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# ACTIVITIES AND ACTIVITY COEFFICIENTS OF ORGANIC BINARY MIXTURES

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EDWARD NEPARKO

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APPROVED BY

[redacted]

[redacted]

George M. Murphy

J. C. Colbert

[redacted]

S. H. Wender

DISSERTATION COMMITTEE

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# ACTIVITIES AND ACTIVITY COEFFICIENTS OF ORGANIC BINARY MIXTURES

## CHAPTER I

## INTRODUCTION

Knowledge of the activities of components in volatile mixtures is of great importance for a number of reasons. From the practical side, it is essential in the design and construction of distillation equipment for the separation of mixtures. In addition, the activity data are a valuable contribution to the thermodynamic data on solutions. In theoretical calculations, the activity data are a prime necessity in the formulation of a general solution theory capable of explaining the behavior of components when mixed together to form a solution.

The activity of a component in solution is defined as the ratio of the fugacity of the component in solution to the fugacity of the pure component at the same temperature. In many systems, the fugacities may be replaced by the partial pressures of the components without appreciable error in the subsequent calculations. Once the activities have been determined for a binary system, it is then possible

to calculate other thermodynamic quantities of interest. These quantities include, for example, heats of mixing and free energies of mixing. The values of the quantities can be compared with those for the same system at different temperatures or analogous systems in an attempt to explain the magnitude of these quantities and their deviations from the expected values if the solutions behaved in an ideal manner. These deviations may be interpreted as due to molecular interactions in the solution and preferred orientation of the species in solution. Ultimately, the activity data and the thermodynamic quantities calculated from them can be used as a basis for the presentation of a molecular picture of the liquid phase in terms of a statistical model. The model can finally be applied in a general manner in an attempt to include all liquids.

Most vapor pressure methods for determining activities and activity coefficients of components of volatile binary organic mixtures have made use of the following equations:

$$y_1 p = p_1; \quad (1 - y_1)p = p_2 \tag{1}$$

and

$$p_1/(x_1 p_1^o) = \gamma_1; \quad p_2/(1 - x_1)p_2^o = \gamma_2 \tag{2}$$

where $x_1$ and $y_1$ are the mole fractions of component 1 in the liquid and vapor phase, respectively; $p_1$ and $p_2$ are the partial pressures of components 1 and 2 above the equilibrium mixture; $p_1^o$ and $p_2^o$ are the vapor pressures of pure 1 and

pure 2; p is the total vapor pressure and $\gamma_1$ and $\gamma_2$ are the activity coefficients of component 1 and 2. Equations (1) and (2) assume ideality of the vapor phase. A common procedure is to determine p, $x_1$ and $y_1$ experimentally and then calculate $\gamma_1$ and $\gamma_2$ from equations (1) and (2).

The determination of activities of volatile binary mixtures has been the object of many investigators using a variety of methods. An excellent summary of these methods is given by Hala et al.[1] One of the most accurate methods in use has been the equilibrium still as developed by Scatchard and his associates.[2] It is a still with the provision for the circulation of both liquid and vapor phases. In the direct experimental determination of vapor-liquid equilibrium, the samples of liquid and vapor must be separated at true equilibrium and the concentration of both phases determined analytically. The method of Scatchard allows the precise determination of the boiling point of the solution. It is applicable to low and medium pressures and only for homogeneous systems, but has the added advantage of using a small sample in the still.

Many more stills are available for the investigation of solutions, and these differ essentially in certain design features that were incorporated to eliminate drawbacks of previous stills or were necessitated by the peculiar properties of the system to be studied. The determination of the equilibrium curves can be carried out at constant temperature

or constant pressure. The design and construction of the stills may be a source of error in some cases, while in others, the nature of the system will contribute to the error. In all the stills in use, the time-consuming factor is the establishing of true equilibrium before sampling can take place.

In addition to the dynamic method as in the equilibrium still, static methods are available. In these methods, the solution is put into a closed container which is immersed in a thermostated bath and agitated until equilibrium is established in the system. Samples are then removed from both phases for analysis. Although the method is extremely simple, at low pressures the amount of vapor necessary for sampling is almcst the same as the total amount of vapor above the solution. The removal of this vapor may then greatly affect the equilibrium. Consequently, this method is not too widely used, especially at low or moderate pressures. At higher pressures it does find more applications.

In the distillation method a small amount of liquid is distilled from a flask which contains a large charge. The method is very simple, but it has the disadvantage that a large liquid charge is needed in the flask and it allows only a small amount of the distillate to be removed, since the composition of the liquid must essentially remain constant. Furthermore, errors arise due to condensation on the walls of the vessel so that for practical purposes, the

method is no longer in use for accurate determinations. Another method that has been used is the one developed by Hansen and Miller.[3] This method allows the sampling of the vapor phase by condensing it out in small finger tubes cooled by a suitable freezing mixture. The amount of vapor that is condensed at one time is controlled by a magnetically operated ground glass valve so that the equilibrium is not disturbed by the sampling.

Although the methods involving the equilibrium still are capable of extreme accuracy, they are time consuming in their operation. In some of the stills, equilibrium may be attained in about half an hour, but in others, it may take a whole day to obtain one concentration point for the system. It may be more profitable in some systems to sacrifice some of the accuracy in order to be able to make rapid determinations. In this manner, many more systems may be investigated over shorter periods of time.

The equilibrium still must also provide for the accurate measurement of the boiling point of the solution. For true equilibrium, concentration gradients must not occur in the liquid phase and the equilibrium vapors must not partially condense. Superheating must also be avoided. In addition, the cold condensate returned to the flask must be mixed perfectly with the liquid in order to prevent non-equilibrium vaporization due to its lower boiling point. The vapor which leaves the liquid should not entrain drops

of liquid and carry them over into the condenser. The still should be simple to operate, and it should require only a small amount of solution. It should be applicable to a large number of systems without significant modification.

Despite the inherent drawbacks of the equilibrium still, many working models have been made which are capable of extreme precision, and for accurate work the equilibrium still is one of the best methods available. But in many cases, it is evident that the accuracy of the instrument is made at a sacrifice to the time necessary for experimental determinations.

Along with the techniques already described for the determination of activities, total pressure methods are also finding wider application. The knowledge of the total pressure of a binary mixture as a function of the liquid composition at constant temperature is sufficient for a complete description of the liquid-vapor equilibrium. In theory, the activity and activity coefficients can be derived from the total vapor pressure without the use of the vapor composition. The application to the total pressure data of an independent relation, the Gibbs-Duhem equation, permits the calculation of the partial pressures $p_1$ and $p_2$ and hence, the activity coefficients, $\gamma_1$ and $\gamma_2$. Thus one may write:

$$p_1 + p_2 = p; \quad x_1 \, d \ln p_1 + x_2 \, d \ln p_2 = 0 \qquad (3)$$

and these two equations involve only the two unknown pressures $p_1$ and $p_2$. In these equations, we assume ideality of

the vapor phase and neglect the effect of the total pressure on the activities. Experimentally, only the total pressure and liquid composition need be determined.

Although the experimental method is very simple, it has not found widespread use due to the difficulty in the calculations and the fact that small errors in the vapor pressure measurement lead to larger ones in the calculated activity coefficients.

There have been several discussions of the total pressure method by various authors in the last ten years or so. Redlich and Kister[4,5,6] have made a number of important contributions to this method in a series of articles in which they discuss the total pressure method and the methods used to calculate the activity coefficients from the total pressure and composition data. They point out the applicability of this method to a number of systems and mention the errors involved in these determinations.

Levy[7], in an excellent article, discusses a semi-empirical expression which closely approximates the experimental results for a variety of mixtures. The calculation of liquid-vapor equilibria can be done by a number of equations, mostly empirical, from a relatively small amount of experimental data. These methods are limited in their usefulness, since cumbersome graphical or analytical computations are involved in most cases. The author gives two simplified methods of calculating the relation between partial vapor

pressure and liquid composition of binary mixtures. Using the Gibbs-Duhem equation expressed in terms of the partial pressures and the total pressure as the sum of the partial pressures, the author solves for the partial pressures. He further expresses the activity coefficients as power series of the liquid mole fractions. For many systems, the deviations from ideality are such that the coefficients beyond the first in the expansion can be neglected. Once the activity coefficient expression is found for one of the components, that for the other follows directly. For many other systems, such an approximation is invalid, and more coefficients must be used to give an adequate representation of the system. A more detailed description of the power series expansion of the activity coefficient is given by Hildebrand and Scott.[8]

In recent years, additional attention has been focused on the total pressure technique due to its simplicity experimentally. The main object of current research is the simplification of the mathematical analysis. Scatchard[9] gives a review of the methods now in use. Barker[10] considers the problems involved in this method also. He considers in some detail the deviations of the vapors from ideality and uses the method of least squares to fit the data.

As mentioned by the previous authors, the mathematical analysis of the total pressure data is complicated in most cases. Recently, a number of important advances have

been made in the mathematical analysis of total pressure data. Christian[11] has developed a method for curve fitting total pressure data using an IBM 650 digital computer. Myers and Scott,[12] using the faster IBM 709 digital computer, have developed a program to yield parameters in an equation for the excess free energy from isothermal pressure-liquid composition data.

In the present research, it was decided to use the total pressure method because it presented a very simple and rapid experimental technique. It was proposed that a number of binary systems be investigated, fitting the data with the method of Christian.[11] The computer program makes use of only three experimentally determined pressures and concentrations as well as the pressures of the pure components. For symmetric systems, the experimental points are usually chosen at equal mole fractions to secure a good fit of the data. For systems which show unsymmetric behavior, the points may have to be chosen at irregular concentration points to get a good fit over the whole concentration range. The symmetrical curves can usually be fitted in about five to ten minutes of operating time, but for the unsymmetrical cases, computing time may run as long as half an hour. Although sampling and analysis of the liquid phase is needed, it is possible to investigate a binary system over the whole concentration range in about a day or less, and in addition, pressure values may be recorded at various temperatures for

a given concentration point. Equilibrium is established very rapidly and the fact that no vapor samples are necessary allows the readings to be recorded almost as rapidly as the necessary manipulations can be performed.

The methods outlined up to the present have all been used successfully in many investigations. All these methods, however, require sampling of the liquid or vapor phases or both for the determination of the composition. There is also the added disadvantage in the equilibrium stills of the time consumed in reaching true equilibrium. It would be desirable to devise a new method for the determination of activities which would combine speed with accuracy. To achieve the goal of speed, compositions should be evaluated in a manner other than by direct sampling and analysis. The buoyancy bulb has long been used in the measurement of vapor densities for the calculation of association contants in the vapor phase. It seemed logical that such a method could be extended to the determination of activities of binary mixtures. Thus, a sensitive silica vapor density balance could be used to find the composition of the vapor phase. This knowledge coupled with the total pressure of the system would be sufficient for the calculations of activities. The application of the Gibbs-Duhem equation to these data would allow the calculation of the composition and the activity coefficients of the liquid phase.

# CHAPTER II

## OBJECTIVES

The primary objectives of this research were:

1. To refine the total pressure technique for the determination of activities and activity coefficients of binary mixtures and analyse the data so obtained by means of a high speed digital computer. The simplicity and accuracy of the experimental method coupled with the speed of the data analysis should make this an attractive method for the study of binary systems.

2. To develop a new method for the measurement of activities of binary mixtures based on the vapor density balance. The application of the vapor density balance to the determination of activities appears quite feasible. The advantage of such a method is that there would be no necessity of sampling the liquid or vapor phases for concentration analysis. The composition of the vapor phase would be determined directly from the vapor density and total pressure values; and the activities, liquid phase composition and activity coefficients could be calculated by means of the Gibbs-Duhem equation. A number of binary systems, done

previously by other authors, were to be investigated to allow comparison between the vapor density balance method and other methods for accuracy, speed and precision.

# CHAPTER III

# EXPERIMENTAL

## A. ACTIVITY FROM TOTAL PRESSURE

### I. APPARATUS

The apparatus, shown in Figure 1, consists of a solution vessel (A) which may be opened to vacuum or atmosphere through the two way stopcock (C). The pressure of the system is read on the closed end manometer (G). The solution is stirred by the stirrer bar (D) which is controlled by a magnetic stirrer (E) placed beneath both the solution vessel (A) and the thermostated bath (F). The solution may be sampled or increments of a component added at (B) which can be blown open or closed by heating with a torch.

### II. PROCEDURE

The total pressure of a binary mixture is investigated in the following manner. Component 1 is introduced into the solution vessel (A) through the opening made at (B) by heating with a torch. The opening is sealed, the system is thoroughly evacuated and the pressure is read for component 1. Dry nitrogen is then bled into the system and

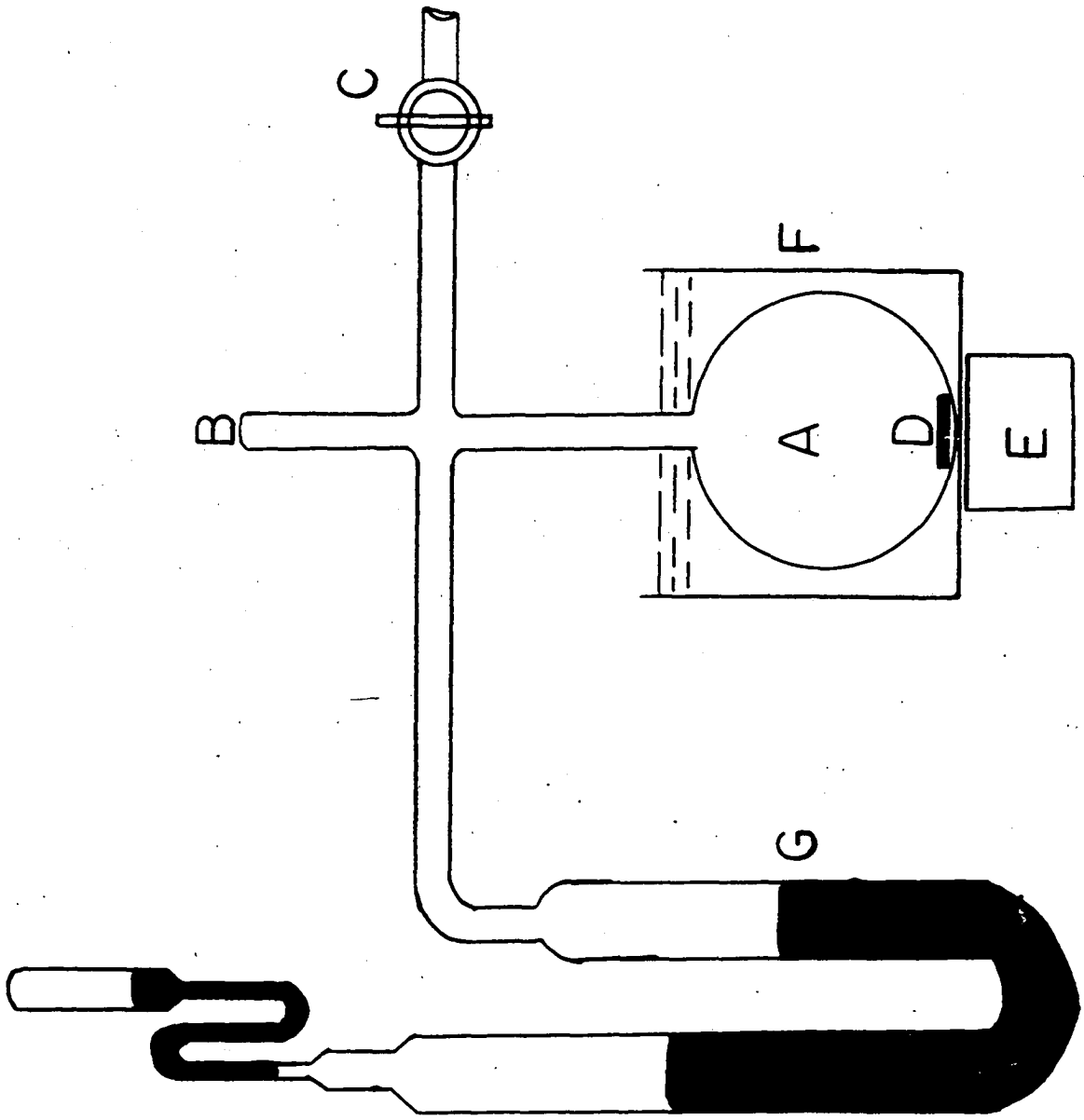


Fig. 1.--Total Pressure Apparatus

a small amount of component 2 is added through the opening at (B). This is then closed with a torch, the system is evacuated and the pressure is recorded. Nitrogen is again bled into the system and the liquid phase is sampled through the opening at (B) with a long, fine pipette made from 8 mm. Pyrex tubing by heating and drawing to a suitable length and diameter. The liquid is sealed into a glass tube for later analysis. Another increment of component 2 is added, the opening at (B) is closed and the pressure determined as before. This is repeated until about half the concentration range is covered. The other half of the concentration is covered in an entirely analogous manner. No vapor samples were ever collected. Provision can be made to do so by a slight modification of the existing system.[3] One of the important advantages of this method is that two or more temperatures can be covered at the same time simply by adjusting the thermoregulator and waiting for thermal equilibrium to be established in the system. With this technique, only one liquid sample is required for the series of temperatures.

The samples obtained in the above manner were analysed wherever possible by comparing the refractive index of the sample with the values of a standard curve prepared for the particularly binary pair. In the case where refractive index could not be used and one of the components was an acid, composition was determined by titration with a

standard base.

## B. ACTIVITY FROM VAPOR DENSITY

### I. APPARATUS

The apparatus, shown in Figure 2, consists of a gas density balance (A) supported on two fine horizontal silica fibers attached to a silica support (B). The entire balance is mounted on a Pyrex glass platform which may be easily removed from the Pyrex glass balance case for adjustment and repair. A large bore glass tube (about 80 mm. in diameter) connects the balance case to the solution vessel (E). It is necessary to use a tube of this size to ensure rapid equilibration between the liquid and vapor phase. The height of the pointer (C) is observed through the window (D) with a precision cathetometer. The solution (E) is stirred by a stirrer bar (F), which is controlled by a magnetic stirrer placed below the thermostated bath (G) and the solution vessel. The pressure of the system is measured by means of a closed manometer. One of the pure components is added to the solution vessel (E) through one of the openings of a Y-tube connecting at (J). The other arm of the Y-tube connects to a sample tube containing a second component, which can be added in incremental amounts by means of a magnetically-operated ground glass valve. The water level in the thermostated bath is kept above the solution vessel (E) but below the balance in order to prevent vapor condensation on the buoyancy bulb.

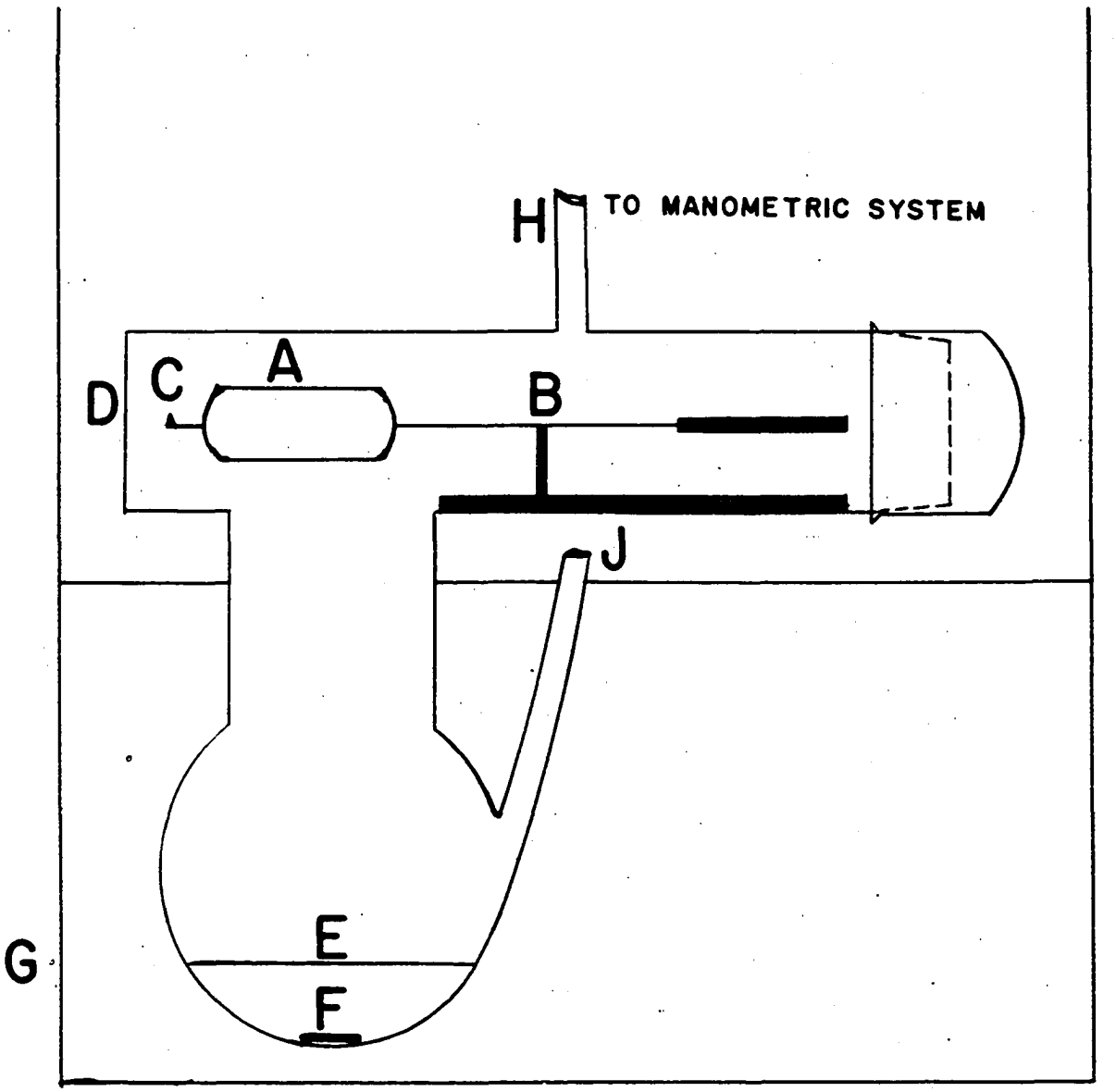


Fig. 2.--Vapor Density Balance Apparatus

## II. PROCEDURE

The apparatus is calibrated in the following manner. The system is evacuated to its lowest pressure, and both the pressure and pointer position are recorded. A small amount of vapor of known molecular weight is bled into the system and the pressure, and pointer positions are recorded. This is repeated in intervals up to a total of about 100 mm. A plot of scale deflection vs. pressure yields a straight line passing through the origin and from the slope of this line, the force constant of the balance is calculated. Two liquids, benzene and carbon tetrachloride, were used in the calibration of the balance. These were chosen because they are ideal in the vapor phase and because of the wide difference in molecular weights which allows a good check of the operating range of the balance.

