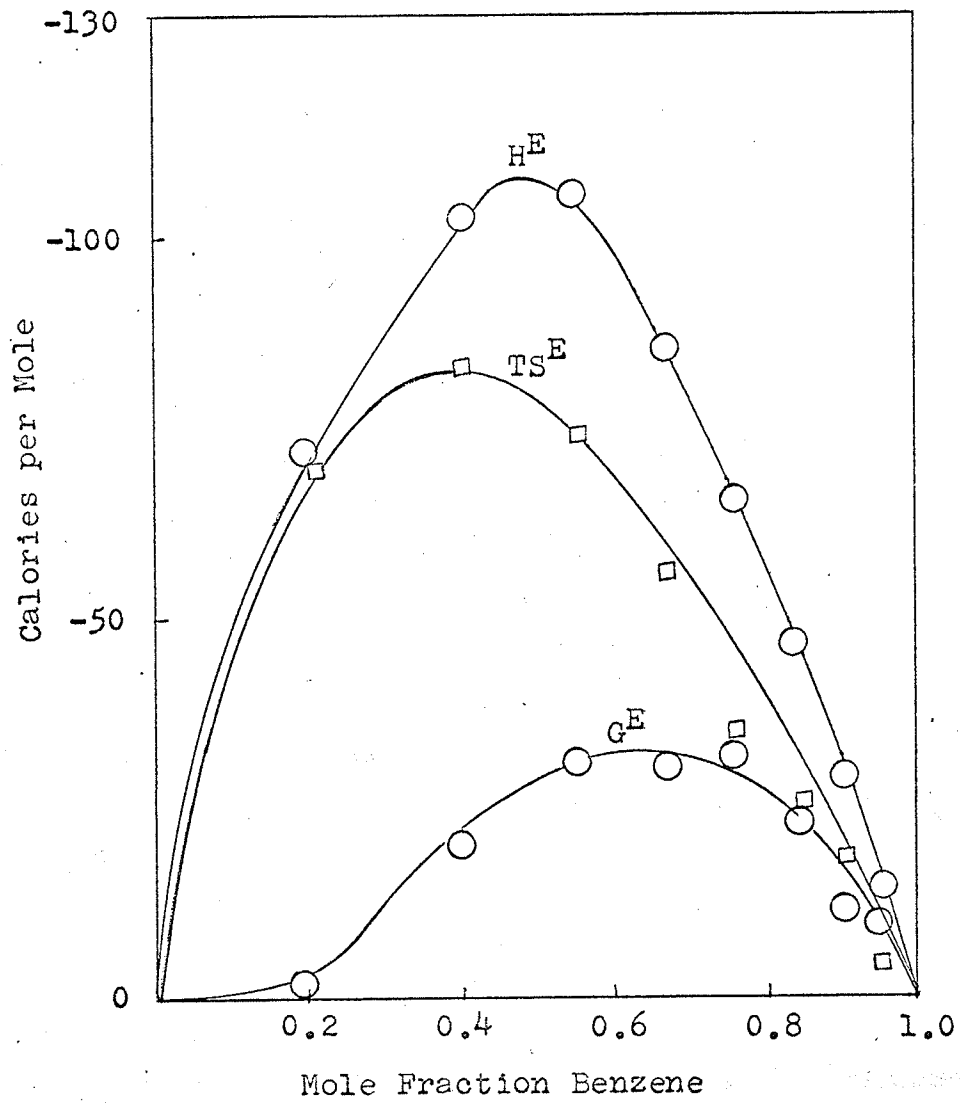


TABLE 26

VAPOUR-LIQUID EQUILIBRIA AND THE VAPOUR PRESSURES
OF THE SYSTEM ACETONE-BENZENE AT 25°C.

LIQUID		VAPOUR		Total Pressure (mm.Hg.)	Partial Pressures (mm.Hg.)	
Wt.% C ₆ H ₆	Mole % C ₆ H ₆	Wt.% C ₆ H ₆	Mole % C ₆ H ₆		Benz.	Acetone
0.00	0.00	0.00	0.00	226.5	0.0	226.5
16.13	12.51	11.75	9.00	218.0	19.6	198.4
30.95	25.00	21.30	16.75	210.1	35.2	174.9
43.62	36.52	29.35	23.60	201.0	47.4	153.6
62.65	55.50	41.36	34.40	184.0	63.3	120.7
77.14	71.50	52.39	45.00	165.0	74.3	90.7
86.37	82.49	63.59	56.50	148.1	83.7	64.4
91.28	88.62	71.93	65.58	133.5	87.5	46.0
96.23	95.00	84.32	80.00	116.2	93.0	23.2
100.00	100.00	100.00	100.00	95.0	95.0	0.0

FIGURE 30. Liquid-Vapour Composition Equilibrium
Curve for the System Acetone-Benzene
at 25°C.

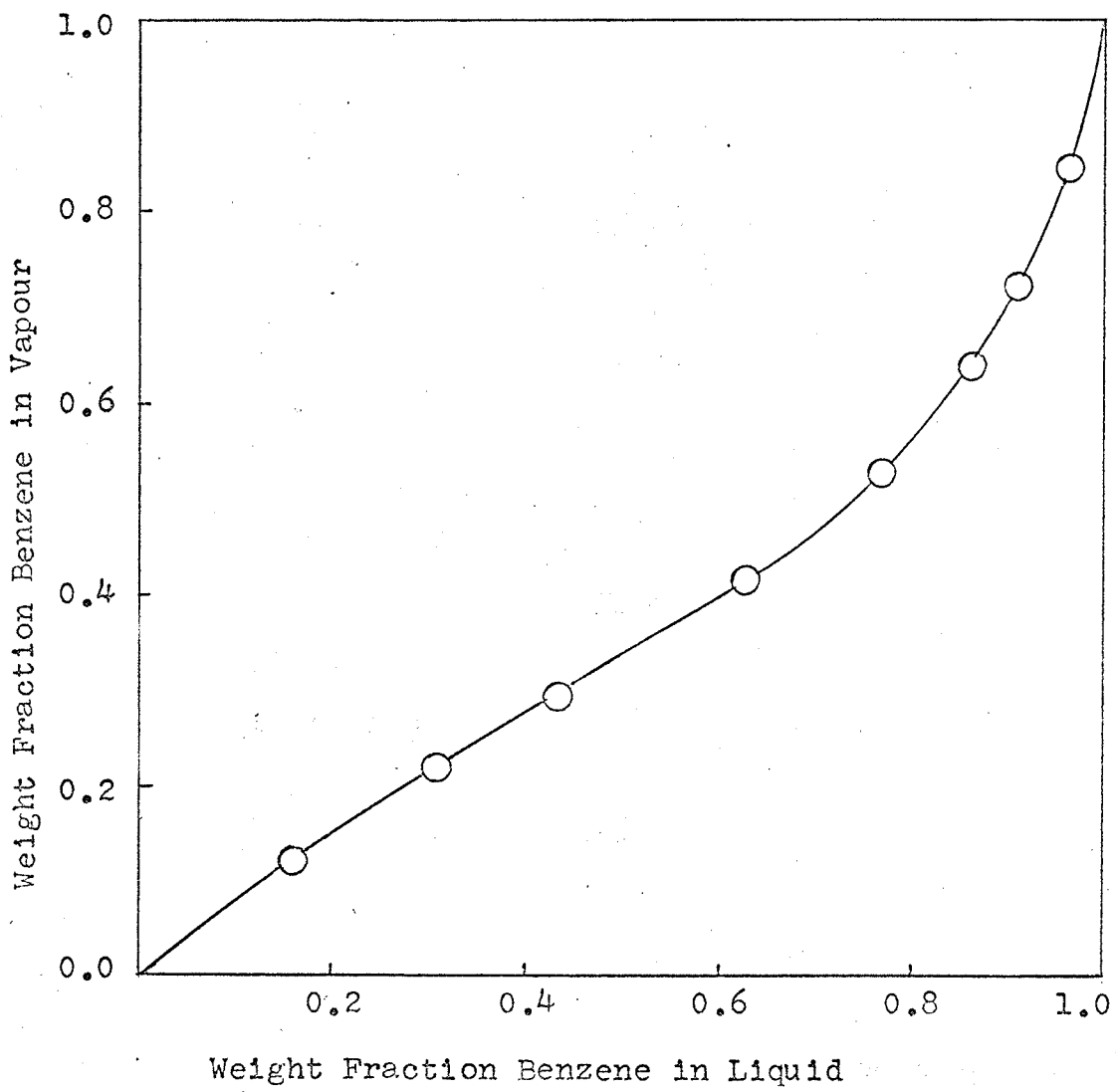


FIGURE 31. Total and Partial Vapour Pressure Curves
for the System Acetone-Benzene at 25°C.

CD Total pressure curve*

BC Partial pressures of Acetone

AD Partial pressures of Benzene

*The straight lines are the "ideal"
curves.

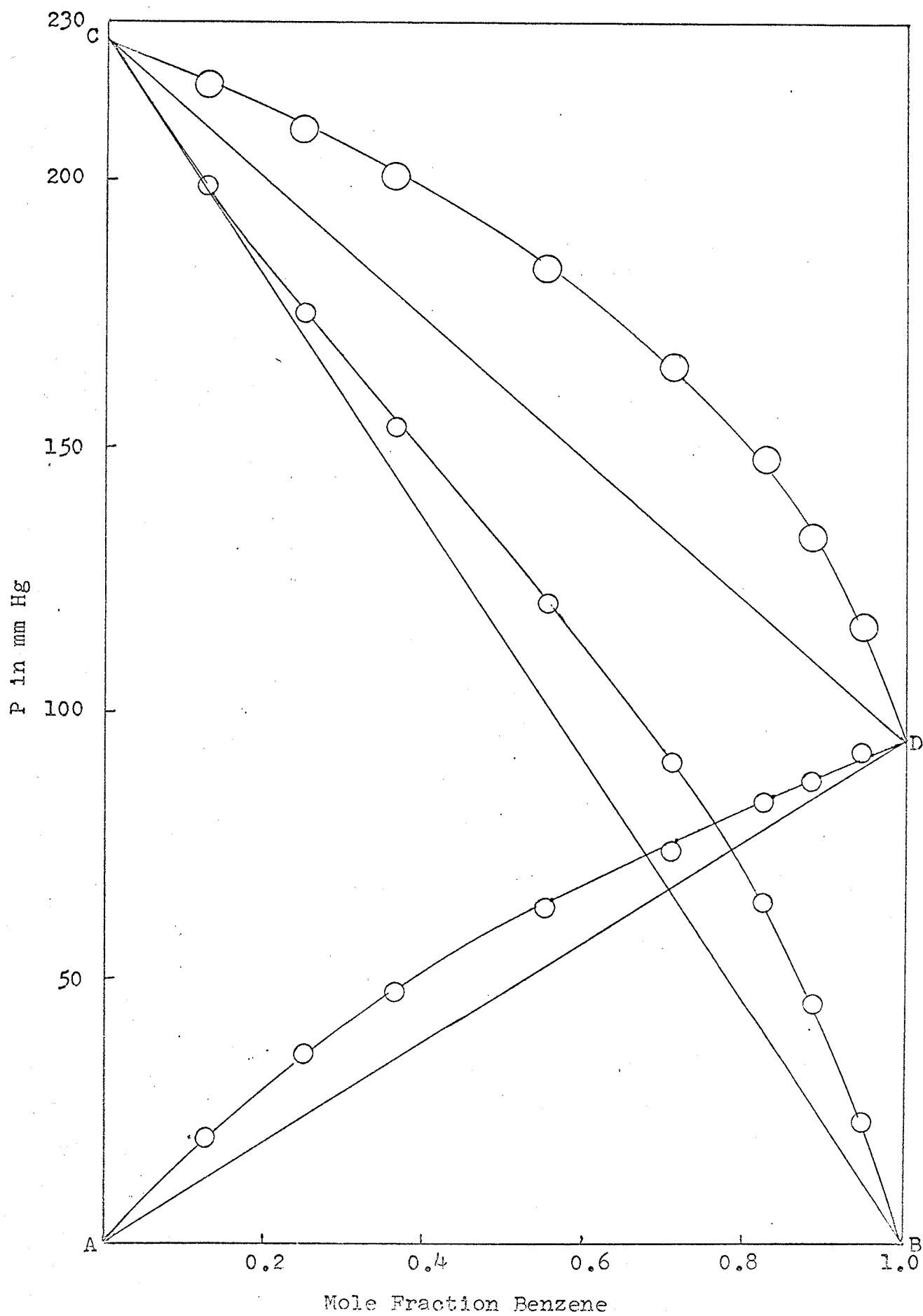


TABLE 27
 EXCESS GIBBS FREE ENERGY FOR THE SYSTEM
 ACETONE-BENZENE AT 25°C

$X_{C_6H_6}$	ACETONE		BENZENE		E_G (Cal/mole)
	α	γ	α	γ	
0.0000	1.000	1.000	-	-	0.0
0.1251	0.8759	1.0011	0.2063	1.6491	37.7
0.2500	0.7722	1.0296	0.3706	1.4824	71.3
0.3652	0.6782	1.0684	0.4990	1.3664	92.5
0.5550	0.5329	1.1975	0.6664	1.2007	107.7
0.7150	0.4004	1.4049	0.7822	1.0940	95.4
0.8249	0.2843	1.6236	0.8811	1.0681	82.5
0.8862	0.2031	1.7847	0.9212	1.0395	59.5
0.9500	0.1024	2.0480	0.9791	1.0306	38.2
1.0000	-	-	1.0000	1.0000	0.0

for acetone and for benzene, and the total excess Gibbs free energy of the system. From the data of Campbell et al and G^E values obtained in this research, the function TS^E was calculated by means of relation (24). The results of these calculations are given in Table 28 and Figure 32.

THE SYSTEM ACETONE-BENZENE-CHLOROFORM

Table 29 shows the vapour-liquid equilibrium compositions in the system Acetone-Benzene-Chloroform obtained from isothermal distillation. The total pressure data are shown in Table 30. In this table, the partial pressures have been calculated using the interpolated vapour compositions obtained from the data of Table 29. Table 31 shows the values of activity, activity coefficient and partial molal excess Gibbs free energy for the components and the total excess Gibbs free energy for the system. From these data of excess Gibbs free energy, the curve showing the concentrations for which the excess Gibbs free energy is zero, has been interpolated in Figure 33, making use of the binary data at the same time.