A binary mixture is investigated by introducing component 1 into the sample tube and degassing by a number of freezing-thawing cycles. The ground glass valve is closed and component 1 is frozen with liquid air or a dry ice-acetone mixture. The system is swept out a number of times with dry air to eliminate vapors of component 1. To prevent the possibility of an explosion from residual vapors, dry nitrogen is bled into the system, component 2 is introduced into the vessel (E) through one arm of the Y-tube which can be blown open or closed by heating with a torch. The system is thoroughly degassed and the pressure and pointer deflection

for pure component 2 are recorded. The temperature of the vapor is recorded from a thermometer resting against the side of the balance case. An increment of component 1 is added by removing the freezing mixture and heating gently with a torch until the liquid boils vigorously; the magnetic valve being held open by a permanent magnet supported outside the tube. Component 1 is frozen again, the system is briefly evacuated and the pointer and pressure readings are recorded. Increments of component 1 are added in this manner until an entire run, covering half the concentration range, is covered. The other half of the concentration range is covered in an analogous manner.

In early runs, it was found that in time the glass sample tube would crack due to the severe temperature range imposed on the cell. This was remedied by making the cell of Kovar metal. This method of addition was then satisfactory for components of low boiling, but when components of higher boiling point were used, severe bumping would occur upon heating causing the balance to oscillate for a period of time before coming to its equilibrium position. In addition, the vapor would condense on the bulb and the balance case adding to the time necessary for the system to reach equilibrium.

These defects were eliminated by the use of the following addition system. A Pyrex glass cell having a magnetically operated ground glass valve is connected to one

arm of the Y-tube by means of small bore polyethylene tubing which allows almost unrestricted flexibility of the glass cell during the addition of a component. The tubing is sealed to the glass portion of the apparatus by heating the glass sections and then pressing the polyethylene tubing over it and holding until the polyethylene tubing is solidified. In addition, molten polyethylene is run over the joints and in each case, vacuum tight joints can be obtained. The component to be added is degassed by a number of freezing-thawing cycles as before, but in adding it to the vessel, it is melted by immersing the cell in warm water and the liquid is run into the solution vessel with the magnetic valve being held open by a permanent magnet outside the cell. This method of addition proved to be quite reliable without the drawbacks of the first method.

It should be noted that once the pure components are degassed and the system is evacuated, no air is admitted during the rest of the run. Attainment of equilibrium is so rapid that the readings can be taken almost as quickly as the above manipulations can be performed. Furthermore, the only two places where the vapors of the system can come in contact with stopcock grease is the joint at the end of the barrel and the two way stopcock controlling the vacuum or admittance of air into the system. In no case does the liquid come in contact with stopcock grease in the system.

## C. MATERIALS

The quartz rod used in the construction of the silica balance was supplied by The Willoughby Quartz Plant of Willoughby, Ohio. All the reagents were either A. R. or C. P. grade and were further purified by distillation through a 30-plate Oldershaw column at a minimum reflux ratio of 10-1. Only the middle fractions were used and boiling points corrected to 760 mm. pressure were:

| | Boiling Range (°C) |
|---|---|
| Acetic Acid | 117.6 - 117.8 |
| Benzene | 79.5 - 79.8 |
| Carbon Tetrachloride | 76.2 - 76.5 |
| Ethyl Acetate | 76.5 - 76.8 |
| Ethyl Alcohol | 78.3 - 78.4 |
| Methyl Alcohol | 64.0 - 64.3 |
| N-Hexane | 68.6 - 68.8 |
| Trifluoroacetic Acid | 71.1 - 71.4 |

# CHAPTER IV

## METHODS OF CALCULATION

### A. TOTAL PRESSURE DATA

The total pressure data were analysed using the method developed by Christian.[11] According to Hildebrand and Scott,[8] the logarithm of the activity coefficients of components in binary mixtures are expressible in power series of the liquid mole fraction. In this work, the expansion was limited to three terms. The total pressure may be written as the sum of the partial pressures of the components in the binary mixture. Furthermore, the partial pressure of each component may be expressed in terms of the vapor pressure of the pure component, its mole fraction in the liquid phase and its activity coefficient to yield:

$$p = x_1 p_1^o \exp (1 - x_1)^2 (A + Bx_1 + Cx_1^2) +$$
$$K_1 x_1^2 p_1^{o2} \exp 2(1 - x_1)^2 (A + Bx_1 + Cx_1^2) +$$
$$(1 - x_1) p_2^o \exp x_1^2 \left[(A - B/2) + (B - 2C/3) x_1 + Cx_1^2\right] \quad (4)$$

where $p_1^o$ and $p_2^o$ are the vapor pressures of pure dimer of component 1 and pure component 2 respectively and $K_1$ is the dimerization constant of component 1 in the vapor phase. The data were fitted according to equation (4). Thus,

fitting total pressure as a function of $x_1$ in this form, the constants A, B and C, and hence, activity coefficients could be determined. Because of the shape of the total pressure curves of the systems investigated, equal mole fractions and their corresponding pressure values could not be used for the input data to obtain a satisfactory fit of the experimental points. Consequently, points were chosen so as to give the best analytical fit over the whole concentration range. The dimerization constants of trifluoroacetic acid used here were those determined by Christian.[13] The dimerization constants of acetic acid were taken from the work of MacDougall.[14] The dimer pressure of acetic at 10°C was found by plotting log dimer pressure vs. 1/T and extrapolating to 10°C.

## B. VAPOR DENSITY BALANCE DATA

The vapor density, d, of the equilibrium vapors is determined directly from the position of the pointer on the silica balance. In cases of systems whose components obey the ideal gas law, the activity of each component may be calculated from the expressions:

$$dRT = \bar{M}p = p_1M_1 + (p - p_1)M_2 \qquad (5)$$

and

$$a_1 = p_1/p_1^o; \quad a_2 = (p - p_1)/p_2^o \qquad (6)$$

where $\bar{M}$ is the average molecular weight of the vapors, $M_1$ and $M_2$ are the molecular weights of the pure components 1 and 2, and $a_1$ and $a_2$ are the activities of components 1 and 2.

In the case of systems in which one of the components dimerizes (e. g. the system $CCl_4$-$CH_3COOH$) expressions corresponding to (5) and (6) may be written in terms of the dimerization constant $K_D$ and the partial pressure of the monomer of the associating compound, $p_1$. Thus:

$$dRT = p_1M_1 + 2K_Dp_1^2M_1 + (p - p_1 - K_Dp_1^2)M_2 \qquad (7)$$

and

$$a_1 = p_1/p_1^o; \quad a_2 = (p - p_1 - K_Dp_1^2)/p_2^o \qquad (8)$$

where the assumption is made that the monomers and dimers obey the ideal gas laws. Similar expressions may be developed for systems in which both components associate in the vapor phase.

The calculation of the liquid phase composition can be made in the following manner. The constant temperature, constant pressure form of the Gibbs-Duhem equation may be rearranged to give:

$$-d \ln a_2 \; / \; (d \ln a_1 - d \ln a_2) = x_1 \qquad (9)$$

The determination of $\ln a_2$ and $\ln a_1$ as functions of any arbitrary variable, $x_1^*$ would allow the calculation of $x_1$ according to the equation

$$\frac{-(d \ln a_2/dx_1^*)}{(d \ln a_1/dx_1^*) - (d \ln a_2/dx_1^*)} = x_1 \qquad (10)$$

It can be shown that for systems deviating but slightly from ideality

$$x_1 = \frac{(1 - a_2)}{(1 - a_2) + (1 - a_1)} \qquad (11)$$

For this reason, the function $x_1^* = (1 - a_2) / (2 - a_1 - a_2)$ was chosen in equation (11) as the independent variable. Defining

$$\gamma_1^* = a_1/x_1^* \text{ and } \gamma_2^* = a_2/(1 - x_1^*) \qquad (12)$$

one can determine expressions of the type

$$\ln \gamma_1^* = (1 - x_1^*)^2 \sum_{i=0} A_1 x_1^{*i}$$

and

$$\ln \gamma_2^* = x_1^{*2} \sum_{i=0} B_i x_1^{*i} \qquad (13)$$

directly from experimental values of $a_1$ and $a_2$.

Actually, only one of the expressions in (13) need be used, since it is obvious that once either $\gamma_1^*$ or $\gamma_2^*$ is fit as a function of $x_1^*$, the other $\gamma^*$ is determined by equations (12).

Equations (12) can be differentiated to give

$$d \ln a_1/dx_1^* = d \ln \gamma_1^*/dx_1^* + 1/x_1^*$$

and

$$d \ln a_2/dx_1^* = d \ln \gamma_2^*/dx_1^* - 1/(1 - x_1^*) \qquad (14)$$

From equations (12) and (13), expressions for $d \ln \gamma_1^*/dx_1^*$ and $d \ln \gamma_2^*/dx_1^*$ can be calculated and substituted into equations (14). Hence, application of equation (10) will yield $x_1$ as a function of $x_1^*$ and the activity coefficients $\gamma_1$ and $\gamma_2$ may be calculated.

The curve fitting technique involving the $\ln\gamma_1^*$ expansion was used only for the systems $C_6H_6$-$CCl_4$, $C_6H_6$-n-hexane, $CCl_4$-n-hexane and $CCl_4$-ethylacetate. All these systems were readily fitted with a one constant equation. A consequence of this was that in every case, $x_1$ and $x_1^*$ were identical.

For other systems, such as those containing an alcohol as one of the components, a different curve fitting technique was used since a single constant expansion was inadequate for these systems. The data were curve fitted using the following equation:

$$(a_1 + a_2 - 1) / a_2 = Aa_1 + Ba_1^2 + Ca_1^3 \qquad (15)$$

where $a_1$ and $a_2$ are experimentally determined activities obtained directly from the output of a computer program developed by Affsprung[15] for the analysis of the vapor density balance data. The constants A, B and C are determined from another computer program developed by Gibbard[16] for curve fitting the experimental activities. For simplicity in the discussion, let f replace the left hand side of equation (15). For an ideal solution, $a_1 + a_2 = 1$, so that a plot of f vs. $a_1$ would give a straight line corresponding to f = 0 for all values of $a_1$. In addition, each of the constants A, B and C would identically be zero. For a real solution with positive deviation from ideality, the limiting values of f can be established as follows. In the case of a very dilute

solution of component 2 in component 1, $a_1 = x_1$ and $a_2 = k_2(1 - x_1)$ where $k_2$ is the Henry's Law constant for component 2. Substituting these values of $a_1$ and $a_2$ into equation (15) and rearranging gives the result:

$$f = 1 - 1/k_2 \tag{16}$$

As $k_2$ becomes very large, the limiting value of f will be 1. On the other hand, for a very dilute solution of component 1 in component 2, $a_2 = x_2$ and $a_1 = k_1(1 - x_2)$ where $k_1$ is the Henry's Law constant for component 1. Substituting these values of $a_1$ and $a_2$ into equation (15) and rearranging gives the result:

$$f = \frac{(k_1 - 1)(1 - x_2)}{x_2} \tag{17}$$

In the limit with $x_2 = 1$, the value of f becomes equal to zero.

The Henry's Law constants for both components can also be evaluated. For the case of component 2, equations (15) and (16) may be combined to give:

$$1 - 1/k_2 = Aa_1 + Ba_1^2 + Ca_1^3 \tag{18}$$

But for a very dilute solution of component 2 in component 1, $a_1$ may be replaced by $x_1$ and in the limit as $x_1$ 1, equation (18) reduces to:

$$1 - 1/k_2 = A + B + C \tag{19}$$

For the Henry's Law constant for component 1, $df/da_1$ can be evaluated from equation (15) which will involve the ratio.

$da_2/da_1$. Using the condition for a dilute solution of component 1 in component 2, namely $a_2 = (1 - x_1)$ and $a_1 = k_1 x_1$, $da_2/da_1$ can be evaluated to give $df/da_1$ in terms of $a_1$ and $k_1$ only. Applying the limiting condition on $df/da_1$ as $a_1 \longrightarrow 0$ gives the result:

$$1 - 1/k_1 = A \tag{20}$$

For the calculation of the liquid phase composition, equation (10) may be rearranged to yield:

$$(1 - a_2 da_1/a_1 da_2) = 1 \; / \; x_1 \tag{21}$$

This equation may be solved by direct differentiation of equation (15) and substituting for the value of $da_1/da_2$ so obtained. An alternate method is to use a computer program to solve for $x_1$ by a $\Delta$ process. Choosing a value of $a_1$ allows the calculation of the corresponding value of $a_2$ from equation (15). A new value of $a_1$ corresponding to $a_1 + \Delta a_1$ is chosen and the above calculations are repeated to yield a new value of $a_2$ equal to $a_2 + \Delta a_2$. For small values of $\Delta a_1$ and $\Delta a_2$, it is possible to replace $da_1$ by $\Delta a_1$ and $da_2$ by $\Delta a_2$ in equation (18) to give:

$$(1 - a_2 \Delta a_1/a_1 \Delta a_2) = 1 \; / \; x_1 \tag{22}$$

Hence, values of $x_1$ can be determined in this manner. Consequently, the activity coefficients can also be calculated for the system.

# CHAPTER V

## RESULTS

The experimental data for the total pressures, partial pressures and activity coefficients for the systems acetic acid-$CCl_4$ and trifluoroacetic acid-$CCl_4$ at 10, 20 and 25 $^{o}C$ as determined by the total pressure apparatus are given in Tables 1-6. Table 7 lists the constants determined from equation (4) for each system in the curve fitting program. Figures 3-8 represent the total and partial pressures plotted on the basis of the mole fraction of acid based on the dimer molecular weight of the acid for each system at each temperature. Points are experimental, and the curves are calculated from the best fit of the experimental data. Figures 9-10 are the calculated activity coefficients for each system.

Tables 8-11 list the experimental activities, the calculated mole fraction of the liquid phase, the calculated activity coefficients and the calculated activities for the systems $C_6H_6$-$CCl_4$, $C_6H_6$-n-hexane, $CCl_4$-n-hexane and $CCl_4$-ethylacetate at 20°. In addition, Table 8 lists the activities as calculated from the data of Scatchard.[17] The

activity coefficients expressed as a function of the mole fraction of the liquid phase are also listed below the table for each of the above systems. Figures 11-14 show a plot of $a_1$ vs. $a_2$ for each system and Figures 15-18 show a plot of the activity coefficients of each component vs. mole fraction of the liquid phase for each system.

Tables 12-15 list the total pressures, the calculated activities, the calculated mole fraction of the liquid phase and the calculated activity coefficients for the systems $CCl_4$-methanol, $CCl_4$-ethanol, $C_6H_6$-methanol and $C_6H_6$-ethanol at $10^{\circ}$. Table 15 lists the constants determined from equation (15) for each system in the curve fitting of the activities. Figures 19-22 show a plot of $a_1$ vs. $a_2$ for each system and Figures 23-26 show a plot of the activity coefficients of each component vs. mole fraction of the liquid phase for each system.

Table 1

System Acetic Acid-$CCl_4$ Dependence of Total Pressure, Partial Pressures and Activity Coefficients on Liquid Mole Fraction at 10°

| $X_d$ | $P_T$ | $p^{calc}_m$ | $p^{calc}_d$ | $p^{calc}_2$ | $p^{calc}_T$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|---|---|
| .0000 | 56.76 | 0.000 | 0.000 | 56.76 | 56.76 | 3.810 | 1.000 |
| .0976 | 54.70 | 0.451 | 1.557 | 52.65 | 54.66 | 2.925 | 1.020 |
| .1678 | 52.57 | 0.533 | 2.220 | 49.85 | 52.60 | 2.632 | 1.050 |
| .2928 | 48.86 | 0.610 | 2.881 | 45.80 | 49.29 | 1.800 | 1.150 |
| .3857 | 47.32 | 0.647 | 3.240 | 43.50 | 47.39 | 1.525 | 1.250 |
| .4814 | 43.64 | 0.675 | 3.548 | 40.35 | 44.57 | 1.350 | 1.375 |
| .5637 | 41.11 | 0.700 | 3.780 | 37.35 | 41.83 | 1.238 | 1.495 |
| .6233 | 39.57 | 0.715 | 3.975 | 34.90 | 39.59 | 1.175 | 1.613 |
| .4836 | 44.01 | 0.676 | 3.550 | 40.30 | 44.56 | 1.347 | 1.379 |
| .4821 | 42.97 | 0.675 | 3.545 | 40.15 | 44.37 | 1.349 | 1.377 |
| .6820 | 36.36 | 0.731 | 4.175 | 32.00 | 36.91 | 1.120 | 1.765 |
| .7467 | 33.08 | 0.750 | 4.400 | 28.00 | 33.15 | 1.075 | 1.952 |
| .8264 | 27.06 | 0.775 | 4.700 | 22.00 | 27.48 | 1.037 | 2.213 |
| .8903 | 22.16 | 0.801 | 4.930 | 16.85 | 22.56 | 1.013 | 2.530 |
| 1.0000 | 6.16 | 0.826 | 5.334 | 00.00 | 6.16 | 1.000 | 3.605 |

Table 2

System Acetic Acid-$CCl_4$ Dependence of Total Pressure, Partial Pressures and Activity Coefficients on Liquid Mole Fraction at 20°

| $X_d$ | $P_T$ | $P_m^{calc}$ | $P_d^{calc}$ | $P_2^{calc}$ | $P_T^{calc}$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|---|---|
| .0000 | 90.97 | 0.000 | 0.000 | 90.97 | 90.97 | 5.400 | 1.000 |
| .0576 | 90.23 | 0.883 | 2.200 | 86.85 | 89.93 | 3.875 | 1.008 |
| .1074 | 87.78 | 1.063 | 3.320 | 84.00 | 88.38 | 3.025 | 1.032 |
| .1614 | 87.00 | 1.168 | 3.945 | 81.45 | 86.46 | 2.450 | 1.075 |
| .2461 | 84.44 | 1.260 | 4.590 | 78.65 | 84.60 | 1.875 | 1.158 |
| .3131 | 82.03 | 1.305 | 4.900 | 76.55 | 82.76 | 1.613 | 1.215 |
| .3831 | 79.23 | 1.350 | 5.225 | 73.75 | 80.23 | 1.420 | 1.305 |
| .4684 | 76.11 | 1.412 | 5.700 | 69.20 | 76.30 | 1.250 | 1.415 |
| .5515 | 70.38 | 1.473 | 6.200 | 63.54 | 71.21 | 1.150 | 1.560 |
| .5748 | 69.49 | 1.485 | 6.340 | 61.65 | 69.47 | 1.137 | 1.587 |
| .6877 | 59.01 | 1.578 | 7.100 | 50.50 | 59.18 | 1.065 | 1.750 |
| .7436 | 52.73 | 1.622 | 7.515 | 43.55 | 52.69 | 1.037 | 1.875 |
| .8148 | 44.14 | 1.682 | 8.100 | 33.65 | 43.43 | 1.017 | 2.000 |
| .8832 | 33.79 | 1.740 | 8.655 | 21.20 | 31.60 | 1.009 | 2.150 |
| .9588 | 20.15 | 1.788 | 9.300 | 9.00 | 20.09 | 1.001 | 2.330 |
| 1.000 | 11.50 | 1.810 | 9.690 | 0.00 | 11.50 | 1.000 | 2.380 |

Table 3

System Acetic Acid-$CCl_4$ Dependence of Total Pressure, Partial Pressures and Activity Coefficients on Liquid Mole Fraction at 25°

| $X_d$ | $P_T$ | $P_m^{calc}$ | $P_d^{calc}$ | $P_2^{calc}$ | $P_T^{calc}$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|---|---|
| .0000 | 114.58 | 0.000 | 0.000 | 114.58 | 114.58 | 3.835 | 1.000 |
| .0576 | 111.99 | 1.068 | 2.225 | 108.90 | 112.19 | 3.100 | 1.007 |
| .1074 | 109.55 | 1.421 | 3.785 | 104.90 | 110.11 | 2.625 | 1.022 |
| .1614 | 107.13 | 1.615 | 4.700 | 100.85 | 107.17 | 2.300 | 1.050 |
| .2461 | 103.85 | 1.793 | 5.835 | 95.40 | 103.18 | 1.848 | 1.103 |
| .3131 | 98.91 | 1.900 | 6.520 | 91.50 | 99.92 | 1.613 | 1.152 |
| .3831 | 95.91 | 1.992 | 7.195 | 87.00 | 96.19 | 1.413 | 1.213 |
| .4684 | 89.86 | 2.080 | 7.900 | 80.85 | 90.83 | 1.313 | 1.335 |
| .5515 | 85.17 | 2.172 | 8.580 | 74.34 | 85.09 | 1.218 | 1.444 |
| .5748 | 82.45 | 2.192 | 8.800 | 72.00 | 82.99 | 1.195 | 1.475 |
| .6877 | 71.96 | 2.305 | 9.725 | 60.45 | 72.48 | 1.110 | 1.690 |
| .7436 | 65.76 | 2.360 | 10.20 | 53.85 | 66.41 | 1.074 | 1.840 |
| .8148 | 56.72 | 2.490 | 10.79 | 43.20 | 56.48 | 1.036 | 2.060 |
| .8832 | 46.61 | 2.513 | 11.46 | 31.30 | 45.27 | 1.016 | 2.326 |
| .9588 | 28.61 | 2.592 | 12.26 | 13.85 | 28.70 | 1.005 | 2.713 |
| 1.000 | 15.33 | 2.632 | 12.70 | 00.00 | 15.33 | 1.000 | 2.965 |

Table 4

System Trifluoroacetic Acid-$CCl_4$ Dependence of Total Pressure, Partial Pressures and Activity Coefficients on Liquid Mole Fraction at 10°

| $X_d$ | $P_T$ | $p^{calc}_m$ | $p^{calc}_d$ | $p^{calc}_2$ | $p^{calc}_T$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|---|---|
| .0000 | 57.34 | 0.000 | 0.00 | 57.34 | 57.34 | 13.020 | 1.000 |
| .0585 | 85.64 | 4.952 | 22.30 | 54.70 | 81.95 | 8.505 | 1.012 |
| .1605 | 91.13 | 6.172 | 33.30 | 52.20 | 91.68 | 4.800 | 1.102 |
| .2549 | 92.16 | 6.300 | 34.30 | 51.90 | 92.50 | 3.150 | 1.220 |
| .2805 | 91.84 | 6.250 | 34.20 | 51.95 | 92.45 | 2.845 | 1.280 |
| .3503 | 92.20 | 6.180 | 34.06 | 52.34 | 92.58 | 2.258 | 1.400 |
| .3783 | 92.29 | 6.225 | 33.60 | 52.30 | 92.13 | 2.120 | 1.505 |
| .4473 | 92.34 | 6.220 | 33.50 | 52.60 | 92.32 | 1.735 | 1.670 |
| .5767 | 92.25 | 6.172 | 33.80 | 52.35 | 92.32 | 1.365 | 2.180 |
| .7432 | 89.51 | 6.190 | 35.35 | 47.30 | 88.84 | 1.110 | 3.135 |
| .9020 | 73.44 | 6.677 | 38.55 | 27.50 | 72.73 | 1.014 | 5.582 |
| 1.0000 | 50.64 | 7.035 | 43.60 | 00.00 | 50.63 | 1.000 | 6.665 |

Table 5

System Trifluoroacetic Acid-$CCl_4$ Dependence of Total Pressure, Partial Pressures and Activity Coefficients on Liquid Mole Fraction at 20°

| $X_d$ | $P_T$ | $p_m^{calc}$ | $p_d^{calc}$ | $p_2^{calc}$ | $P_T^{calc}$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|---|---|
| .0000 | 90.90 | 00.00 | 00.00 | 90.90 | 90.90 | 16.180 | 1.000 |
| .0629 | 138.33 | 9.690 | 41.80 | 87.00 | 137.49 | 8.950 | 1.015 |
| .1297 | 149.70 | 10.820 | 53.00 | 84.90 | 148.72 | 5.550 | 1.090 |
| .1972 | 149.03 | 11.000 | 54.45 | 84.85 | 150.30 | 3.850 | 1.150 |
| .2592 | 149.36 | 11.002 | 54.50 | 84.65 | 150.15 | 2.850 | 1.255 |
| .3361 | 149.27 | 11.000 | 54.60 | 84.50 | 150.10 | 2.200 | 1.320 |
| .3812 | 149.34 | 11.005 | 54.60 | 84.60 | 150.20 | 1.955 | 1.430 |
| .5033 | 149.46 | 11.190 | 56.60 | 82.08 | 149.79 | 1.520 | 1.815 |
| .5574 | 149.44 | 11.300 | 57.85 | 80.40 | 149.35 | 1.405 | 2.030 |
| .6026 | 148.98 | 11.430 | 59.35 | 77.70 | 148.35 | 1.325 | 2.145 |
| .7044 | 146.07 | 11.710 | 62.00 | 71.00 | 144.70 | 1.190 | 2.616 |
| .7067 | 146.21 | 11.720 | 62.10 | 71.00 | 144.82 | 1.190 | 2.615 |
| .8734 | 131.27 | 12.200 | 67.50 | 50.50 | 130.20 | 1.038 | 4.385 |
| 1.000 | 86.97 | 12.750 | 74.22 | 00.00 | 86.97 | 1.000 | 8.260 |

Table 6

System Trifluoroacetic Acid-$CCl_4$ Dependence of Total Pressure, Partial Pressures and Activity Coefficients on Liquid Mole Fraction at 25°

| $X_d$ | $P_T$ | $p_m^{calc}$ | $p_d^{calc}$ | $p_2^{calc}$ | $p_T^{calc}$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|---|---|
| .0000 | 114.72 | 00.00 | 00.00 | 114.72 | 114.72 | 12.172 | 1.000 |
| .0629 | 170.92 | 12.20 | 45.00 | 109.00 | 166.20 | 7.450 | 1.014 |
| .1297 | 182.27 | 14.40 | 61.20 | 106.00 | 181.60 | 4.935 | 1.045 |
| .1972 | 186.92 | 14.95 | 66.00 | 104.50 | 185.45 | 3.555 | 1.125 |
| .2592 | 186.98 | 15.18 | 68.00 | 103.60 | 186.78 | 2.740 | 1.250 |
| .3361 | 186.91 | 15.30 | 69.00 | 103.00 | 187.30 | 2.150 | 1.350 |
| .3812 | 186.92 | 15.40 | 70.00 | 102.10 | 187.50 | 1.950 | 1.440 |
| .5033 | 186.96 | 15.65 | 73.15 | 98.40 | 187.20 | 1.504 | 1.728 |
| .5574 | 186.92 | 15.85 | 74.80 | 96.40 | 187.05 | 1.390 | 1.875 |
| .6026 | 187.91 | 16.00 | 76.20 | 93.50 | 185.70 | 1.310 | 2.045 |
| .7044 | 182.73 | 16.40 | 80.25 | 85.25 | 182.20 | 1.150 | 2.500 |
| .7067 | 182.88 | 16.50 | 80.20 | 85.25 | 181.95 | 1.150 | 2.500 |
| .8734 | 163.15 | 17.20 | 88.00 | 59.00 | 164.20 | 1.030 | 4.000 |
| 1.0000 | 112.49 | 17.91 | 95.48 | 00.00 | 112.49 | 1.000 | 7.228 |

Table 7

Tabulation of the Constants Derived from the Curve Fitting of the Total Pressure Curves

| System | Temp. $^{o}C$ | A | B | C |
|---|---|---|---|---|
| Acetic Acid-$CCl_4$ | 10 | 1.338 | -1.165 | 0.995 |
| Acetic Acid-$CCl_4$ | 20 | 1.686 | -2.839 | 1.800 |
| Acetic Acid-$CCl_4$ | 25 | 1.344 | -1.516 | 1.500 |
| Trifluoroacetic Acid-$CCl_4$ | 10 | 2.570 | -2.273 | 1.385 |
| Trifluoroacetic Acid-$CCl_4$ | 20 | 2.783 | -4.664 | 4.988 |
| Trifluoroacetic Acid-$CCl_4$ | 25 | 2.500 | -3.633 | 3.893 |

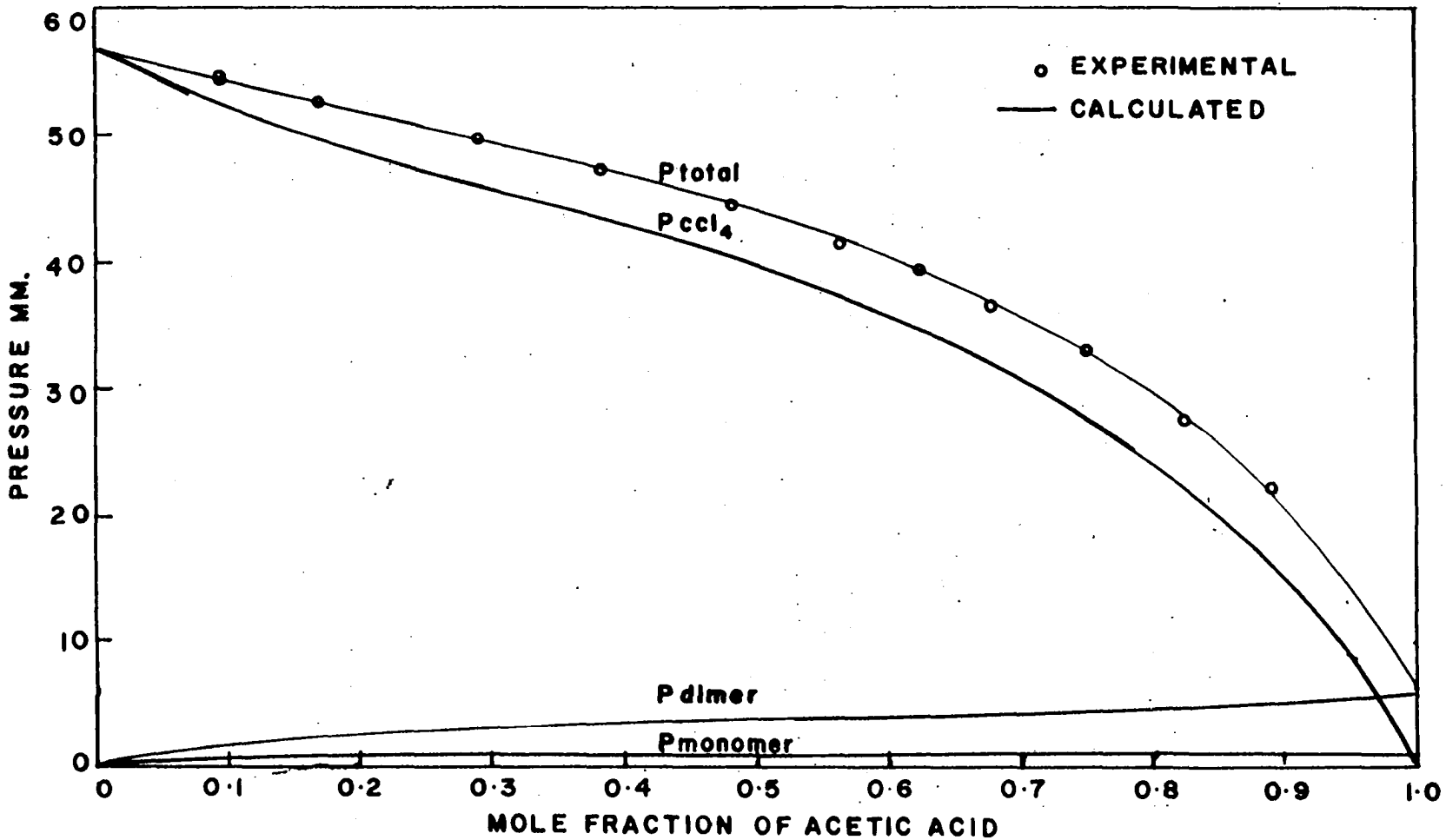


Fig. 3.--Partial and Total Pressures for the System Acetic Acid-$CCl_4$ at $10^{o}$

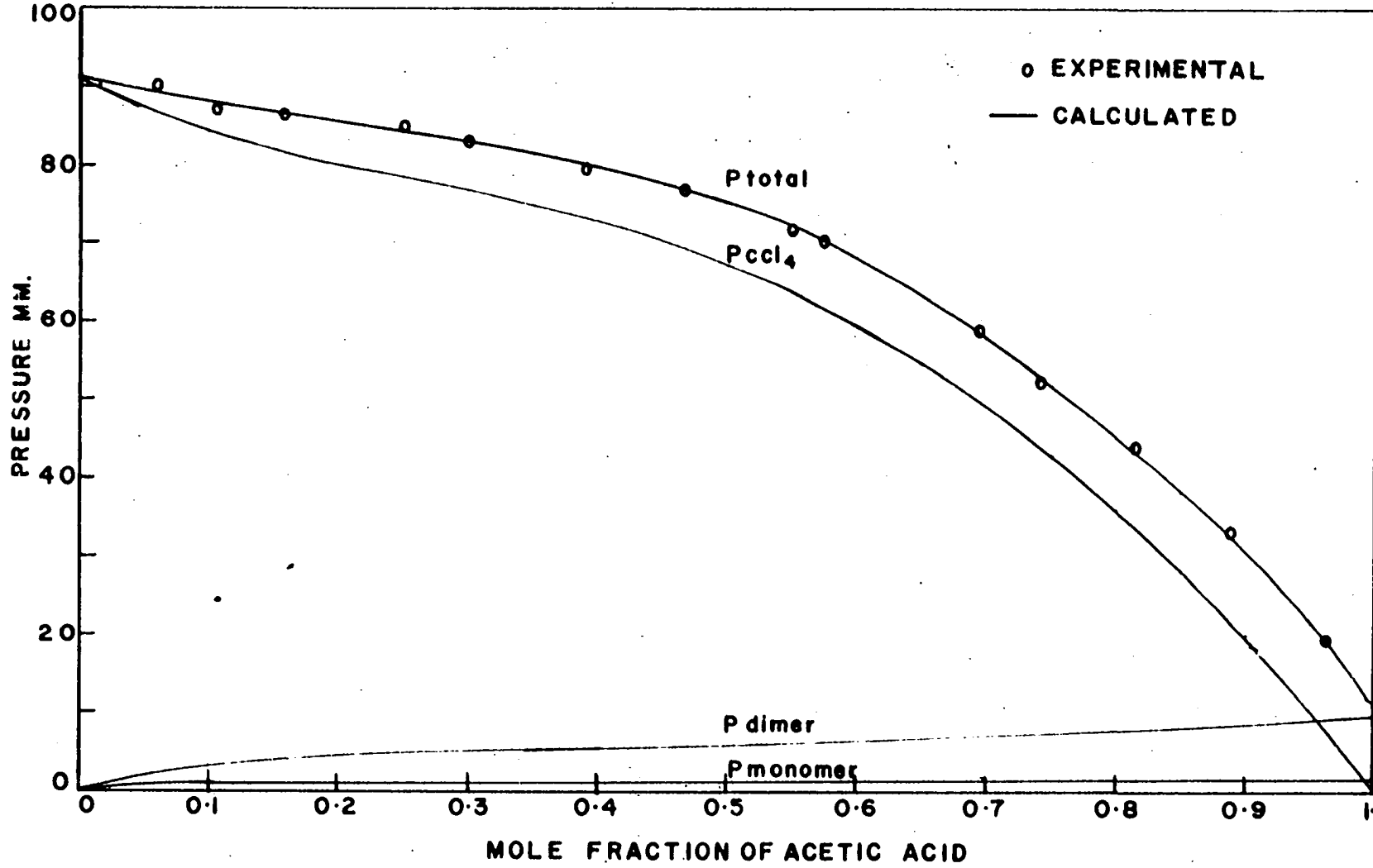


Fig. 4.--Partial and Total Pressures for the System Acetic Acid-$CCl_4$ at 20°

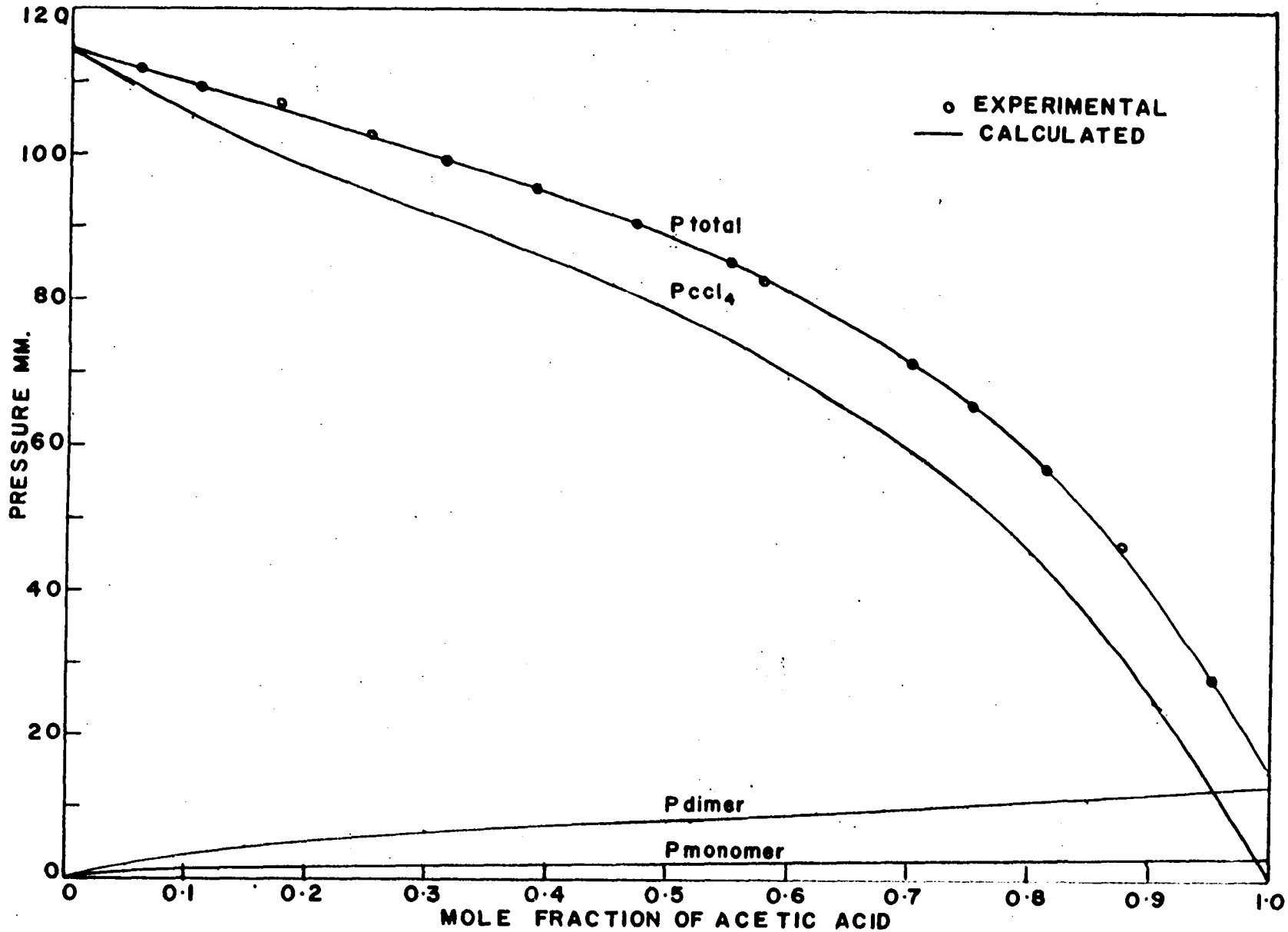


Fig. 5.--Partial and Total Pressures for the System Acetic Acid-$CCl_4$ at 25°

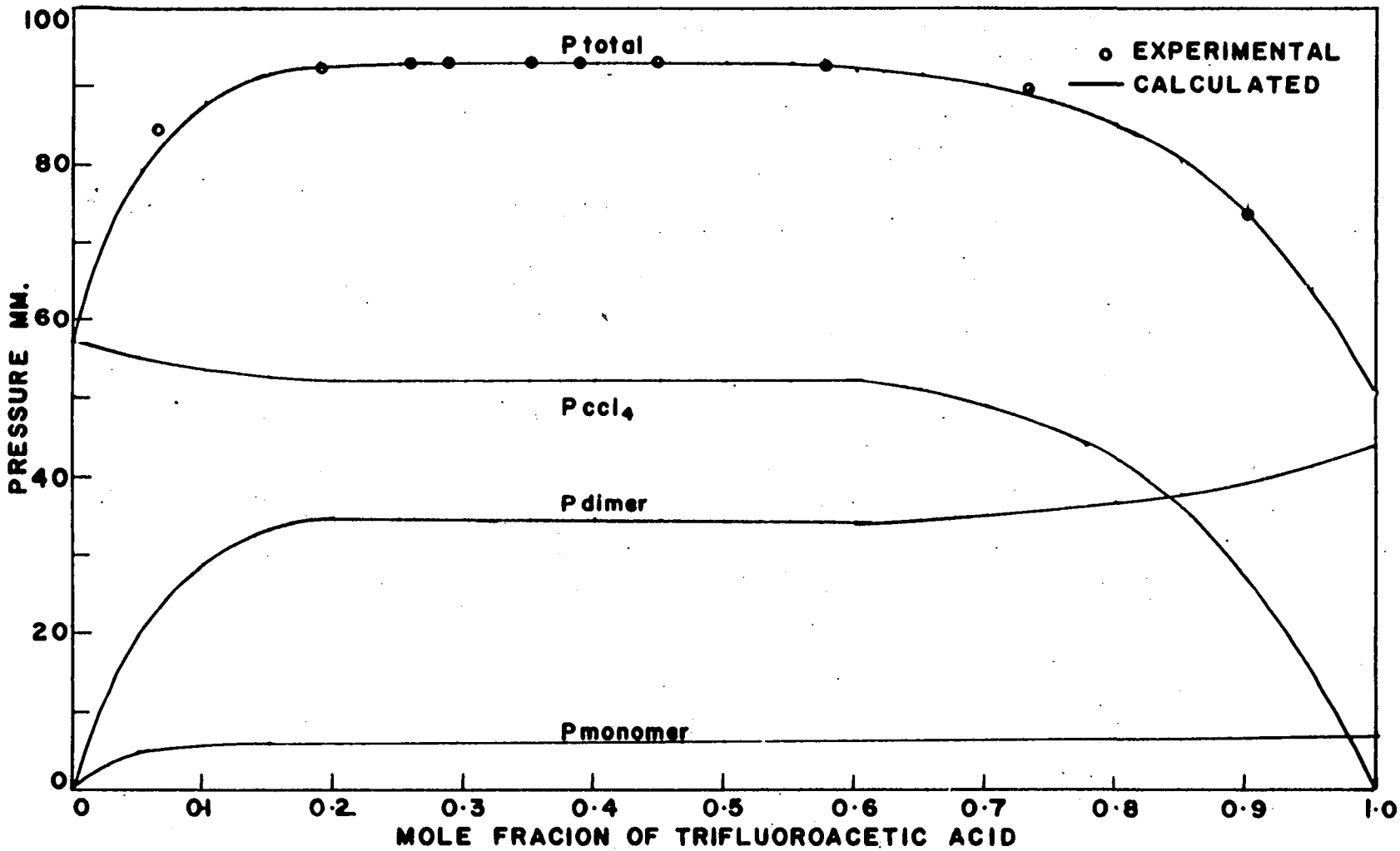


Fig. 6.--Partial and Total Pressures for the System Trifluoroacetic Acid-$CCl_4$ at $10^o$