TABLE 28
EXCESS FUNCTIONS OF MIXING FOR THE SYSTEM
ACETONE-BENZENE AT 25°C

$X_{C_6H_6}$	G^E (Cal/mole)	H^E (Cal/mole)	TS^E (Cal/mole)
0.1251	37.7	14.2	-23.5
0.2500	71.3	27.1	-44.2
0.3652	92.5	38.6	-53.9
0.5550	107.7	45.0	-62.7
0.7150	95.4	33.3	-62.1
0.8249	82.5	22.1	-60.4
0.8862	59.5	14.8	-44.7
0.9500	38.2	6.7	-31.5

FIGURE 32. Excess Functions of Mixing for the
System Acetone-Benzene at 25°C.

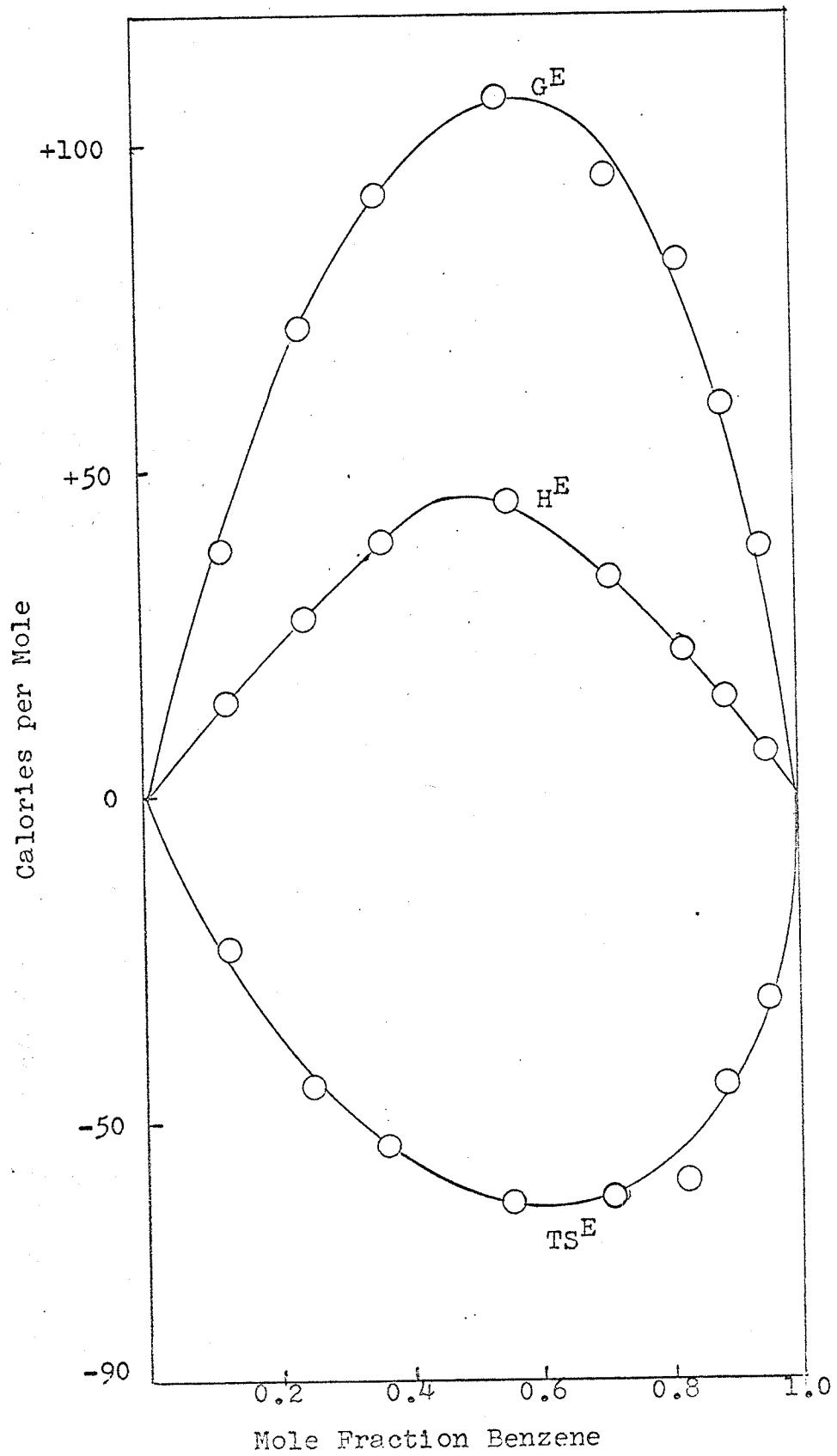


TABLE 29

VAPOUR-LIQUID EQUILIBRIUM COMPOSITIONS IN THE
SYSTEM ACETONE-BENZENE-CHLOROFORM AT 25°C

LIQUID COMPOSITION			VAPOUR COMPOSITION		
Mole percentages			Mole percentages		
Acetone	Benzene	Chloroform	Acetone	Benzene	Chloroform
44.2	46.2	9.6	61.2	31.6	7.2
39.0	45.3	15.7	55.8	32.1	12.1
34.2	42.7	23.1	48.1	31.7	20.2
47.1	48.5	4.4	64.7	31.6	3.7
20.2	55.6	24.2	32.8	42.3	24.9
27.8	58.1	14.1	44.3	43.0	12.7
5.6	84.3	10.1	15.1	72.4	12.5
18.8	76.2	5.0	36.3	58.6	5.1
8.1	89.3	2.6	20.0	76.9	3.1
27.6	64.4	8.0	46.1	46.7	7.2
7.4	70.2	22.4	13.6	58.3	28.1
8.5	50.8	40.7	11.5	38.6	49.9
8.2	20.0	71.8	7.6	12.4	80.0
24.6	37.5	37.9	34.2	27.5	38.3
44.0	27.1	28.9	56.1	20.4	23.5
34.6	16.9	48.5	40.2	12.3	47.6
53.6	16.7	29.7	64.4	12.4	23.2
67.6	15.4	17.0	77.6	11.1	11.3
64.6	25.5	9.9	76.3	17.4	6.3
75.5	16.6	7.9	84.0	11.1	4.9