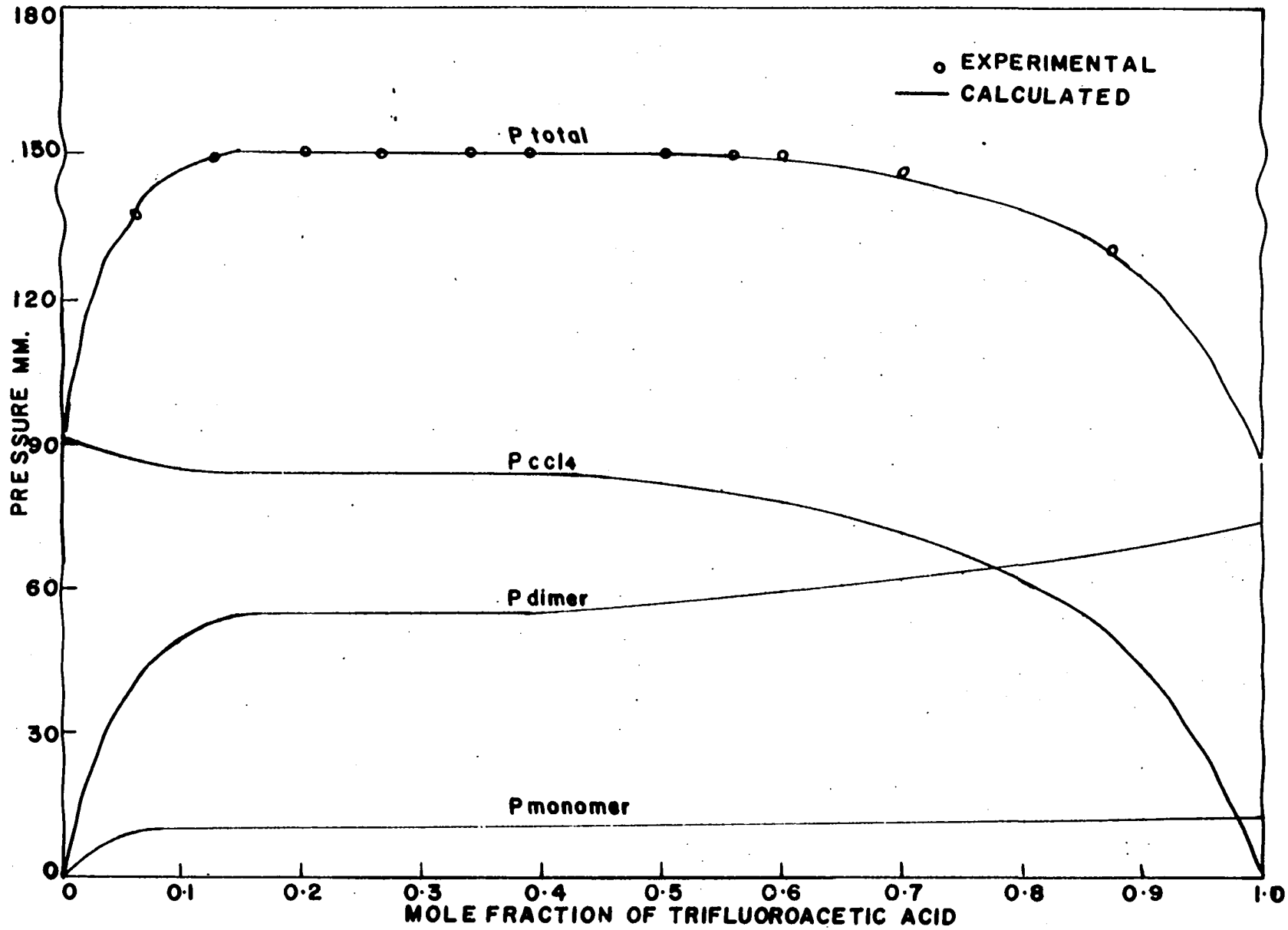


Fig. 7.--Partial and Total Pressures for the System Trifluoroacetic Acid-$CCl_4$ at 20°

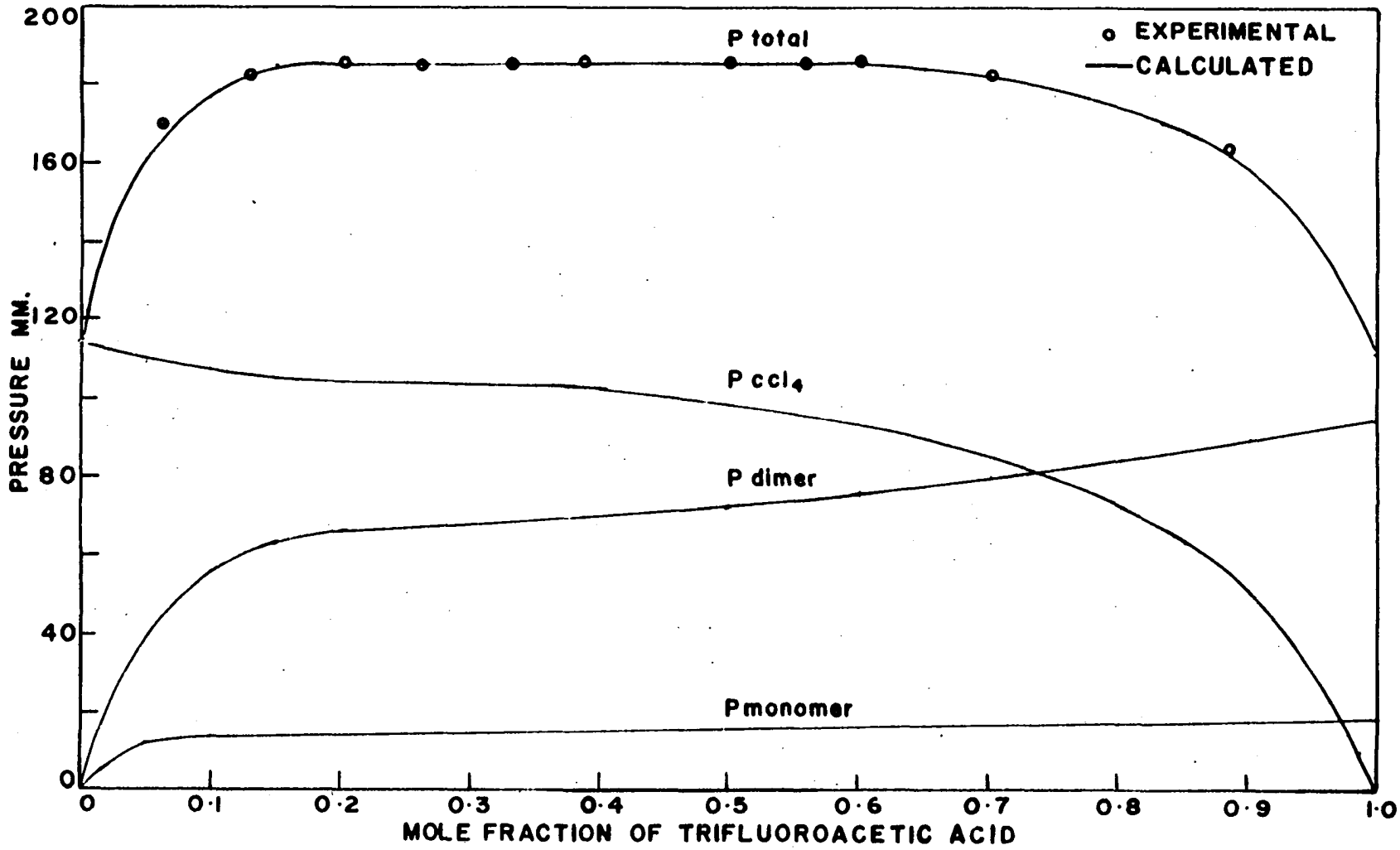


Fig. 8.--Partial and Total Pressures for the System Trifluoroacetic Acid-$CCl_4$ at 25°

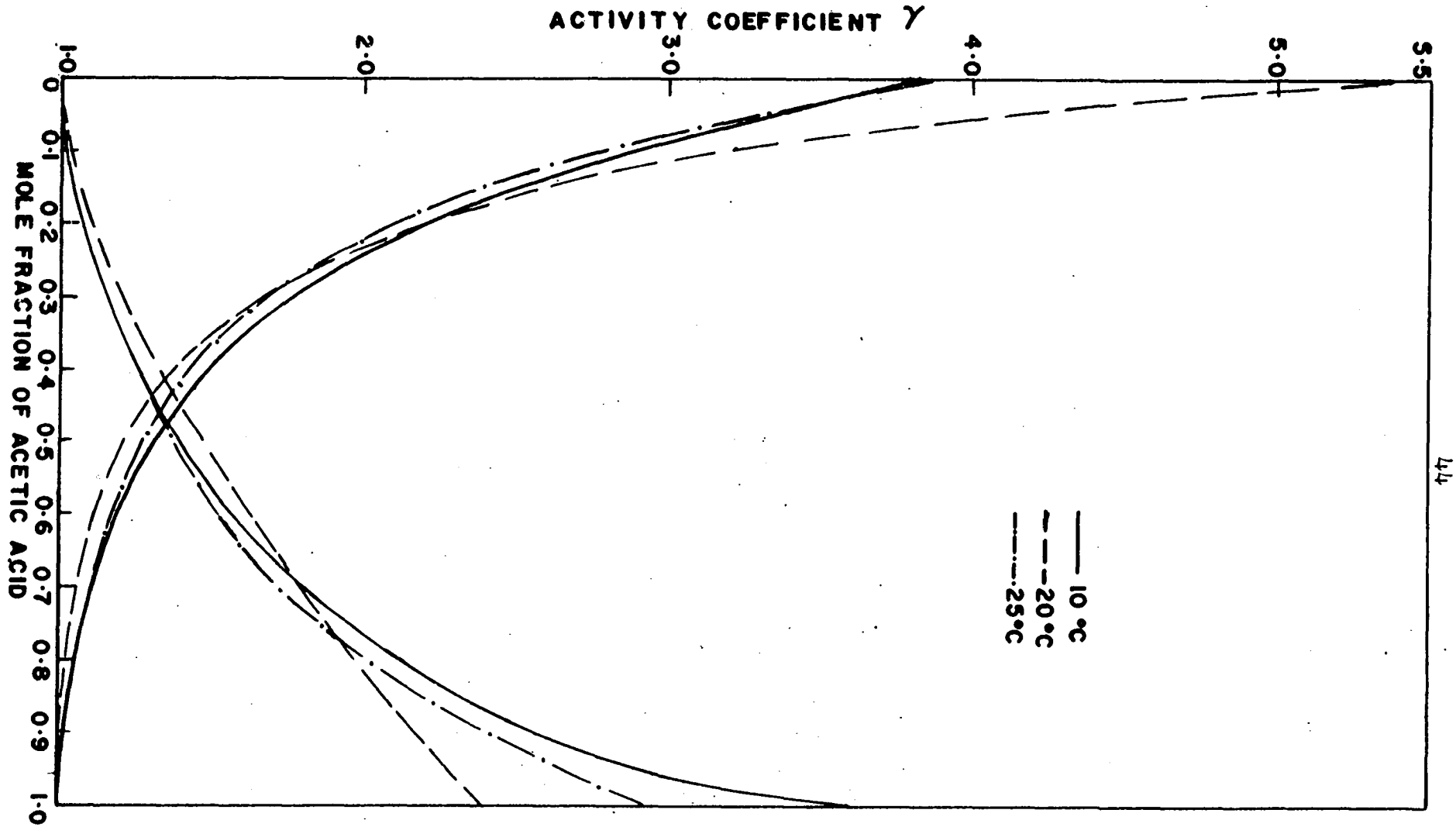


Fig. 9.--Activity Coefficients of the System Acetic Acid-$CCl_4$

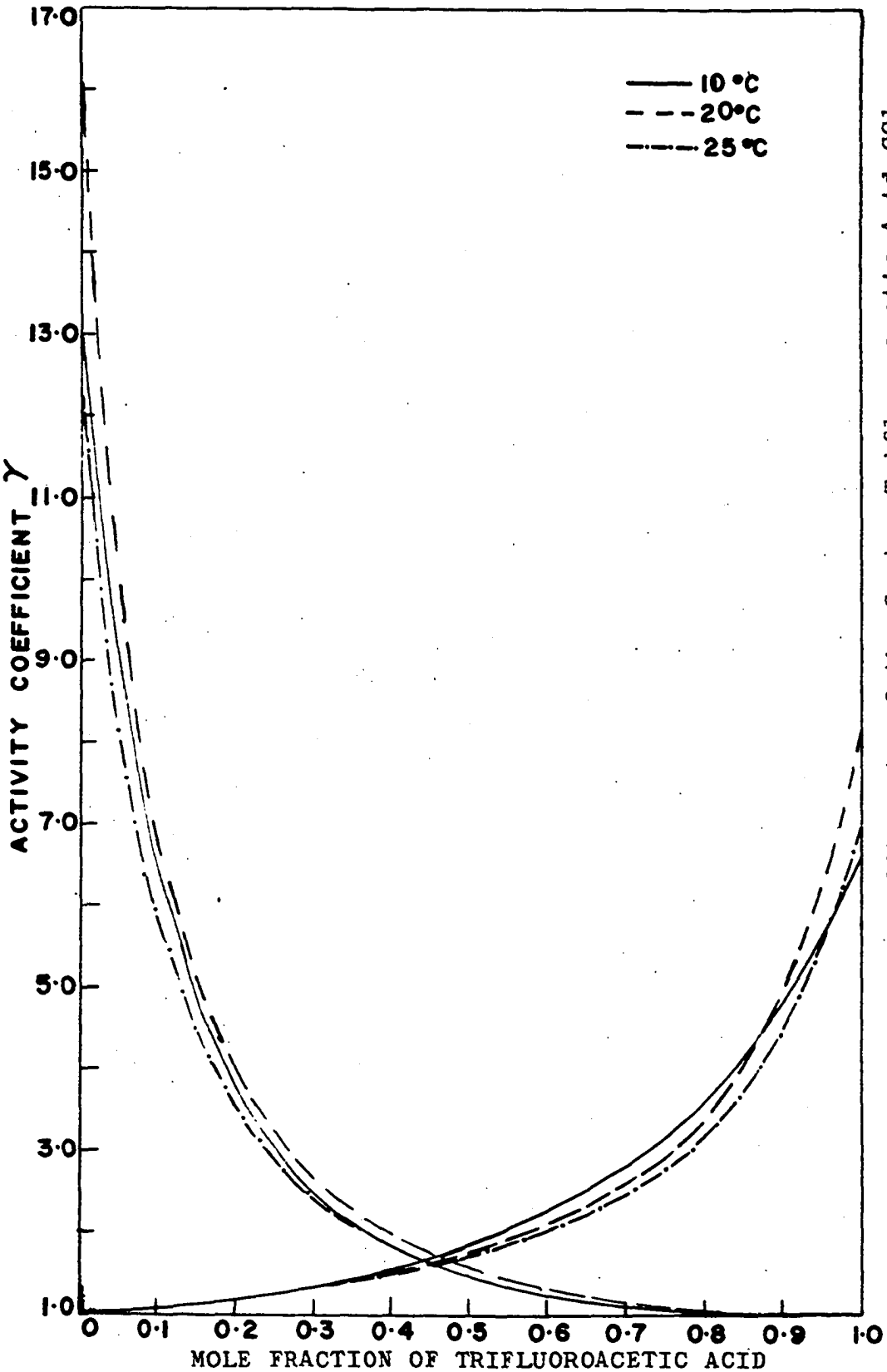


Fig. 10.--Activity Coefficients of the System Trifluoroacetic Acid $CCl_4$

Table 8

System $C_6H_6$-$CCl_4$

Dependence of Activities and Activity Coefficients on Liquid Mole Fraction at 20°

| $a_1$ | $a_2$ | $x_1^*$ | $x_1^1$ | $\gamma_{1\,calc}^*$ | $\gamma_{2\,calc}^*$ | $a_{1\,calc}$ | $a_{2\,calc}$ | $a_1(S)^*$ | $a_2(S)^*$ |
|---|---|---|---|---|---|---|---|---|---|
| 1.000 | 0.000 | 1.000 | 1.000 | 1.000 | | 1.000 | 0.000 | 1.000 | 0.000 |
| 0.937 | 0.069 | 0.937 | 0.937 | 1.000 | 1.131 | 0.937 | 0.071 | 0.937 | 0.071 |
| 0.878 | 0.133 | 0.877 | 0.877 | 1.002 | 1.114 | 0.879 | 0.137 | 0.879 | 0.136 |
| 0.797 | 0.214 | 0.795 | 0.795 | 1.006 | 1.092 | 0.800 | 0.223 | 0.799 | 0.224 |
| 0.759 | 0.266 | 0.753 | 0.753 | 1.008 | 1.083 | 0.760 | 0.267 | 0.759 | 0.267 |
| 0.688 | 0.333 | 0.681 | 0.681 | 1.014 | 1.067 | 0.690 | 0.340 | 0.691 | 0.339 |
| 0.648 | 0.379 | 0.638 | 0.638 | 1.019 | 1.059 | 0.650 | 0.383 | 0.649 | 0.383 |
| 0.629 | 0.402 | 0.615 | 0.615 | 1.022 | 1.054 | 0.628 | 0.406 | 0.628 | 0.404 |
| 0.592 | 0.444 | 0.577 | 0.577 | 1.025 | 1.048 | 0.594 | 0.443 | 0.591 | 0.443 |
| 0.519 | 0.520 | 0.499 | 0.499 | 1.036 | 1.035 | 0.517 | 0.518 | 0.517 | 0.518 |
| 0.517 | 0.523 | 0.497 | 0.497 | 1.037 | 1.035 | 0.515 | 0.521 | 0.514 | 0.520 |
| 0.469 | 0.570 | 0.447 | 0.447 | 1.045 | 1.028 | 0.467 | 0.568 | 0.466 | 0.568 |
| 0.319 | 0.699 | 0.307 | 0.307 | 1.068 | 1.013 | 0.328 | 0.702 | 0.328 | 0.702 |
| 0.260 | 0.756 | 0.248 | 0.248 | 1.083 | 1.009 | 0.262 | 0.759 | 0.262 | 0.758 |
| 0.204 | 0.812 | 0.191 | 0.191 | 1.094 | 1.005 | 0.209 | 0.813 | 0.208 | 0.813 |
| 0.107 | 0.902 | 0.099 | 0.099 | 1.123 | 1.001 | 0.111 | 0.902 | 0.109 | 0.903 |
| 0.000 | 1.000 | 0.000 | 0.000 | | 1.000 | 0.000 | 1.000 | 0.000 | 1.000 |