TABLE 30

TOTAL PRESSURES, INTERPOLATED VAPOUR COMPOSITIONS
AND PARTIAL PRESSURES IN THE SYSTEM
ACETONE-BENZENE-CHLOROFORM AT 25°C

<u>Liquid Mole Percents</u>		<u>Vapour Mole Percents</u>		Total Press.	<u>Partial Pressures</u>		
Acet.	Benz.	Acet.	Benz.	(mm.Hg.)	Acet.	Benz.	Chlor.
	Chlor.	Acet.	Chlor.	(mm.Hg.)	(mm.Hg.)	Chlor.	
44.9	22.8	32.3	17.0	173.1	97.1	29.4	46.6
32.2	42.5	25.3	31.7	153.9	71.9	48.8	33.2
57.9	28.0	14.1	20.0	183.8	130.1	36.8	16.9
47.0	40.4	12.6	28.4	173.0	108.5	49.1	15.4
41.4	10.4	48.2	7.9	166.0	78.5	13.1	74.4
40.4	54.7	4.9	37.4	169.1	99.1	63.2	6.8
35.4	52.8	11.8	39.9	160.6	80.6	64.1	15.9
48.9	33.4	17.7	23.6	175.6	111.3	41.4	22.9
14.1	67.6	18.3	54.6	134.0	33.8	73.2	27.0
11.1	51.5	37.4	39.2	138.8	23.9	54.4	60.5
24.1	59.1	16.8	44.6	146.9	57.4	65.5	24.0
69.6	22.9	7.5	15.4	198.5	158.6	30.6	9.3
80.1	10.0	9.9	6.9	206.5	180.3	14.2	12.0
6.9	78.8	14.3	67.8	123.1	18.2	83.5	21.4
88.0	7.8	4.2	4.8	215.0	199.3	10.3	5.4
28.8	51.2	20.0	37.7	153.2	69.5	57.8	25.9

TABLE 31

EXCESS GIBBS FREE ENERGY IN THE SYSTEM ACETONE-

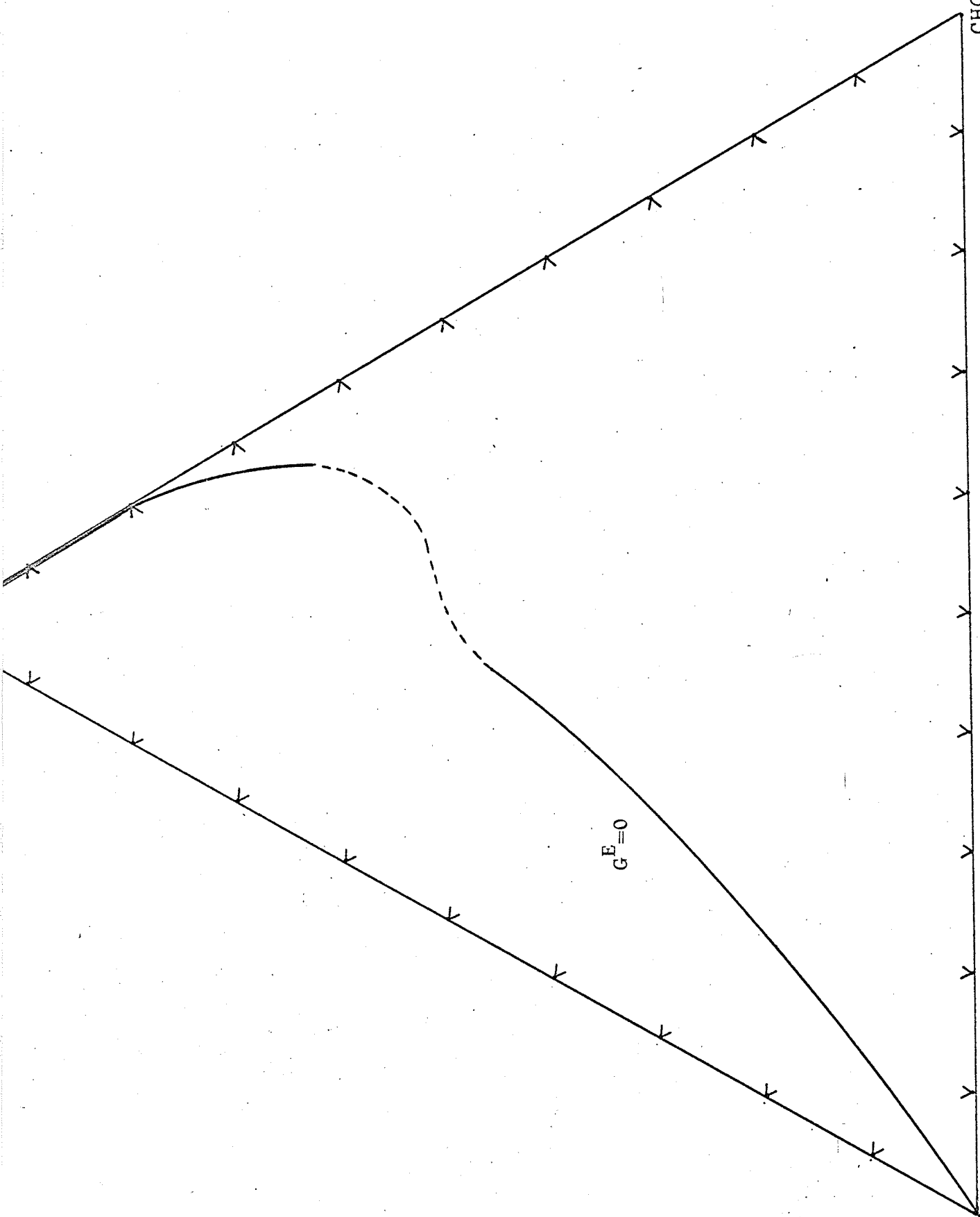
BENZENE-CHLOROFORM AT 25°C

Liquid Mole Percent Acet. Benz.	Acetone			Benzene			Chloroform			
	<i>a</i>	<i>γ</i>	μ^E (Cal/ mole)	<i>a</i>	<i>γ</i>	μ^E (Cal/ mole)	<i>a</i>	<i>γ</i>	μ^E (Cal/ mole)	G^E (Cal/ mole)
44.9	0.4287	0.9548	-27.4	0.3095	1.3574	+181.1	0.2363	0.7316	-185.2	-30.8
32.2	0.3174	0.9857	-8.6	0.5137	1.2087	+112.3	0.1683	0.6652	-241.6	-16.2
57.9	0.5744	0.9921	-4.8	0.3874	1.3836	+192.4	0.0857	0.6078	-295.1	+9.5
47.0	0.4790	1.0191	+10.9	0.5169	1.2795	+146.1	0.0781	0.6198	-283.5	+28.4
41.4	0.3466	0.8372	-105.3	0.1379	1.3260	+167.2	0.3773	0.7828	-145.1	-96.1
40.4	0.4375	1.0829	+47.2	0.6653	1.2163	+116.0	0.0345	0.7041	-207.9	+72.4
54.7	0.3558	1.0051	+3.0	0.6748	1.2780	+145.4	0.0806	0.6831	-225.9	+51.2
35.4	0.4914	1.0049	+2.9	0.4358	1.3048	+157.7	0.1161	0.6559	-249.9	+9.9
48.9	0.1492	1.0582	+33.4	0.7706	1.1400	+77.6	0.1369	0.7481	-172.0	+25.7
14.1	0.1055	0.9505	-30.0	0.5727	1.1120	+62.9	0.3068	0.8203	-117.4	-14.8
11.1	0.2534	1.0514	+29.7	0.6895	1.1666	+91.4	0.1217	0.7244	-191.1	+29.1
59.1	0.7002	1.0060	+3.4	0.3221	1.4065	+202.2	0.0472	0.6293	-274.5	+28.1
22.9	0.7960	0.9938	-3.7	0.1495	1.4950	+238.3	0.0609	0.6152	-287.9	-7.7
69.6	0.0803	1.1594	+87.6	0.8790	1.1155	+64.8	0.1085	0.7587	-163.6	+33.7
80.1	0.8800	1.0000	0.0	0.1084	1.3897	+195.1	0.0274	0.6524	-253.1	+4.6
6.9	0.3068	1.0653	+37.5	0.6085	1.1885	+102.4	0.1313	0.6565	-249.4	+13.3

FIGURE 33. Zero Excess Gibbs Free Energy Curve
in the System Acetone-Benzene-Chloroform
at 25°C.

CHCl₃

Acetone



$G^E=0$

A = Acetone
B = Benzene
C = Chloroform

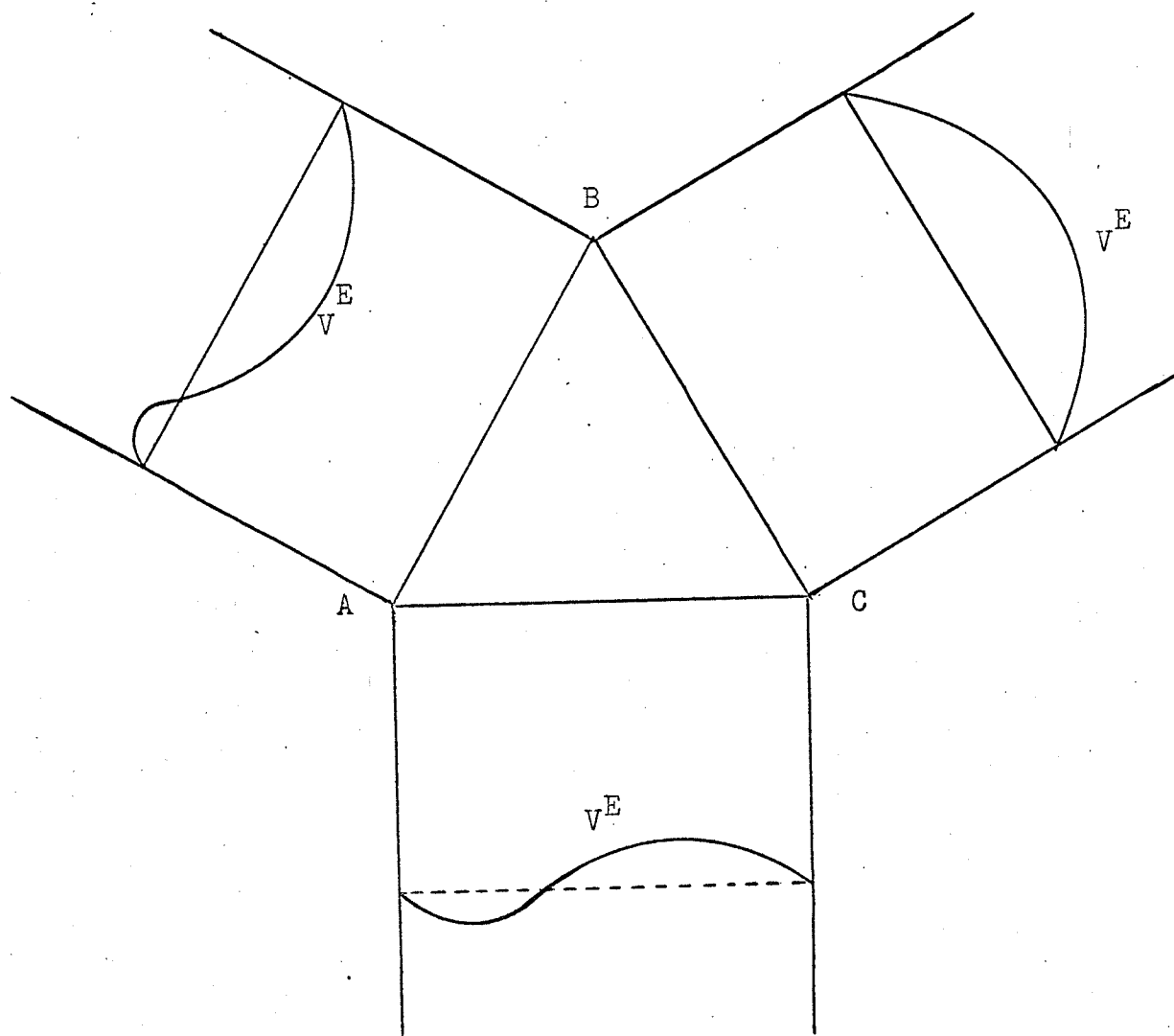


Figure- 34 Exploded Diagram showing the Excess Volume Functions in the contiguous binary systems of Acetone-Benzene-Chloroform

CHAPTER V

DISCUSSION

A. THE SYSTEM ACETONE-CHLOROFORM

In this system a volume contraction occurs on mixing of the components (Figure 7) until a concentration of about 68 mole-percent acetone is reached where V^E changes sign and becomes positive. The values of V^E are seen to pass through a maximum when the mole-percentage of acetone is 86, and a minimum when the mole-percentage is 32. The maximum value of V^E for this system is +0.05 ml. per mole and the minimum recorded is -0.152 ml. per mole. Figure 8 shows that the partial molal volume of acetone passes through a maximum and the partial molal volume of chloroform through a minimum when the molar ratio is approximately unity.

From density measurements at 25° and 35.17°C, Hubbard (39) found that while V^E is positive at high acetone concentrations, it is negative over most of the range of composition. His results at 25°C are comparable to my values except for slight differences in magnitude. Since a direct method was used in this research better accuracy is claimed for volume changes. Excess volumes calculated from Reinder and de Minjer's (1) density data could not be appropriately plotted; there is a considerable scatter

of their experimental points. Staveley *et al.*, (30) measured the excess volumes at 25° and 50° for this system and have correlated the function V^E with excess entropy of mixing. In their work, the excess entropy of mixing at constant pressure, S_p^E , is -1.02 cal/mole deg. for the equimolar mixture at 35.17°C. Having known G^E , H^E , S_p^E , and V^E at the same temperature they enquired into the magnitude of the contribution made to H^E and S_p^E by the volume change on mixing. They found that the volume contraction contributed very little to the value of S_p^E , since V^E is 0.19 ml/mole, and $(S_p^E - S_v^E)$ is -0.049 cal/mole deg., from which it follows that S_v^E is -0.97 cal/mole deg. They used the relation

$$S_p^E = S_v^E + \frac{\alpha V^E}{K_T}$$

where the coefficient of expansion, $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$ and isothermal compressibility, $K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$ are measured quantities and S_p^E follows from relation (24). They found that the shape of the V^E curve had the effect of making S_v^E a more symmetrical function of composition than was S_p^E .