$$\ln\gamma_1^* = 0.14(1 - x_1^*)^2 \text{ and } x_1 = x_1^*$$

Table 9

System $C_6H_6$-n-Hexane

Dependence of Activities and Activity Coefficients on Liquid Mole Fraction at 20°

| $a_1$ | $a_2$ | $x_1^*$ | $x_1^1$ | $\gamma_1^{calc}$ | $\gamma_2^{calc}$ | $a_1^{calc}$ | $a_2^{calc}$ |
|---|---|---|---|---|---|---|---|
| 1.000 | 0.000 | 1.000 | 1.000 | 1.000 | | 1.000 | 0.000 |
| 0.935 | 0.085 | 0.934 | 0.934 | 1.002 | 1.305 | 0.936 | 0.086 |
| 0.844 | 0.202 | 0.836 | 0.836 | 1.009 | 1.244 | 0.844 | 0.204 |
| 0.760 | 0.307 | 0.742 | 0.742 | 1.023 | 1.193 | 0.760 | 0.307 |
| 0.680 | 0.403 | 0.651 | 0.651 | 1.043 | 1.148 | 0.679 | 0.401 |
| 0.598 | 0.495 | 0.557 | 0.557 | 1.069 | 1.112 | 0.595 | 0.496 |
| 0.524 | 0.567 | 0.477 | 0.477 | 1.096 | 1.080 | 0.522 | 0.565 |
| 0.499 | 0.602 | 0.443 | 0.443 | 1.110 | 1.069 | 0.492 | 0.596 |
| 0.514 | 0.590 | 0.458 | 0.458 | 1.103 | 1.073 | 0.505 | 0.582 |
| 0.457 | 0.644 | 0.384 | 0.384 | 1.133 | 1.051 | 0.434 | 0.648 |
| 0.338 | 0.735 | 0.285 | 0.285 | 1.179 | 1.029 | 0.337 | 0.735 |
| 0.202 | 0.829 | 0.177 | 0.177 | 1.231 | 1.002 | 0.217 | 0.825 |
| 0.150 | 0.885 | 0.119 | 0.119 | 1.271 | 1.001 | 0.152 | 0.885 |
| 0.000 | 1.000 | 0.000 | 0.000 | | 1.000 | 0.000 | 1.000 |

$$\ln\gamma_1^* = 0.35(1 - x_1^*) \quad \text{and} \quad x_1 = x_1^*$$

Table 10

System $CCl_4$-n-Hexane

Dependence of Activities and Activity Coefficients on Liquid Mole Fraction at 20°

| $a_1$ | $a_2$ | $x_1^*$ | $x_1$ | $\gamma_1^{calc}$ | $\gamma_2^{calc}$ | $a_1^{calc}$ | $a_2^{calc}$ |
|---|---|---|---|---|---|---|---|
| 1.000 | 0.000 | 1.000 | 1.000 | 1.000 | | 1.000 | 0.000 |
| 0.963 | 0.044 | 0.963 | 0.963 | 1.001 | 1.176 | 0.963 | 0.044 |
| 0.839 | 0.191 | 0.834 | 0.834 | 1.005 | 1.125 | 0.839 | 0.187 |
| 0.775 | 0.264 | 0.766 | 0.766 | 1.010 | 1.115 | 0.774 | 0.261 |
| 0.689 | 0.355 | 0.675 | 0.675 | 1.020 | 1.082 | 0.688 | 0.352 |
| 0.628 | 0.421 | 0.609 | 0.609 | 1.028 | 1.067 | 0.626 | 0.417 |
| 0.568 | 0.481 | 0.545 | 0.545 | 1.039 | 1.054 | 0.567 | 0.480 |
| 0.525 | 0.524 | 0.500 | 0.500 | 1.045 | 1.040 | 0.523 | 0.520 |
| 0.473 | 0.575 | 0.447 | 0.447 | 1.055 | 1.036 | 0.472 | 0.573 |
| 0.456 | 0.589 | 0.430 | 0.430 | 1.058 | 1.034 | 0.455 | 0.589 |
| 0.449 | 0.596 | 0.424 | 0.424 | 1.060 | 1.032 | 0.449 | 0.595 |
| 0.420 | 0.621 | 0.395 | 0.395 | 1.066 | 1.028 | 0.421 | 0.622 |
| 0.350 | 0.687 | 0.325 | 0.325 | 1.080 | 1.019 | 0.351 | 0.688 |
| 0.241 | 0.792 | 0.215 | 0.215 | 1.111 | 1.008 | 0.239 | 0.791 |
| 0.137 | 0.886 | 0.117 | 0.117 | 1.145 | 1.002 | 0.134 | 0.885 |
| 0.071 | 0.940 | 0.061 | 0.061 | 1.160 | 1.001 | 0.070 | 0.940 |
| 0.000 | 1.000 | 0.000 | 0.000 | | 1.000 | 0.000 | 1.000 |

$\ln \gamma_1^* = 0.18(1 - x_1^*)^2$ and $x_1 - x_1^*$

Table 11

System $CCl_4$-Ethylacetate

Dependence of Activities and Activity Coefficients on Liquid Mole Fraction at 20°

| $a_1$ | $a_2$ | $x_1^*$ | $x_1$ | $\gamma_1^{calc}$ | $\gamma_2^{calc}$ | $a_1^{calc}$ | $a_2^{calc}$ |
|---|---|---|---|---|---|---|---|
| 1.000 | 0.000 | 1.000 | 1.000 | 1.000 | | 1.000 | 0.000 |
| 0.969 | 0.042 | 0.969 | 0.969 | 1.000 | 1.375 | 0.969 | 0.043 |
| 0.890 | 0.161 | 0.884 | 0.884 | 1.005 | 1.313 | 0.889 | 0.153 |
| 0.830 | 0.230 | 0.819 | 0.819 | 1.012 | 1.283 | 0.829 | 0.232 |
| 0.775 | 0.295 | 0.758 | 0.758 | 1.023 | 1.229 | 0.776 | 0.297 |
| 0.705 | 0.369 | 0.681 | 0.681 | 1.039 | 1.180 | 0.706 | 0.376 |
| 0.649 | 0.429 | 0.619 | 0.619 | 1.055 | 1.150 | 0.654 | 0.437 |
| 0.619 | 0.462 | 0.585 | 0.585 | 1.065 | 1.130 | 0.633 | 0.468 |
| 0.600 | 0.488 | 0.561 | 0.561 | 1.077 | 1.126 | 0.605 | 0.494 |
| 0.451 | 0.637 | 0.398 | 0.398 | 1.140 | 1.063 | 0.453 | 0.640 |
| 0.430 | 0.659 | 0.375 | 0.375 | 1.156 | 1.056 | 0.433 | 0.660 |
| 0.431 | 0.662 | 0.373 | 0.373 | 1.157 | 1.056 | 0.431 | 0.663 |
| 0.432 | 0.666 | 0.369 | 0.369 | 1.160 | 1.054 | 0.428 | 0.665 |
| 0.405 | 0.690 | 0.342 | 0.342 | 1.173 | 1.048 | 0.402 | 0.690 |
| 0.357 | 0.729 | 0.296 | 0.296 | 1.198 | 1.035 | 0.355 | 0.728 |
| 0.131 | 0.905 | 0.099 | 0.099 | 1.325 | 1.004 | 0.131 | 0.905 |
| 0.000 | 1.000 | 0.000 | 0.000 | | 1.000 | 0.000 | 1.000 |