The viscosity data appearing in Figure 16 have been replotted in Figure 17 to find the actual deviation from ideal behaviour as differences of the experimental points from the corresponding points on the straight line joining the viscosities of the pure components. If viscosity is

considered a normal thermodynamic property related to the mole-fraction in the same way as volume or chemical potential is, giving rise to the actual value of the thermodynamic function for the binary mixture, it is justifiable to plot such excess functions on the basis of deviations from ideality. The differences from ideal behaviour show a maximum positive deviation in viscosity at a concentration of 60 mole-percent chloroform as is evident from Figure 17. This treatment calls for some explanation. Kendall (123) has treated a few binary solutions of alcohols by a cube-root equation, where the viscosity of the mixture is given by

$$\eta^{\frac{1}{3}} = x_1 \eta_1^{\frac{1}{3}} + x_2 \eta_2^{\frac{1}{3}}$$

in which η_1 and η_2 are the viscosities of the pure components and x_1 and x_2 are their respective mole-fractions. As Kendall's equation has been found to give results close to experimental data for the three alcohol mixtures studied, it may be considered one of the properties of a perfect solution but this needs further experimental evidence to be acceptable. Nevertheless I thought the general method of thermodynamic excess functions applied to viscosity might be useful to represent the deviations in the present work. It certainly gives better indication of the deviation if representation of the viscosity of ideal binary solution is made along the straight line joining the viscosities of

the pure components. As such in Figure 17, the $\Delta\eta$ plot signifies the excess values over ideal ones in the binary solution represented as differences. It may be worthwhile to compare the maximum positive deviation of viscosity occurring at 60 mole-percent CHCl_3 with the "Acetone-Chloroform" total vapour pressure curve which has the greatest deviation also at this concentration. Beckman and Faust (124) also observed the greatest deviation of viscosity at this concentration (60 mole percent chloroform) at 28.15°C , although they observed a maximum which changed strongly with temperature and finally disappeared at higher temperatures.

A study of Figure 23 shows that an azeotropic point occurs in this system at 25°C . A strong negative deviation from Raoult's law is apparent from Figure 24. This implies that G^E is strongly negative.

The vapour pressures recorded for acetone in the literature are not at all concordant, as has been pointed out by Beare, McVicar and Ferguson (125); my result for 25°C agrees most closely with those of Mathews (126), Parks and Chaffee (118), Mueller and Kearns (71) and the one calculated using the Antoine equation with the constants taken from Dreisbach and Martin (127).

My vapour pressure for chloroform, 197.2 mm. at 25°C is definitely below that recorded by Beckman and Liesche

(128) which is 199.1 mm at 25°C. The value obtained by me may be compared with those given by Scatchard et al., (129), Rock and Schroder (70), Mueller and Kearns (71), and Dreisbach (130).

The partial pressures plotted in Figure 24 are thermodynamically consistent and the treatment suggested by von Zawidzki applies to this binary system. In Table 22 the partial pressures calculated from the Gibbs-Duhem-Margules equation reproduce the measured values fairly well and that confirms the thermodynamic consistency of the data.

From Figure 26 it follows that the curves for all the excess functions of mixing G^E , H^E and TS^E are unsymmetrical. Haase (26) has pointed out that the evidence of a great many data on various systems seems to indicate that as a rule the function $V^E(X)$ has a behaviour similar to that of the function $S^E(X)$. This, however, is clearly not the case in the system acetone-chloroform. Gieskes (131) recently reported the deviation from this generalization for his system acetic acid-chloroform and also quoted Scott et al., (132) who found a similar phenomenon in the system 1-hydro-n-perfluoroheptane and acetone. The latter observed a very large positive V^E , while S^E had a negative sign.

The classification of the system according to the rules of Kamke and Kummerle (24) may therefore be done

as follows:

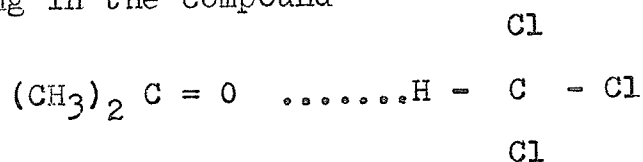
$$G^E(X) < 0, \text{ no point of inflexion}$$

$$H^E(X) < 0, \text{ no point of inflexion}$$

$$S^E(X) < 0, \text{ no point of inflexion}$$

$$V^E(X) \lesssim 0, \text{ no point of inflexion}$$

Campbell and Kartzmark (67) have proved the existence of a 1:1 compound in this system. They proposed hydrogen bonding in the compound



The energy of the hydrogen bond has been calculated by them to be -2.7 kcal per mole. Kearns (66) has evaluated the heat of association as -2.4 kcal/mole.

Due to hydrogen bonding between the two components, this system shows negative deviations from Raoult's law, and there is a considerable evolution of heat on mixing. Staveley et al., (30) and Hubbard (39) found that the volume contraction increases with rising temperature, in spite of the fact that the degree of association of the two components must decrease.

Many theoretical and semi-theoretical treatments have been given for this system (74, 76, 77, 78, 79, 133, 134).

Munster (134) and Barker and Smith (133) attempted to predict the thermodynamic mixing functions by consideration of ordering or orientation forces.

Although there is no doubt about the presence of hydrogen bonding as evident from the results of ultraviolet spectroscopy (134), measurement of supersonic waves (136), proton magnetic resonance (137) and other measurements in this system, complications arise when one attempts to construct a theory, because of the fact that both acetone (138) and chloroform (139) are known to associate in the pure state.

Munster (134) envisages a solute-solvent interaction in this system. The chloroform (solvent) molecules are oriented by the acetone (solute) molecules whilst in the pure solvent free rotation occurs. Obviously, the sign of the excess entropy of mixing is negative ($\Delta S^E < 0$) in this case. On the other hand, it may be that the excess entropy of dilution $\Delta S_2^E < 0$, because the number of molecules oriented on average by a solute molecule decreases when the latter form clusters at increased concentrations.

It can be seen from the Trouton-Hildebrand constant of chloroform (=21.7) that in the pure solvent there is little co-operative orientation (140). In acetone (140), the interaction is greater (Trouton-Hildebrand constant = 22.5). On the other hand, the chloroform molecules should be strongly oriented by acetone because in the former the

carbon-hydrogen bond is considerably loosened (141) and hydrogen bonding with acetone is probable (142). Seguin (143) came to the same conclusion on the basis of measurements of the magnetic susceptibility. Briegleb (144) observed the displacement of CO bands in the absorption spectrum of the mixture which indicates that there is strong localized interaction between the chloroform and acetone molecules. This explains why they mix exothermically, whereas halides and hydrocarbons usually mix endothermically (e.g. cyclohexane and carbon tetrachloride) (145).

Munster (134) stressed that it is not the interaction between the molecules of the solvent and the solute (solvation) as such, which is the essential factor, but rather that the number of possible orientations of the solvent molecules is reduced by the neighbouring solute molecules. In terms of Kirjew (146) this is regarded as a compound formation.

It has been seen that the molecules of acetone have a much greater attraction for one another than the chloroform molecules have for each other. In the pure state, therefore, acetone molecules tend largely to associate, although such association is undoubtedly indefinite and not strictly stoichiometric. At low concentrations of CHCl_3 , these attractive forces in the acetone are weakened

and as a result there might be a dissociation or break-up of the more or less indefinitely associated groups accompanied by an increase in volume. This might explain the positive V^E in Figure 7. The question at once arises why then G^E and H^E are negative in this region. It might perhaps be said that the process of compound formation commences as soon as a small quantity of CHCl_3 is added to pure acetone and it is not certain whether the molecules of acetone have a greater attraction for one another than for chloroform molecules. In any case if the dissociation of pure acetone has to take place it is expected that G^E and H^E measurements should also show similar positive behaviour. As such, the explanation in terms of breaking-up of bigger acetone molecules is somewhat doubtful. The negative V^E with increasing CHCl_3 concentration is, of course, due to the compound formation which tends to bind the two types of molecules.