$$\ln \gamma_1^* = 0.40(1 - x_1^*)^2 \text{ and } x_1 = x_1^*$$

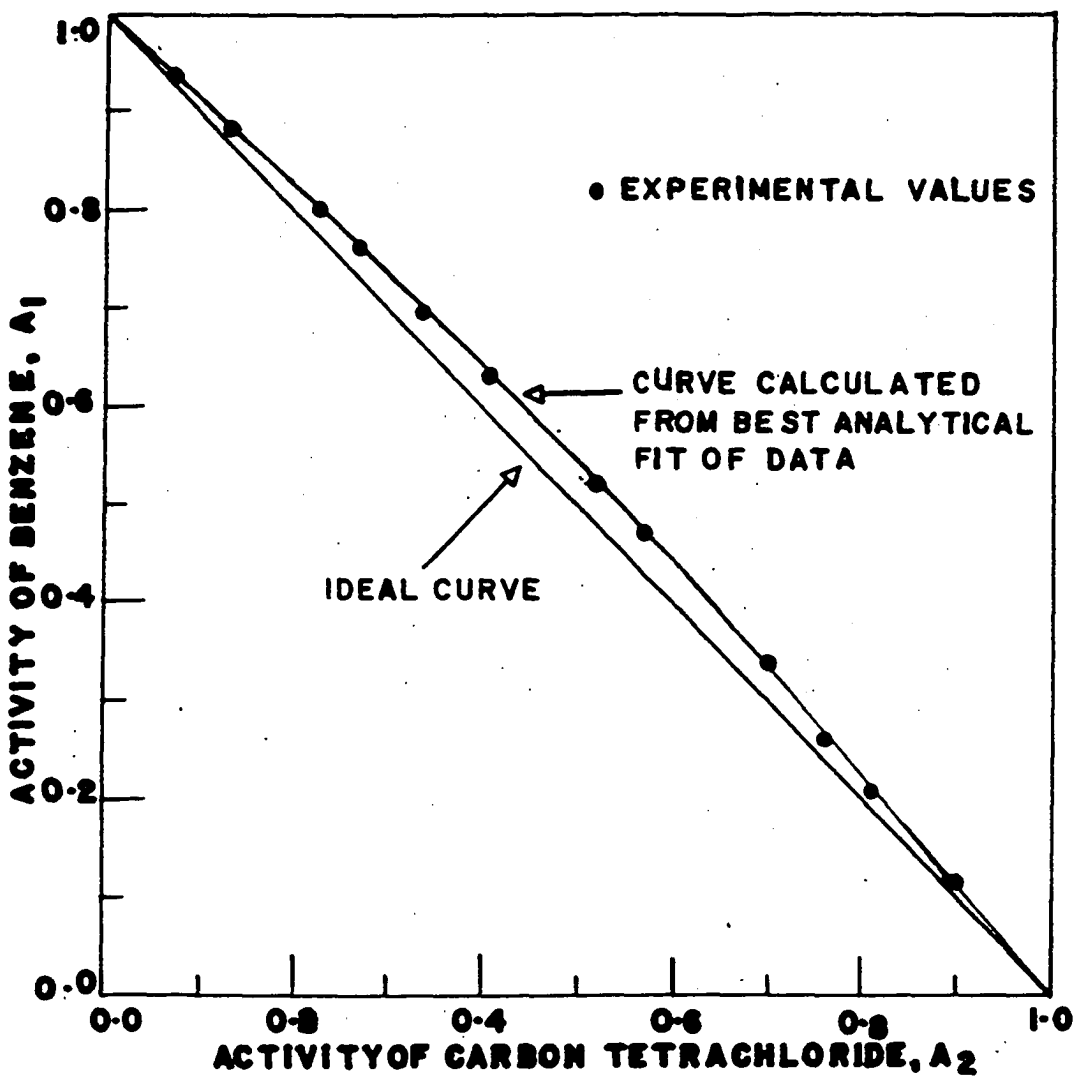


Fig. 11.--Activities of the System $C_6H_6$-$CCl_4$ at 20°

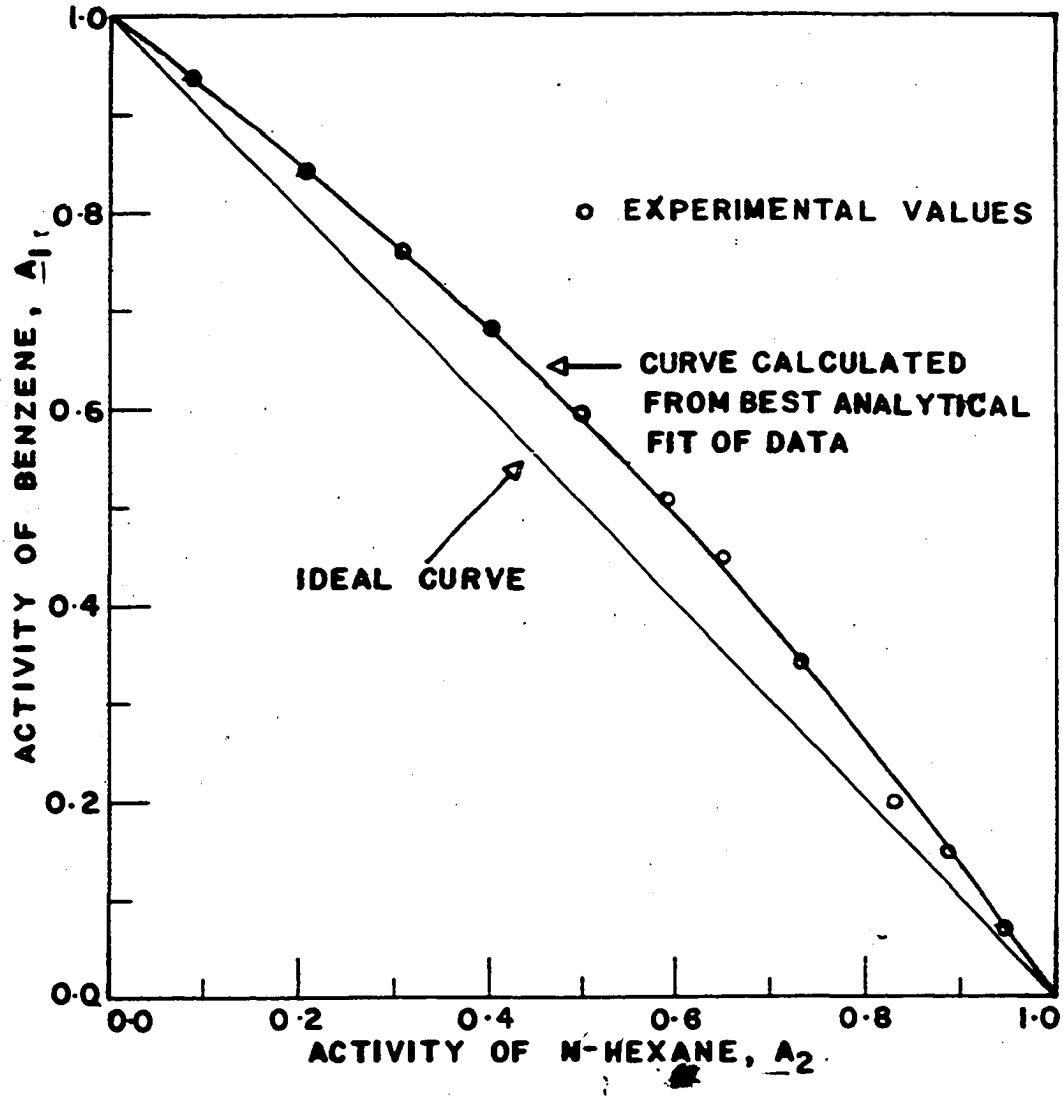


Fig. 12.--Activities of the System $C_6H_6$-n-Hexane at 20°

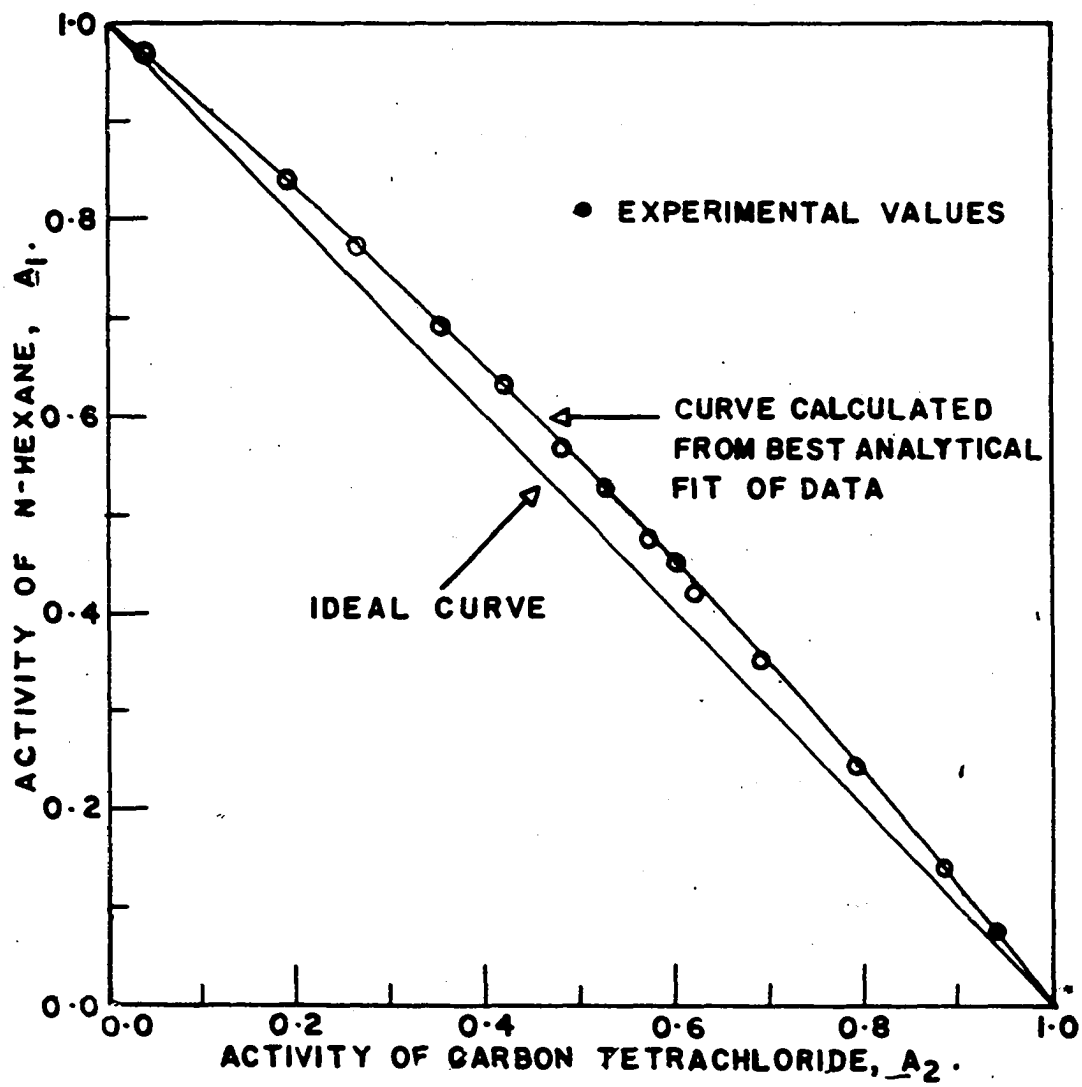


Fig. 13.--Activities of the System $CCl_4$-n-Hexane at 20°

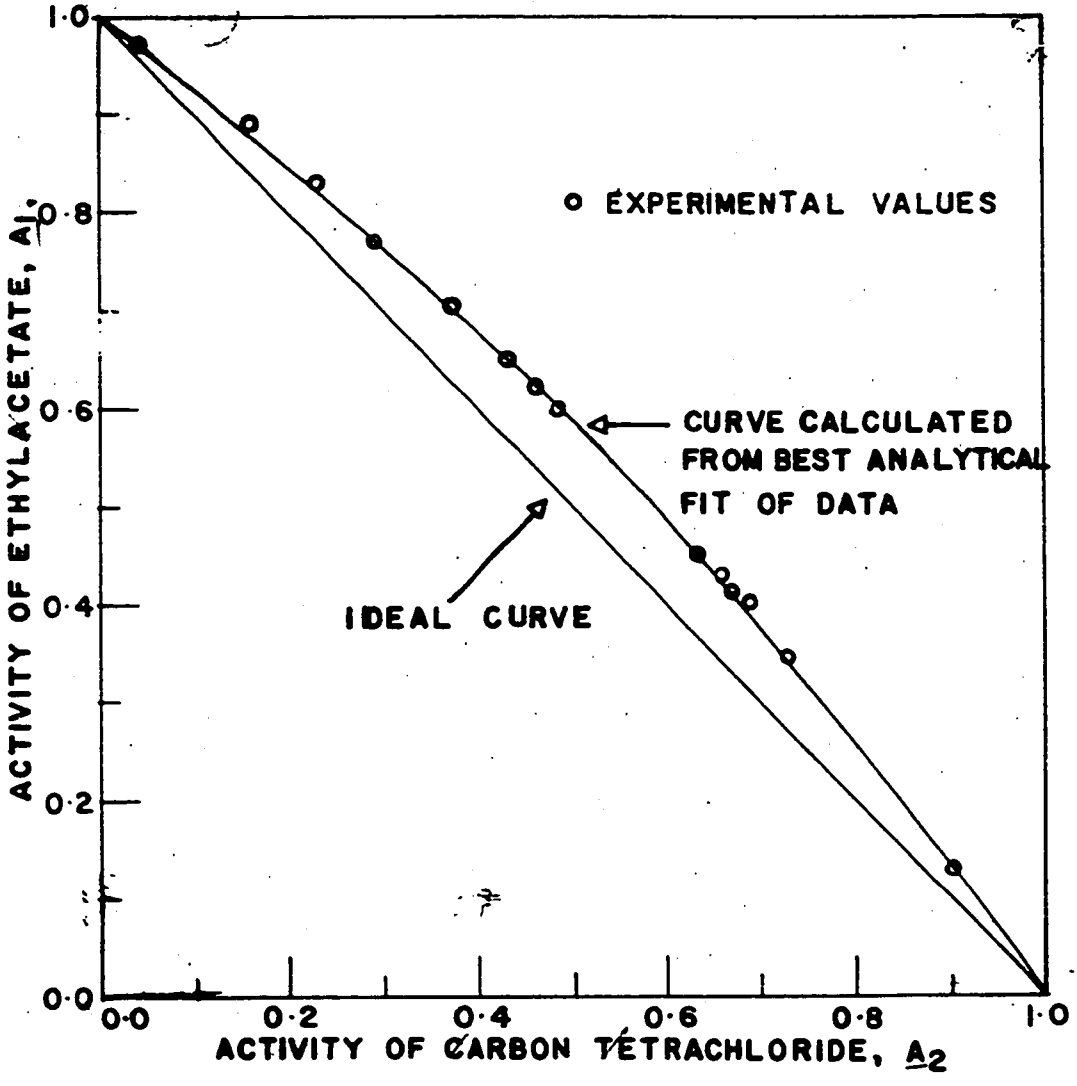


Fig. 14.--Activities of the System $CCl_4$-Ethylacetate at 20°

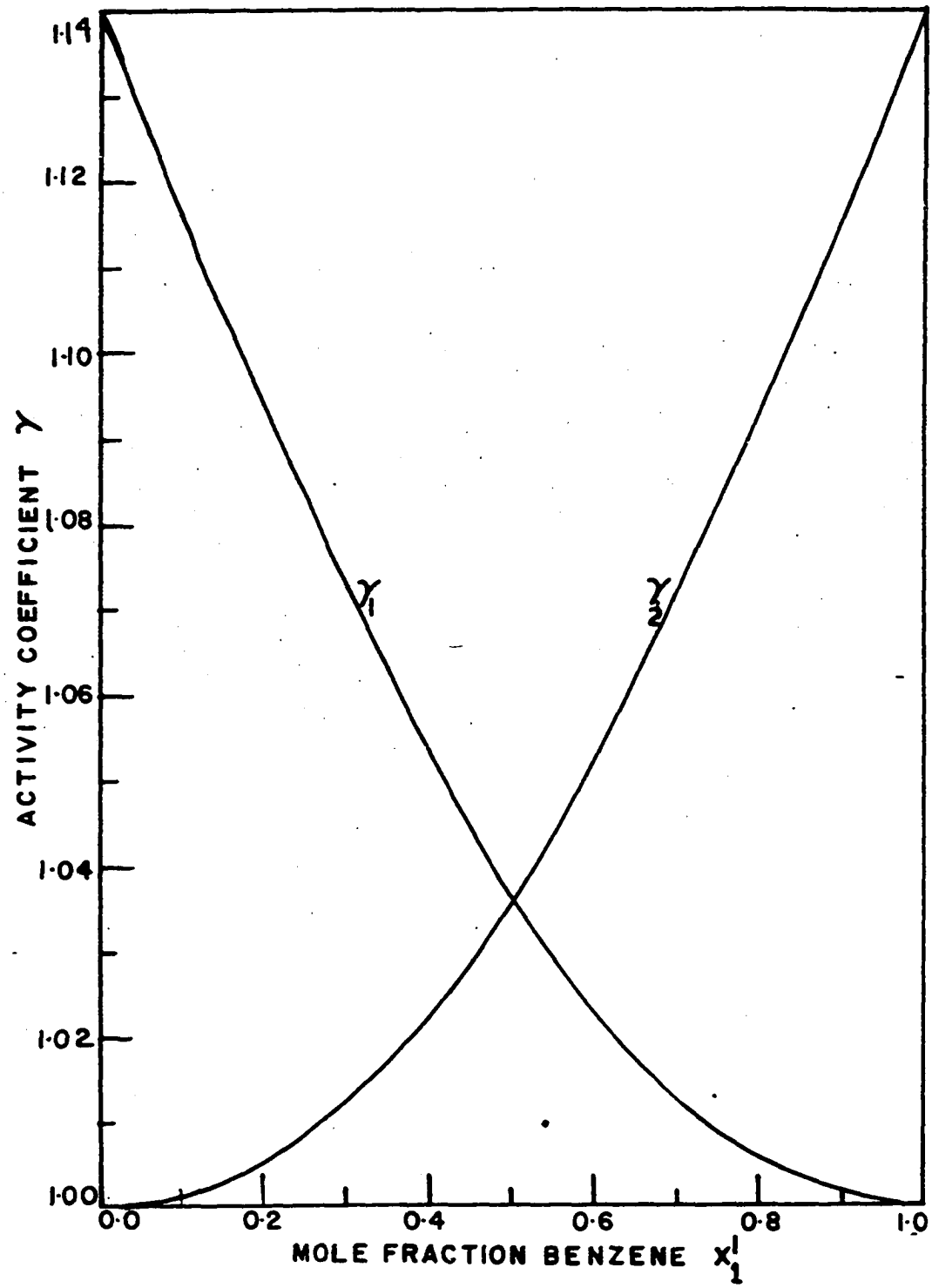


Fig. 15.--Activity Coefficients of the System $C_6H_6$-$CCl_4$ at 20°

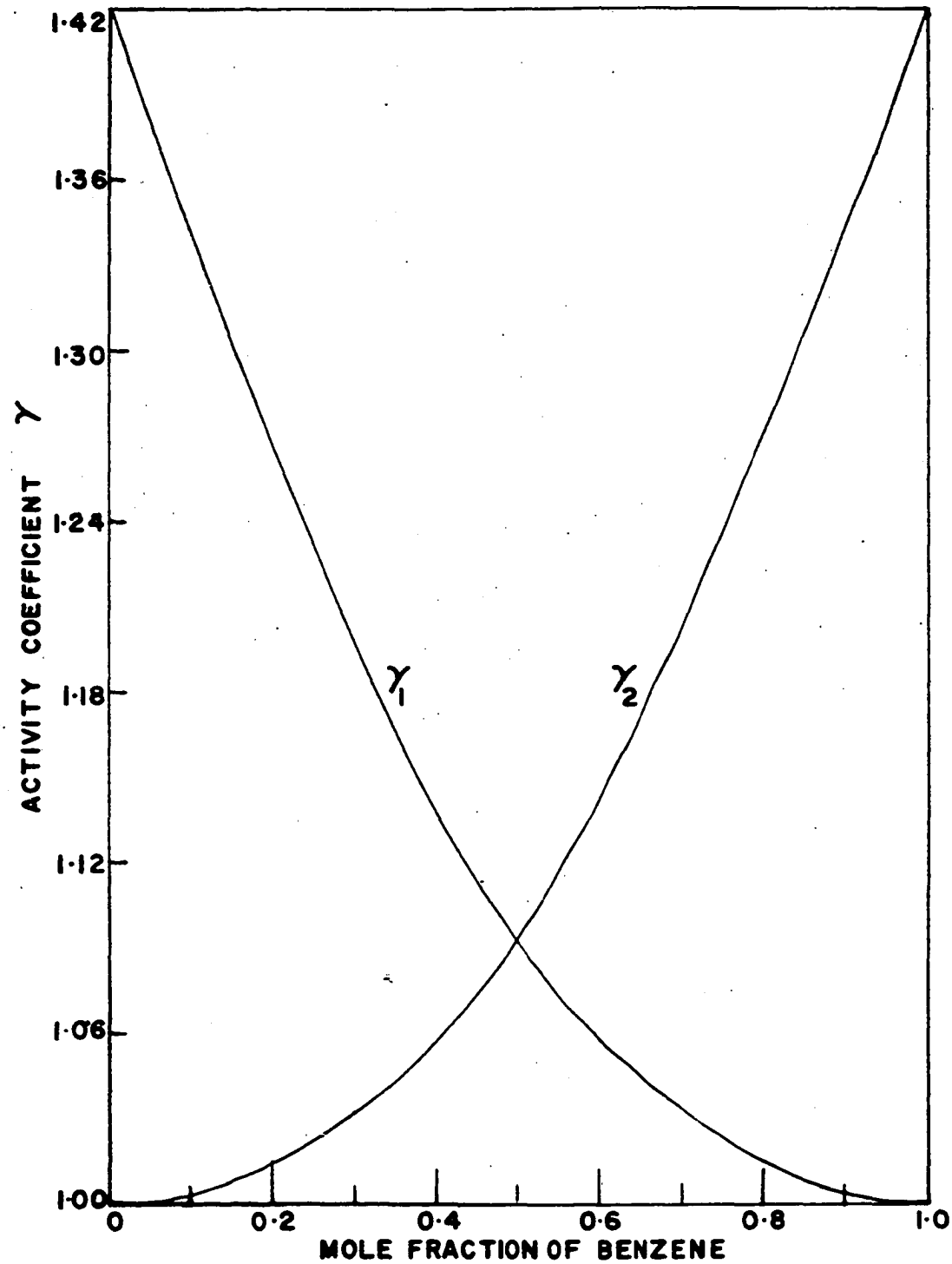


Fig. 16.--Activity Coefficients of the System $C_6H_6$-n-Hexane at 20°

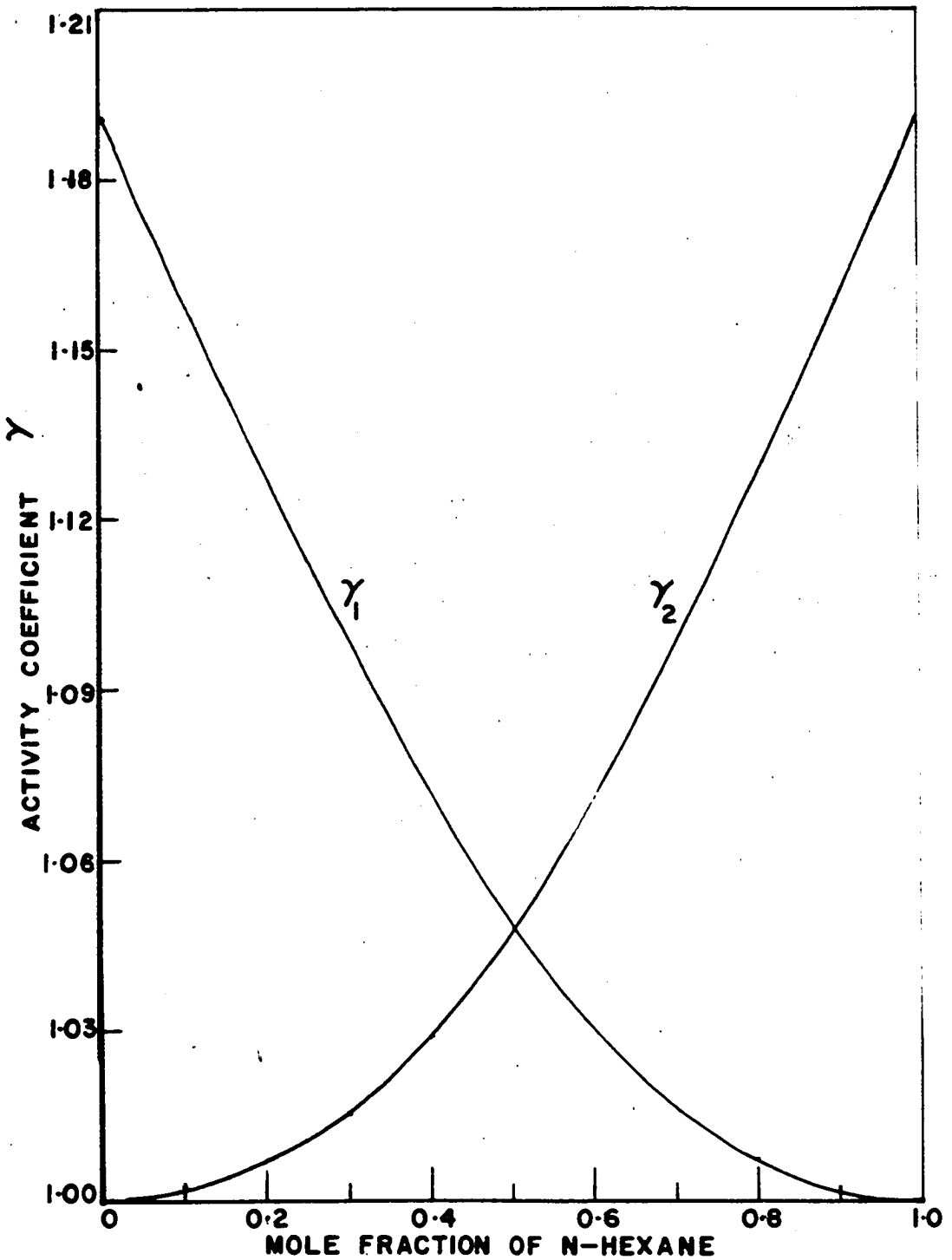


Fig. 17.--Activity Coefficients of the System $CCl_4$-n-Hexane at 20°

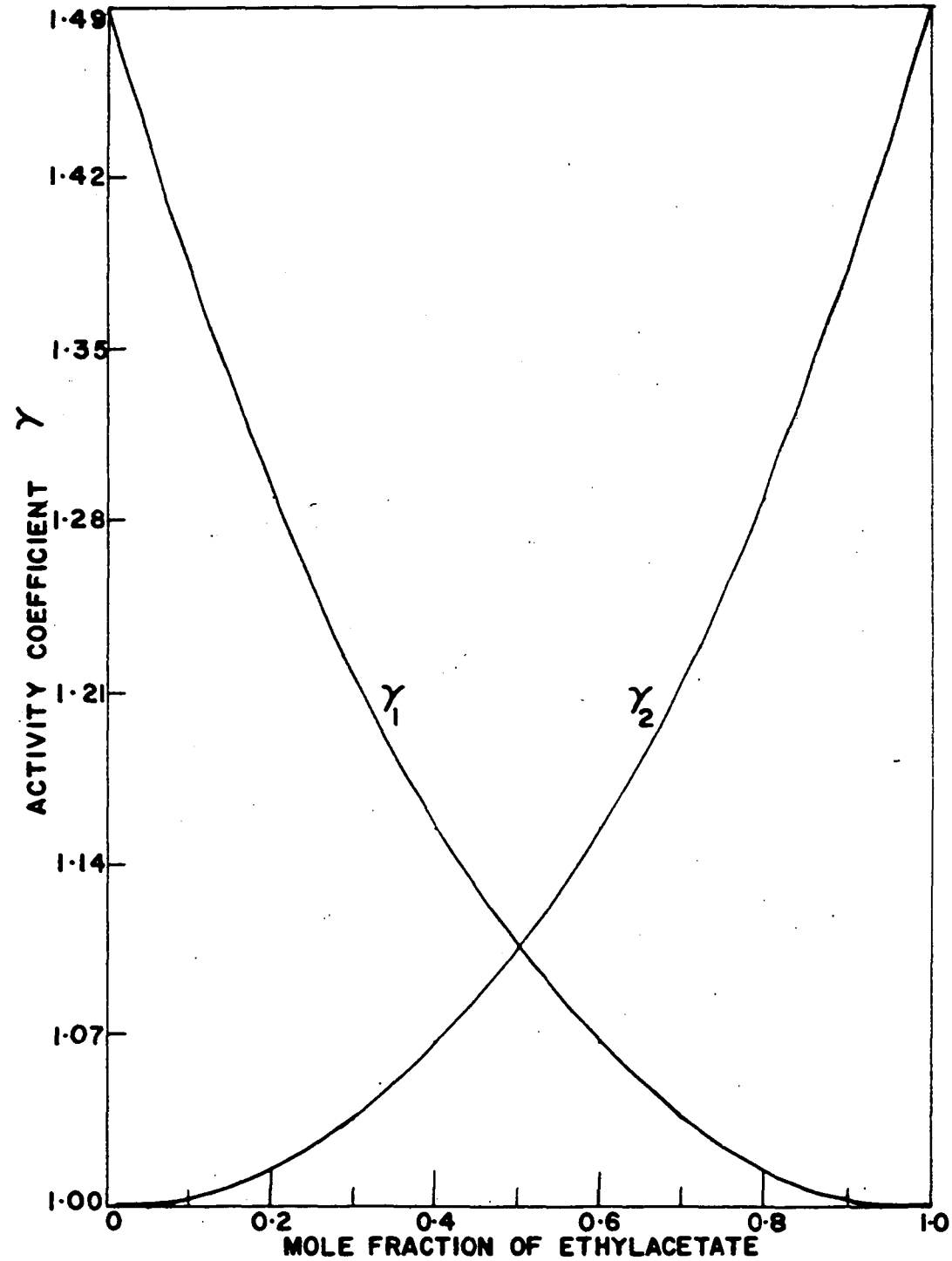


Fig. 18.--Activity Coefficients of the System $CCl_4$-Ethylacetate at 20°

Table 12

System $CCl_4$-methanol

Dependence of Total Pressure, Activities and Activity Coefficients on Liquid Mole Fraction at 10°

| $P_T$ | $a_1$ | $a_2$ | $x_1^{calc}$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|
| 57.04 | 1.000 | 0.000 | 1.000 | 1.000 | 3.953 |
| 96.46 | 0.927 | 0.769 | 0.663 | 1.398 | 2.282 |
| 96.44 | 0.921 | 0.778 | 0.629 | 1.464 | 2.097 |
| 94.48 | 0.860 | 0.805 | 0.424 | 2.028 | 1.398 |
| 93.54 | 0.841 | 0.807 | 0.448 | 1.877 | 1.462 |
| 91.43 | 0.740 | 0.845 | 0.231 | 3.186 | 1.099 |
| 89.65 | 0.736 | 0.871 | 0.195 | 3.795 | 1.082 |
| 88.80 | 0.680 | 0.886 | 0.152 | 4.474 | 1.045 |
| 87.16 | 0.644 | 0.894 | 0.136 | 4.735 | 1.035 |
| 83.90 | 0.582 | 0.899 | 0.118 | 4.932 | 1.019 |
| 74.75 | 0.369 | 0.951 | 0.068 | 5.426 | 1.020 |
| 56.45 | 0.000 | 1.000 | 0.000 | 23.810 | 1.000 |

Table 13

System $CCl_4$-ethanol

Dependence of Total Pressure, Activities and Activity Coefficients ~~on~~ Liquid Mole Fraction at 10°

| $P_T$ | $a_1$ | $a_2$ | $x_1^{calc}$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|
| 57.00 | 1.000 | 0.000 | 1.000 | 1.000 | 20.41 |
| 68.72 | 0.946 | 0.644 | 0.861 | 1.099 | 4.633 |
| 67.59 | 0.889 | 0.731 | 0.674 | 1.319 | 2.242 |
| 65.73 | 0.856 | 0.733 | 0.610 | 1.403 | 1.879 |
| 61.79 | 0.735 | 0.855 | 0.302 | 2.434 | 1.225 |
| 59.13 | 0.662 | 0.915 | 0.184 | 3.598 | 1.121 |
| 57.69 | 0.638 | 0.912 | 0.177 | 3.604 | 1.108 |
| 48.45 | 0.454 | 0.961 | 0.073 | 6.219 | 1.037 |
| 35.60 | 0.216 | 0.988 | 0.020 | 10.80 | 1.008 |
| 29.43 | 0.107 | 0.987 | 0.007 | 15.29 | 1.003 |
| 23.58 | 0.000 | 1.000 | 0.000 | 27.03 | 1.000 |

Table 14

System $C_6H_6$-methanol

Dependence of Total Pressure, Activities and Activity Coefficients on Liquid Mole Fraction at 10°

| $P_T$ | $a_1$ | $a_2$ | $x_1^{calc}$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|
| 45.65 | 1.000 | 0.000 | 1.000 | 1.00 | |
| 84.86 | 0.993 | 0.703 | 0.920 | 1.079 | 8.788 |
| 84.65 | 0.955 | 0.722 | 0.635 | 1.504 | 1.978 |
| 84.08 | 0.902 | 0.762 | 0.402 | 2.244 | 1.274 |
| 84.01 | 0.886 | 0.768 | 0.378 | 2.344 | 1.235 |
| 83.28 | 0.827 | 0.810 | 0.210 | 3.938 | 1.026 |
| 81.57 | 0.772 | 0.824 | 0.203 | 3.803 | 1.073 |
| 79.83 | 0.717 | 0.837 | 0.187 | 3.834 | 1.030 |
| 75.10 | 0.568 | 0.869 | 0.151 | 3.761 | 1.024 |
| 65.80 | 0.270 | 0.949 | 0.060 | 4.500 | 1.009 |
| 56.25 | 0.000 | 1.000 | 0.000 | 5.845 | 1.000 |