The work of Tyrer (74) on latent heat of vapourization of this system is of interest. Tyrer assumed that in acetone-chloroform system the former is an associated liquid and the latter is a normal liquid. For such mixtures, he argued, it is possible to determine from a study of their latent heats of vapourization whether the associated constituent undergoes gradual dissociation as it is diluted with the other constituent, or whether a solvate

(compound) is formed. He found the latent heat at constant composition of a normal mixture is approximately a linear function of the composition. He did not observe any diminution of the apparent latent heat as would be expected from a gradual dissociation of the associated molecules, but, on the contrary, the latent heat over a portion of the range at least, increased with increase of the dilution. This, he argued, could have no other meaning but that solvates are formed in the mixtures. Dolezalek (76) also concluded the existence of a solvate on the basis of his study of vapour pressures.

Barker and Smith (133) calculated the hydrogen bond interaction energy and the van der Waals interaction energy for this system from Zawidzki's (1) data, using a lattice model where the molecules have several contact points. They neglected the dipole interaction, and resulting state of co-operative orientation, in pure acetone. The dipole interaction might explain the unusually large value of the van der Waals interaction obtained by them.

From dielectric constant studies it has been estimated that about 7% of acetone and chloroform are associated in an equimolar mixture at 20° (147). The entropy decrease for dimerization due to a single hydrogen bond is usually between 20 and 26 cal/deg. mole of dimer (27). A value of S_p^E (the excess entropy of mixing at constant pressure) of about 1 cal/mole deg. at 25° for an equimolar

mixture is therefore consistent with a few percent of 1:1 association with about the same entropy change as for dimerization, and the corresponding figure of 450 cal/mole for the heat evolved on mixing is about the amount which might be expected if one fairly strong hydrogen bond is involved in the association of an acetone and a chloroform molecule.

Papoošek and Koochirek (148) considered the isothermal compressibility as consisting of two parts

$$K_T = K_S + K_g$$

K_g is considered to be the geometrical part of the coefficient of compressibility K_T and accounts for the lowering of the intermolecular distances in a solution during its compression. K_S represents the structural part of K_T accounting for the simultaneous increase in the molecular regularity of the liquid with decreasing volume. From comparisons of several methods it was concluded by them that K_S^E is very closely related to the excess volume V^E . This is specially evident since the K_S^E plot in their work changed sign in the same way that V^E has changed sign in this work.

Several other possibilities of complex formation have been cited for this system, such as AB_2 where A = acetone and B = chloroform (66). From the freezing-point diagram of Campbell and Kartzmark (67) it appears that only a 1:1 com-

pound exists in the solid phase. It is very doubtful whether an association might be present in the liquid phase and its presence is not indicated in the freezing-point diagram. The freezing-point diagrams can only indicate the possibility of an association in the liquid phase. But the existing data on this system can be best interpreted from the standpoint of 1:1 compound formation.

B. THE SYSTEM BENZENE-CHLOROFORM

This system shows an increase of volume on mixing. This means that there is a positive excess molar volume function as shown in Figure 9. The maximum value of V^E occurs at 45 mole percent chloroform and the excess partial molal volume curves do not show a symmetry. The data for molar refraction of mixtures in Table 10 and Figure 15 show that the molar refractions are approximately additive and hence that the true molecular volumes remain practically unchanged on mixing.

Figure 18 shows the deviations of viscosity and fluidity from ideal values. In order to find the correct magnitude of the maximum and minimum in the fluidity and viscosity respectively, the differences are plotted in Figures 20 and 19. These figures show the extremum at 33 mole percent chloroform. It may be observed that the maximum fluidity is somewhat flattened compared to the

minimum viscosity which is sharp. Many investigators therefore prefer to plot fluidity. No direct conclusion can be made from these plots.

No azeotropic point is present in this system as apparent from Figure 27. It should therefore be possible to separate the two components completely by means of an isothermal fractional distillation. A slight negative deviation from Raoult's law is observed from Figure 28. This may in the first instance indicate the possibility of compound formation. In this connection, work of Reeves and Schneider (149), and Campbell and Kartzmark (2) may throw some light. The measurements of proton resonance signal of pure CHCl_3 by Reeves and Schneider (149) indicate self-association. Again large total shift of the CHCl_3 proton signal in benzene solution is indicative of complex formation between CHCl_3 and the aromatic hydrocarbon. From the measurements of Campbell et al., (2) it appears that the freezing-point diagram of the binary system benzene-chloroform does not show any compound formation. Though it might be argued that the high melting point of benzene may obscure a molecular compound in the freezing-point diagram, it is very unlikely that a compound exists.

The "interaction" shift observed by Reeves et al., (149) in CHCl_3 in benzene solution is to higher magnetic field. This is in sharp contrast to the corresponding shift to

low field observed in hydrogen bonding involving lone pair donors, as for example in chloroform when it is associated with acetone (137). Reeves and Schneider argued that a specific interaction with benzene occurs such that the chloroform hydrogen is preferentially located above or below the plane of the aromatic ring, since if the mutual orientation of the two kinds of molecules were completely random the field enhancement due to the ring current would be considerably smaller. This might possibly explain the negative deviation from Raoult's law and negative $G^E(X)$ function.

All the thermodynamic functions are negative in Figure 29. The classification of the system according to the rules of Kamke and Kummerle (24) is therefore as follows

$$G^E(X) < 0 \quad \text{no point of inflexion}$$

$$H^E(X) < 0 \quad \text{no point of inflexion}$$

$$S^E(X) < 0 \quad \text{no point of inflexion}$$

$$V^E(X) > 0 \quad \text{no point of inflexion}$$

My values do not show any negative V^E and are in disagreement with those reported by Schmidt (69) at 17°C. His experiments presumably suffered from inaccurate density determinations, since a small pycnometer was used for his measurements.

The vapour pressure for benzene obtained in this research agreed very well with the value calculated using the Antoine equation given by Lange (150).

From my own data and those of Reeves and Schneider (149) the interaction between benzene and chloroform is best explained in terms of non-randomness of the molecules. The deviation is negative because interaction between benzene and chloroform molecules is stronger than that between two identical chloroform molecules. Billes and Varsanyi (151) argued that if one of the components is non-polar while the other is polar with a hydrogen atom linked to the atom of the latter which possesses a free electron-pair, hydrogen-bonding interaction may occur, and the molecules of the second component are able to associate. This is not strictly applicable to the system at hand. Furthermore, this system is another example of deviation from Haase's (26) generalization of parallelism between the V^E and S^E functions.

C. THE SYSTEM ACETONE-BENZENE

This binary system shows contraction on mixing to relatively high mole-percent of acetone and expansion only for a small region of concentration. My accurate determinations showed a positive V^E region hitherto not reported in the literature.

The data of Harms (93) at 6°C are in reasonable agreement with the magnitude of my values but differ in concentration dependence, positive values being absent. The data of McCombie, Roberts and Scarborough (92) at 15°C and of Ebersole (89) at 25°C show a little disagreement, differing again in not having positive values. The data of Brown and Smith (95) are in fair agreement with my values up to about 85 mole-percent acetone. They do not report experimental points above 88.8 mole-percent acetone (152), and this is the region where I have observed positive V^E values. Brown (151) noticed an indication of a small positive value while plotting the V^E curve but a little too low for my values. In the private communication he further suggested that a plot of $\frac{V^M}{X_1X_2}$ versus χ (ratio of an excess function and product of mole-fractions) might show up any discrepancies. Generally a plot of

$$\frac{V^E}{X_1X_2} = A + B(x_1 - x_2) + C(x_1 - x_2)^2$$

versus mole-fraction does not give a straight line and hence is not a good consistency test.

In general the viscosity and excess viscosity data as plotted in Figures 21 and 22 show negative deviation. The measurements of the total and partial vapour pressures in this system as appearing in Figure 31, show positive deviation from Raoult's law. There is no azeotropic point observed in Figure 30, and hence separation by fractional

distillation should be possible.

Function G^E is positive in Figure 32; H^E plotted in Figure 32 is from the data of Campbell et al., (2). The function TS^E has also been plotted. The classification of the system from the standpoint of Kamke-Kummerle rules (24) is therefore as given below:

$G^E(X) > 0$, no point of inflexion

$H^E(X) > 0$, no point of inflexion

$S^E(X) < 0$, no point of inflexion

$V^E(X) < 0$, but changes sign

Scott (153) remarks that in the case of dispersion force solutions the theory of Prigogine and Mathot (154) gives a positive heat of mixing associated with a negative volume change and a negative excess entropy. It does not appear to me that this theory would fit completely the observations in the present system. The question of volume changes in dispersion force solutions is clearly one which requires much more theoretical study and much careful experiment on well-chosen systems. Behaviour of real solutions such as acetone-benzene can not therefore be explained by any of the existing theories of solutions.

D. THE SYSTEM ACETONE-CHLOROFORM-BENZENE

From Figure 13, it appears that in the ternary system

there are two curves along which the excess volume V^E is equal to zero. The ternary plot is confirmed by the nature of the binaries and vice versa. It may be observed from Figure 13 that the curves of zero volume of mixing do not run through pure acetone in the triangular plot. There is no volume change when pure acetone is mixed with pure acetone and obviously the acetone apex of the triangle is a point with zero volume of mixing. It is realized by me that it is a pertinent question. The whole puzzle may be solved by realizing the fact that the plot appearing in Figure 13 is actually a projection of a three-dimensional prism on its base. Looking at Figure 34 it is clear that curves appearing in Figure 13 are the experimentally found concentrations where $V^E = 0$ and also these are the projections of the corresponding points on the binary. It is easy to visualize from the three-dimensional model that the surface of V^E is curved and its projection on the base of the triangle will give the curves as shown in Figure 13. It might be seen that these two curves pass through the apex of pure acetone also. This will be clear if we fold the binary sides in the exploded diagram to form a solid prism and then project the V^E surface on the base keeping specially in mind the two humped regions of the V^E surface at the acetone apex. The curves passing through acetone apex will be the imaginary extensions of the two $V^E = 0$ curves and even though these are imaginary curves, they

are perfectly in order as far as passing through the acetone apex is concerned. This type of behaviour might have been expected even from the nature of the binary systems alone. The ternary data confirm the contention.

The curves of zero excess volume indicate the existence of ideality as far as the volume of the mixture is concerned. The curve of zero heat of mixing obtained in this system by Campbell *et al.*, (2) does not coincide with either of these curves. It was of interest to find whether semi-ideality occurring in Acetic Acid-Chloroform-Water also appeared in Acetone-Chloroform-Benzene. This was not found true in this system, and even pseudo-ideality could not be proved.

The presence of curves of zero excess volumes seems to be the result of the deviations from ideality, which are opposed to each other, in the three binary systems.

A study of the results obtained with the vapour pressures and vapour compositions in the ternary system shows negative as well as positive deviations from Raoult's law (Table 30). The excess Gibbs free energy G^E has been calculated and the interpolated curve of $G^E = 0$ appearing in Figure 33, definitely shows the compensating effects of the binary systems. The reason that there is a positive region as well as a negative region in the composition triangle indicates the presence of $G^E = 0$ curve. From the

nature of the binary systems this was to be expected since no other specific interaction seemed to take place in the ternary system. The measurement of ternary vapour-liquid equilibria confirmed it. The concentrations for which $G^E = 0$, do not coincide with either those concentrations for which $H^E = 0$, or for which $V^E = 0$.

The obvious conclusion from these observations is that the $V^E = 0$, $H^E = 0$ and $G^E = 0$ curves occur in the ternary system as a result of compensating effects of the respective functions in the binary systems. They do not coincide and as such even semi-ideality does not exist in the system.

From the ternary freezing point diagram of Campbell et al., (2) it appears that the compound between acetone and chloroform continues to exist in the ternary system.

CHAPTER VI

SUMMARY

This thesis deals with the following thermodynamic and physical properties of the system Acetone-Chloroform-Benzene and its contiguous binary systems: density, refractive index, excess volume, viscosity, vapour pressure and vapour composition at 25°C. The excess functions G^E and S^E have been calculated making use of vapour-liquid equilibrium data collected in this work and heat of mixing data of Campbell et al., (2).

In acetone-chloroform system the functions are classified according to the rules of Kamke and Kummerle (24).

$$G^E(X) < 0, \text{ no point of inflexion}$$

$$H^E(X) < 0, \text{ no point of inflexion}$$

$$S^E(X) < 0, \text{ no point of inflexion}$$

$$V^E(X) \lesssim 0, \text{ no point of inflexion}$$

A compound exists between chloroform and acetone and the existence of hydrogen bonding is strongly favoured.

The system benzene-chloroform has the following classification according to the rules of Kamke and Kummerle (24),

$$G^E(X) < 0, \text{ no point of inflexion}$$

$$H^E(X) < 0, \text{ no point of inflexion}$$

$S^E(X) < 0$, no point of inflexion

$V^E(X) > 0$, no point of inflexion

A possible interaction of chloroform with benzene occurs such that the chloroform hydrogen is preferentially located above or below the plane of the aromatic ring (148).

In acetone-benzene system the classification of Kamke and Kummerle (24) is

$G^E(X) > 0$, no point of inflexion

$H^E(X) > 0$, no point of inflexion

$S^E(X) < 0$, no point of inflexion

$V^E(X) < 0$, but changes sign

In the case of dispersion force solutions the theory of Prigogine and Mathot (154) gives a positive heat of mixing associated with a negative volume change and a negative excess entropy. The present system can not be fully explained by this theory.

In the ternary system there are curves with $V^E = 0$, $G^E = 0$ and $H^E = 0$ which appear to exist as a result of compensating effects of the binary systems. These curves are not co-incident and therefore no ideality exists.

CHAPTER VII

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