Table 15

System $C_6H_6$-ethanol

Dependence of Total Pressure, Activities and Activity Coefficients on Liquid Mole Fraction at 10°

| $P_T$ | $a_1$ | $a_2$ | $x_1$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|
| 45.68 | 1.000 | 0.000 | 1.000 | 1.00 | 7.575 |
| 58.35 | 0.960 | 0.609 | 0.889 | 1.080 | 5.486 |
| 58.21 | 0.884 | 0.750 | 0.600 | 1.473 | 1.875 |
| 56.45 | 0.813 | 0.813 | 0.387 | 2.101 | 1.326 |
| 55.92 | 0.795 | 0.826 | 0.382 | 2.080 | 1.336 |
| 55.89 | 0.771 | 0.872 | 0.240 | 3.212 | 1.147 |
| 47.35 | 0.539 | 0.920 | 0.065 | 8.292 | 1.027 |
| 36.00 | 0.290 | 0.964 | 0.040 | 7.250 | 1.005 |
| 23.55 | 0.000 | 1.000 | 0.000 | 40.0 | 1.000 |

Table 16

Tabulation of the Constants Derived from the Curve Fitting of the Activity Curves

| System | T °C | A | B | C |
|---|---|---|---|---|
| $C_6H_6$-Methanol | 10 | 0.829 | 0.021 | 0.147 |
| $C_6H_6$-Ethanol | 10 | 0.868 | 0.082 | 0.025 |
| $CCl_4$-Methanol | 10 | 0.747 | 0.264 | -0.053 |
| $CCl_4$-Ethanol | 10 | 0.951 | -0.057 | 0.069 |

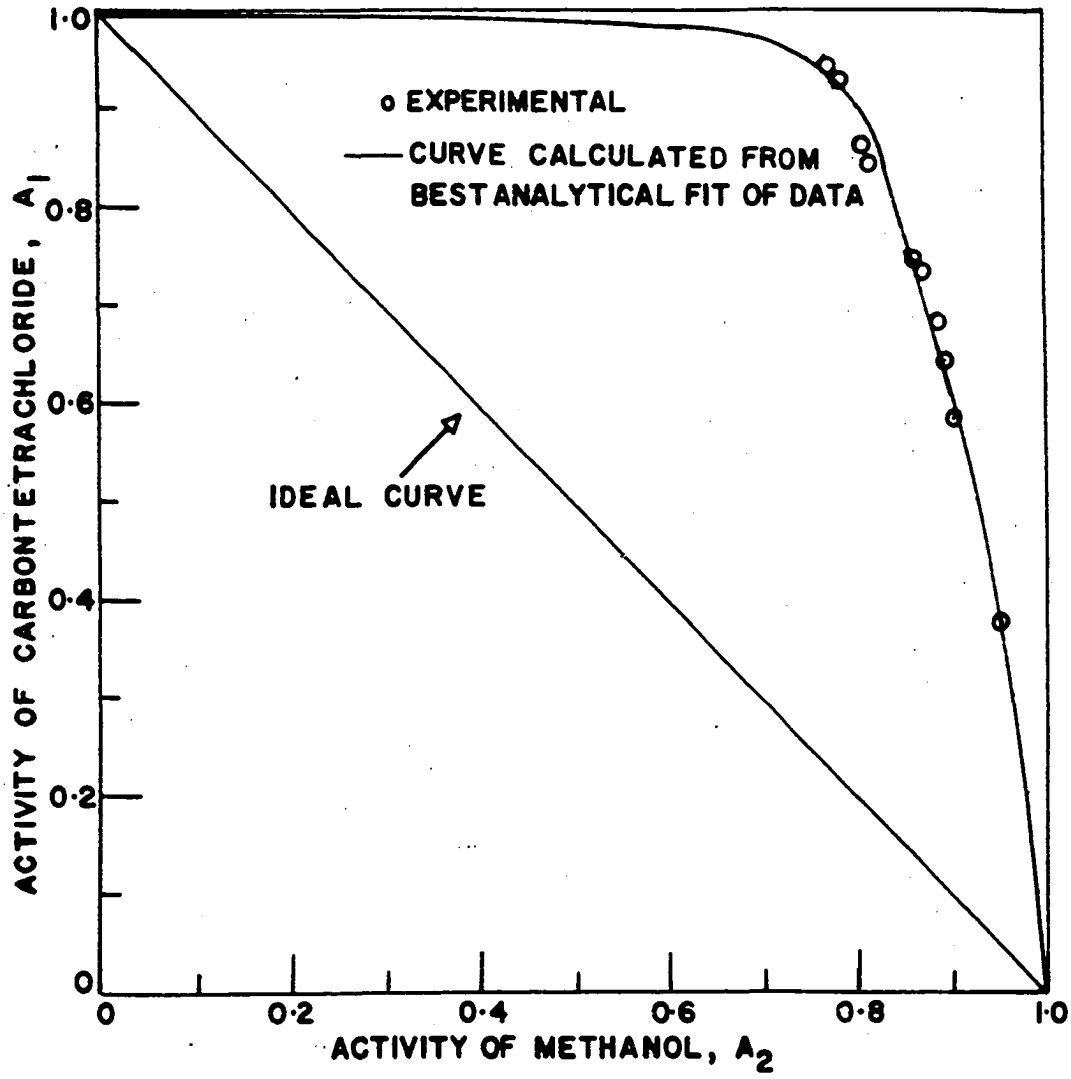


Fig. 19.--Activities of the System $CCl_4$-Methanol at 10°

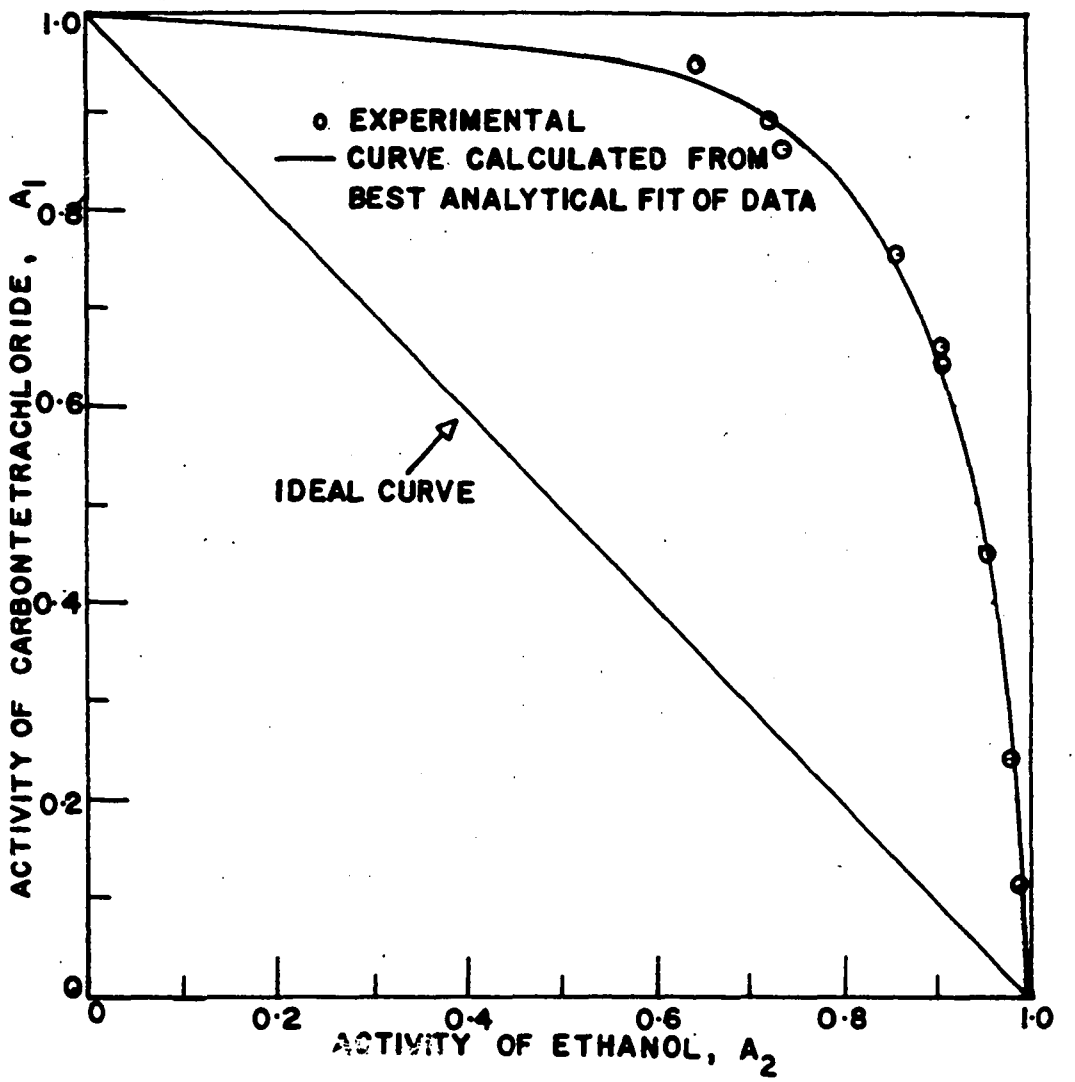


Fig. 20.--Activities of the System $CCl_4$-Ethanol at 10°

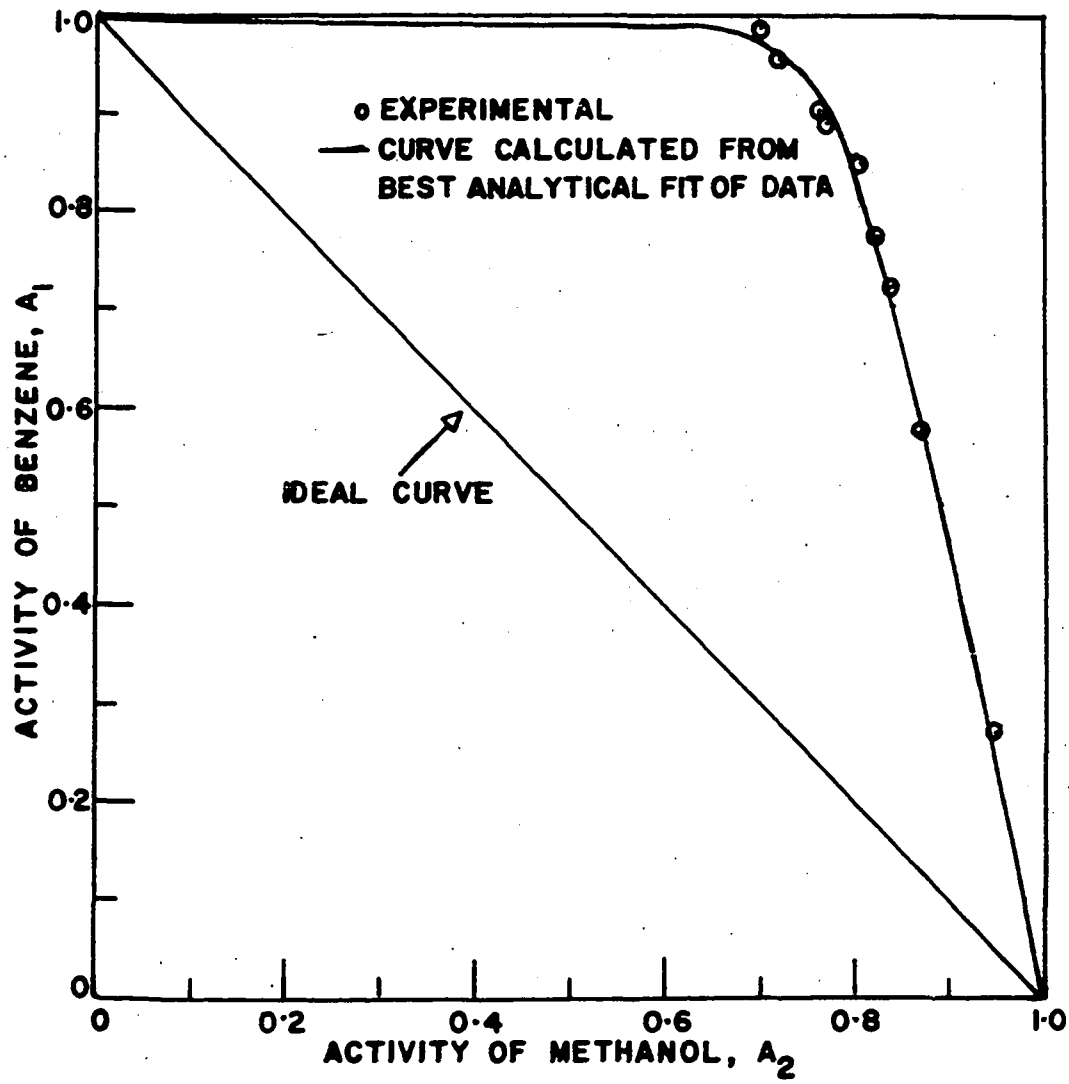


Fig. 21.--Activities of the System $C_6H_6$-Methanol at 10°

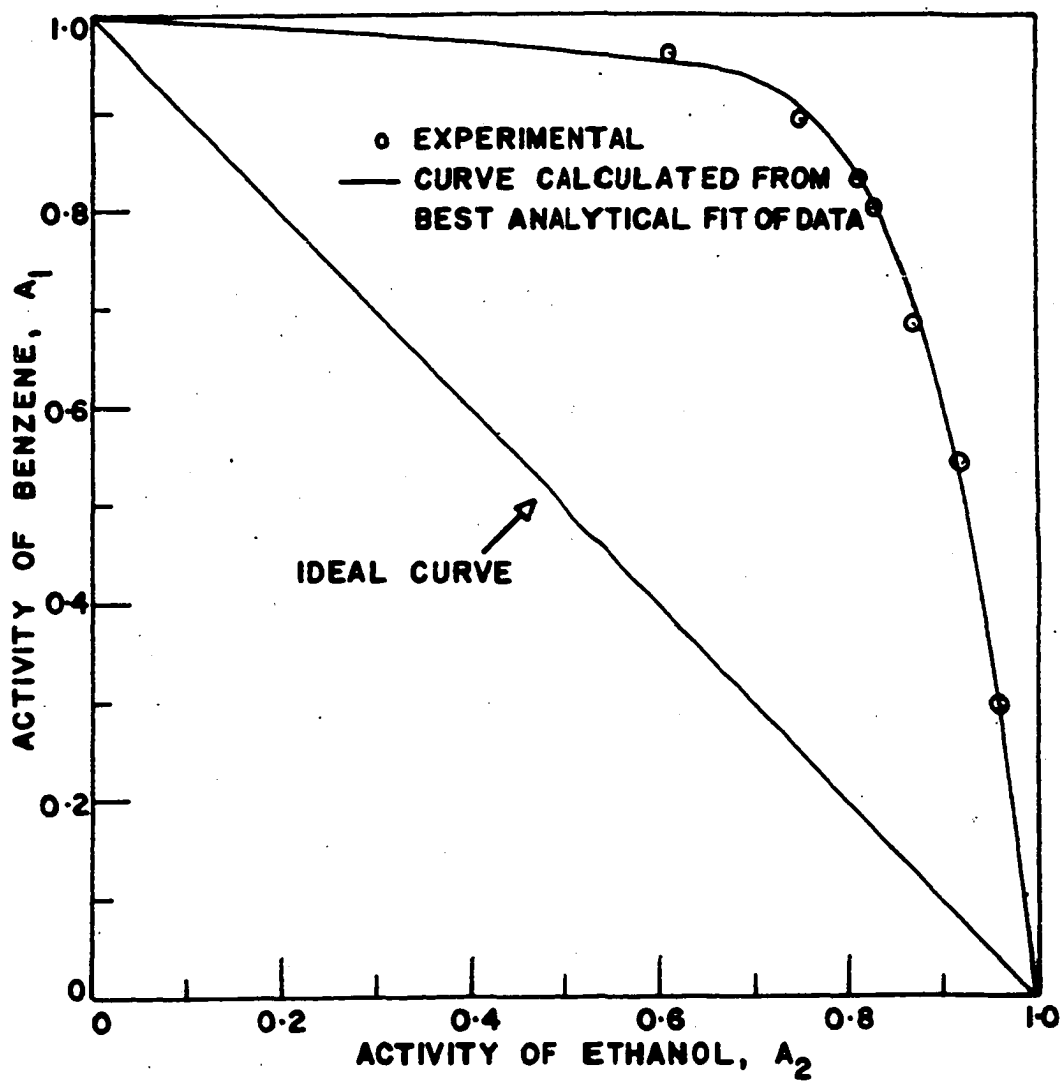


Fig. 22.--Activities of the System $C_6H_6$-Ethanol at 10°

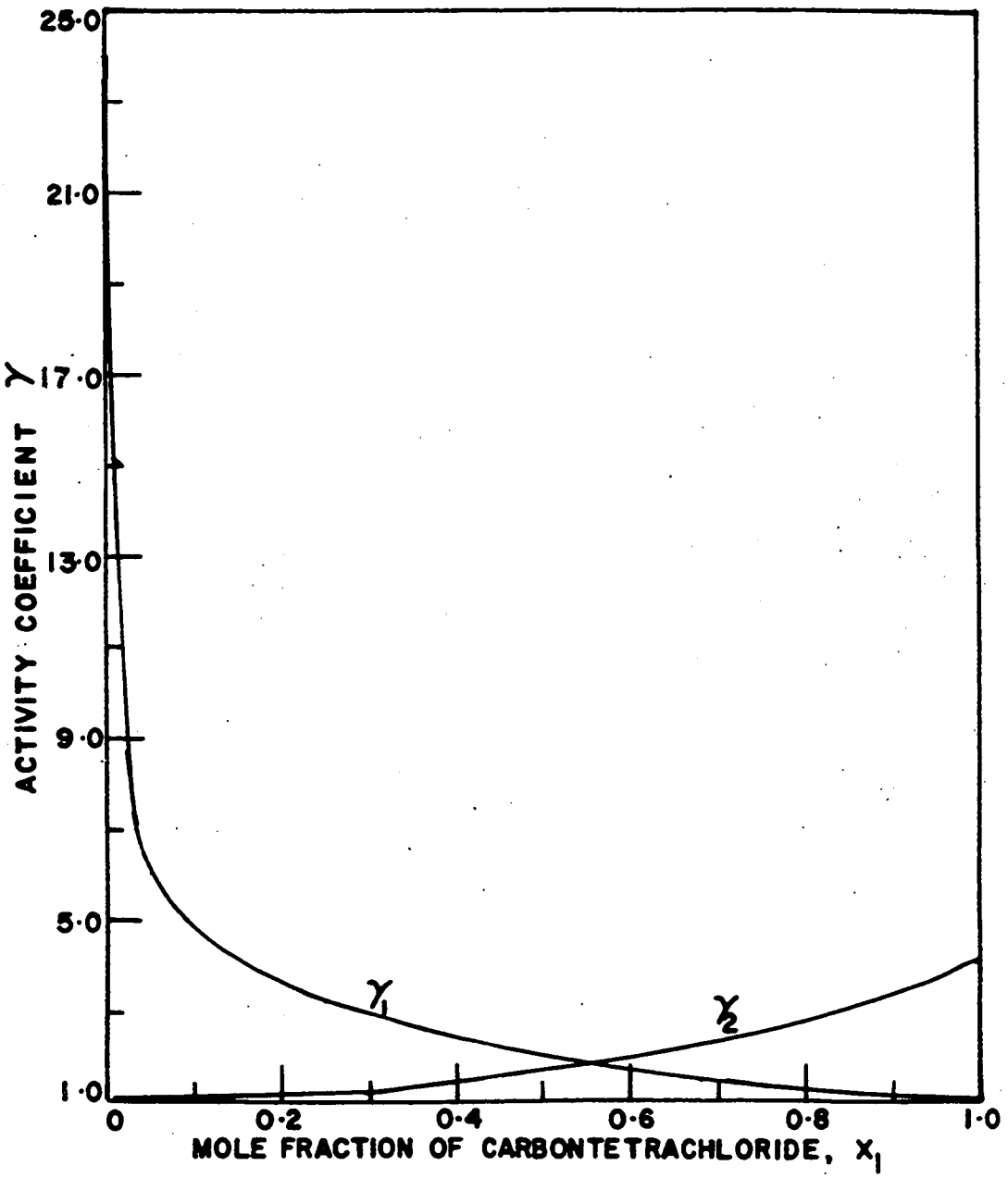


Fig. 23.--Activity Coefficients of the System $CCl_4$-Methanol at 10°

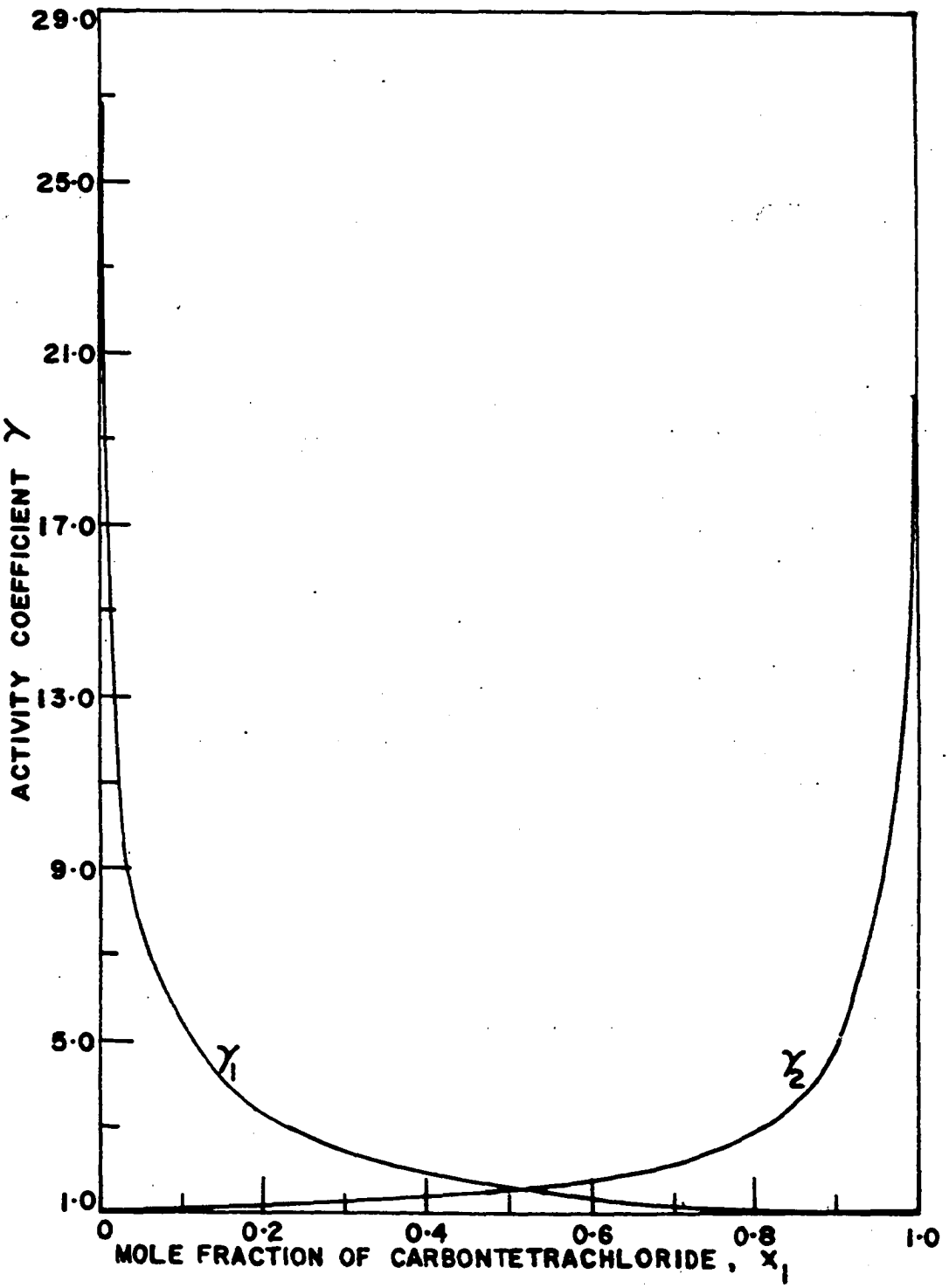


Fig. 24.--Activity Coefficients of the System $CCl_4$-Ethanol at 10°

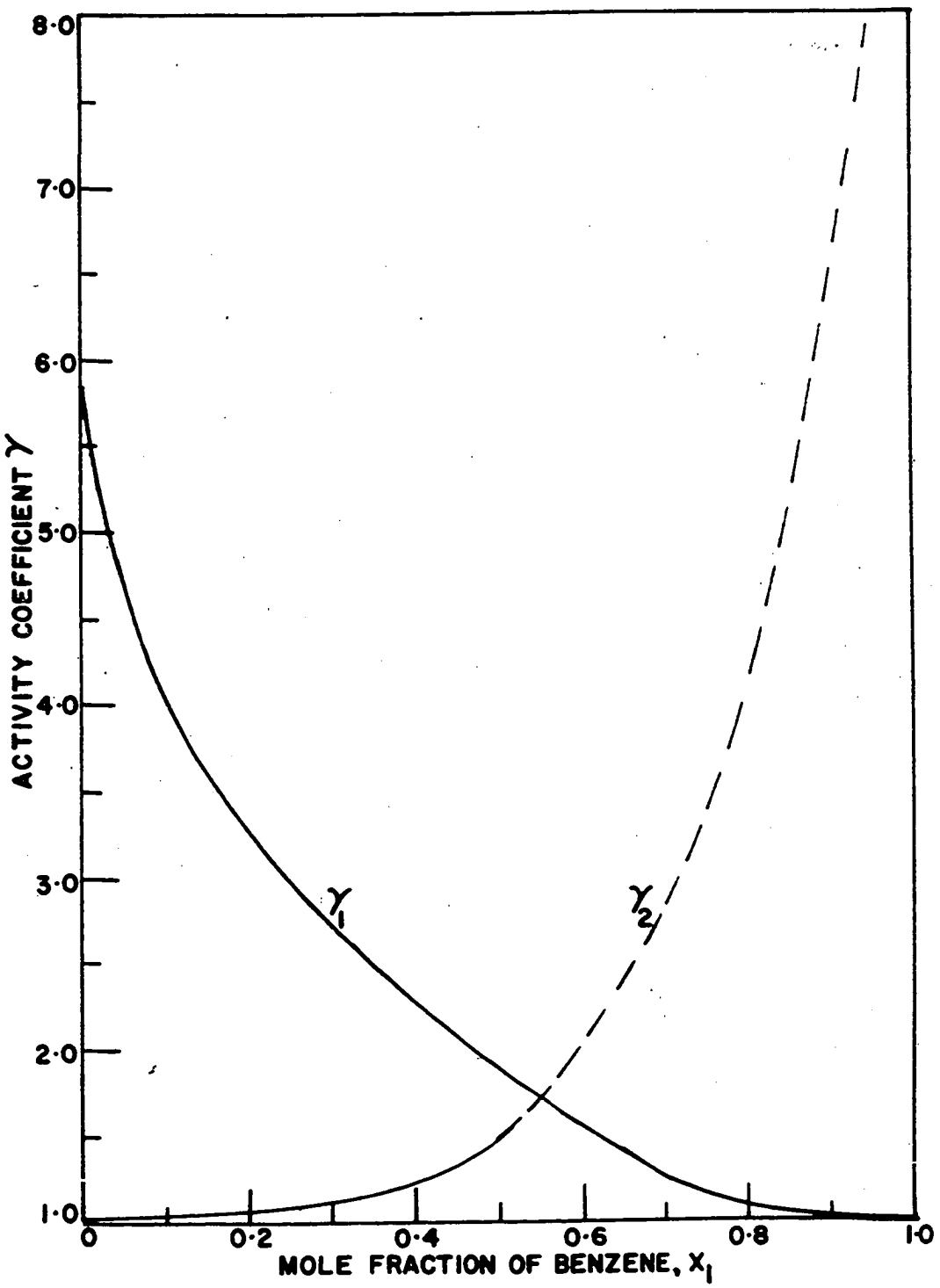


Fig. 25.--Activity Coefficients of the System $C_6H_6$-Methanol at 10°

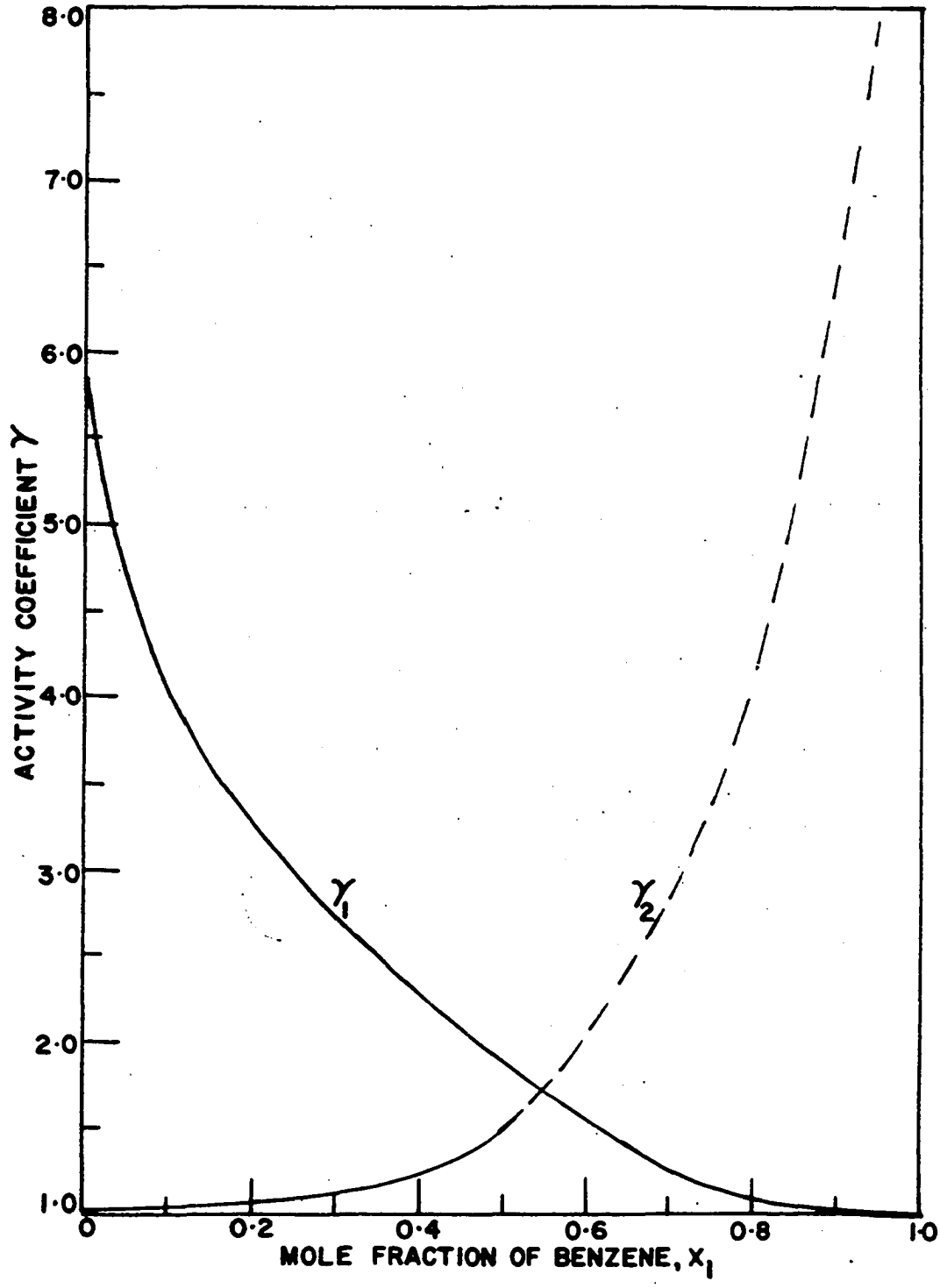


Fig. 25.--Activity Coefficients of the System $C_6H_6$-Methanol at 10°

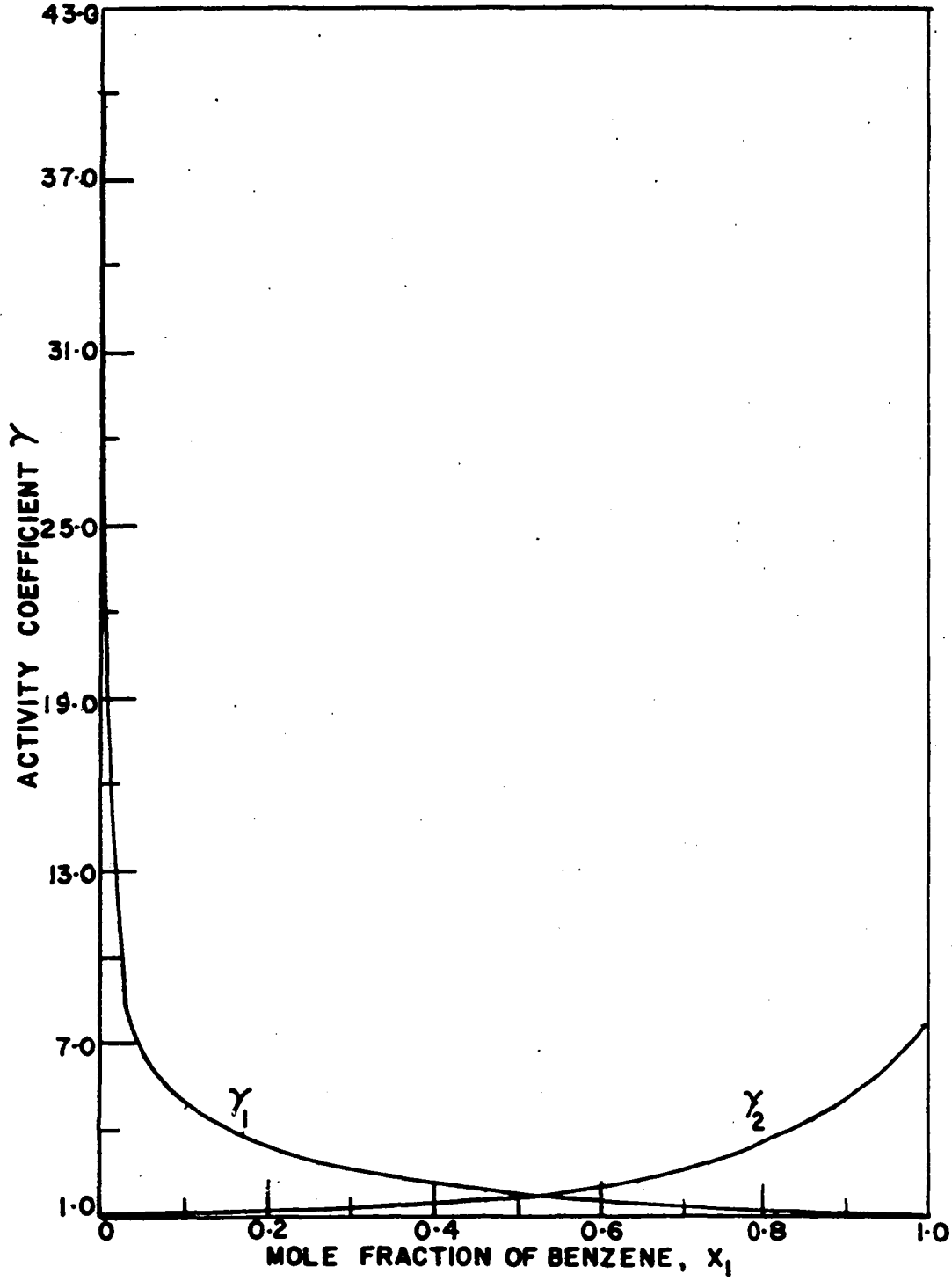


Fig. 26.--Activity Coefficients of the System $C_6H_6$-Ethanol at 10°

# CHAPTER VI

# DISCUSSION

## A. TOTAL PRESSURE METHOD

The systems, acetic acid-$CCl_4$ and trifluoroacetic acid-$CCl_4$, both show positive deviation from ideality, with the latter showing the more non-ideal behavior. Both acids associate in the liquid and vapor phases so that their solutions with components like $CCl_4$ would be expected to show positive deviation. Since the association in the liquid phase is quite pronounced, the curve fitting technique was applied using the mole fraction of the acid calculated on the basis of dimer molecular weight. The curve fitting technique using mole fraction of acid calculated on the acid monomer molecular weight proved to be unsatisfactory, particularly in the region of low acid concentration. It appears that both acids exist almost exclusively in the dimer form, even in relatively dilute solutions in $CCl_4$. Vapor phase association is also quite pronounced as is evident from the small values of the partial pressures of the monomer compared to the total pressure.

The case of the trifluoroacetic acid-$CCl_4$ system is of particular interest due to the length of the flat portion of the total pressure curve, indicating the formation of an azeotrope. The conditions are favorable for the formation of an azeotrope, since both components have closely related boiling points and the acid associates very strongly. Even at the lowest temperature used in this work (10°C), no phase separation was ever observed. Although no detailed study was carried out on the critical solution temperature, phase separation was observed at about 0°C. The peculiar solution properties of the fluorocarbons have been discussed by Scott.[17] The majority of the perfluorinated hydrocarbons are only partially miscible with their hydrocarbon counterparts and this is attributed to the fact that the perfluorinated hydrocarbons have very low values of the solubility parameters. From the difference between the two values of the solubility parameters for two components, it can be predicted whether the two components will be miscible.[8] Assuming that trifluoroacetic acid has a low value of the solubility parameter by analogy with the other fluorinated materials, then it is possible to see why trifluoroacetic acid and $CCl_4$ do show such extreme deviation from ideality.

The limiting values for the activity coefficients for both components in both systems were calculated from the values of the constants determined by the computer program. In neither system was there any regular decrease of the

limiting values with increase in temperature. In addition, there was no order of arrangement of the limiting values with regard to the temperature of the system. Apparently, neither system exhibits a large heat effect on mixing.

In addition to the total curve fitting of the data, each of the pressure curves was fitted separately at each concentration end. In this method, data points were read from the plots and subsequent curve fits would not extend beyond about 0.25 mole fraction at either end before the calculated values of the total pressure would diverge very greatly from the experimental ones. In effect, each total pressure curve would have two sets of constants, one for each end of the pressure curve. The constants determined in this manner were then used to calculate the limiting activity coefficients for the components. The agreement between these values of the activity coefficients and those calculated from fitting the curve with only one set of constants was reasonably good. The numerical values were close to those determined from the curves fitted with only one set of constants and again, there was no order of the values with regard to the increase of temperature. To get a better correlation of the activity coefficients with temperature, it would be necessary to study the systems over a wider temperature range.

The total pressure method is an extremely useful and accurate means of determining the partial pressures and

hence, the activity coefficients of the components of a binary mixture. The method is straightforward and simple and is applicable to a wide variety of binary systems in which at least one component is volatile. The method is comparable in accuracy to methods based on the measurement of partial pressures. Measurements can be made over a range of temperatures so that the data can be used in the calculation of various thermodynamic quantities. Although it is necessary to sample and analyse the liquid phase for composition, the time involved in the determinations is short compared to methods where the vapor phase must be collected and analysed.

The curve fitting technique has been shown to be applicable to systems which differ only moderately from ideality as well as those which differ greatly from ideality. The calculated and experimental pressures agree to within experimental error in almost all cases. However, where the total pressure curve shows a very steep slope, calculated points deviate from experimental values by more than the experimental error. Since the curve fitting is done with a three constant equation, some discrepancy can be expected between calculated and experimental values, particularly in the region of the curve where the slope is very steep. A better fit of the data could be achieved using an equation with additional constants.

In most instances, 20 minutes is sufficient to curve fit a system completely, but for systems where the deviation from ideality is more pronounced, 30 minutes or more may be required. The flexibility of the curve fitting program is shown in that the three inpu points for the calculations may be so chosen as to weight a curve in a given direction for systems showing large deviations from ideality. In a number of instances, actual data points were chosen as the input instead of values read off the total pressure curve. The versatility of the program is demonstrated by the fact that associating components can also be treated in this manner provided that the necessary association constants are available.

The total pressure method is a quick and accurate means of gathering data for binary systems. Coupled with the curve fitting technique used here, it presents a new and more useful method for the evaluation of activity coefficients from total pressure and liquid composition data. It is an improvement over the usual total pressure-partial methods in both the time necessary for the compilation of the data and its mathematical analysis.

## B. VAPOR DENSITY BALANCE

The systems $C_6H_6$-$CCl_4$, $C_6H_6$-n-hexane, $CCl_4$-n-hexane and $CCl_4$-ethylacetate all show positive deviation from ideality. Using the theory of solubility parameters, the differences in the solubility parameters for each pair of

components is sufficient to indicate that positive deviation will occur. For all the systems, it was possible to fit the activity coefficient as a function of the liquid mole fraction of a component in terms of a one constant equation.

The one system for which it was possible to make detailed comparison of results obtained here with previously reported values was the system $C_6H_6$-$CCl_4$. From Table 8 it can be seen that the activity values calculated from the present data by the curve fitting technique described, and those calculated from the data of Scatchard, Wood and Mochel[18] agree in general to within 0.001. The directly measured values of the activity appear to be in general agreement with those of Scatchard et al. to within 0.004. While the activity values obtained by this method are by no means as precise as those of Scatchard and co-workers, the agreement between those data and the data reported here are satisfactory. Hildebrand and Scott[8] point out that the system should show but slight positive deviation from ideality since the two components are similar in internal pressure and there is no tendency to form a minimum boiling mixture.

The system $C_6H_6$-n-hexane has been studied by Myers[19] and Tongberg and Johnston,[20] but mainly from the view of elucidating the vapor-liquid equilibrium curve at atmospheric pressure. Both authors found positive deviation from ideality with no evidence of azeotrope formation and commented upon the fact that the boiling point curve shows a very flat

portion for solutions containing more than 80 mole % n-Hexane, indicating that the vapor enriches very slowly in n-Hexane for these low concentrations of $C_6H_6$. Myers gives limiting activity coefficients for n-Hexane of 1.45 and $C_6H_6$ of 1.65. In this work, the limiting values for both components was 1.42. The difference between the two limiting values may be due in part to the fact that the activity coefficients were fitted as a function of the liquid mole fraction in terms of a one constant equation in this work, while Myers used a graphical integration of the Gibbs-Duhem equation over a temperature range of almost 20°. He further points out that at low mole fractions of a component, a small error in the composition leads to a large error in the activity coefficient, and it is difficult to evaluate the limiting values of the activity coefficient accurately.

The system $CCl_4$-ethylacetate has been investigated by Schutz,[21] who determined the change in the composition of the azeotrope with pressure. The present work also shows the presence of an azeotrope since the total pressure remains constant over a short range of the concentration. Hildebrand and Scott[8] indicate that both components differ sufficiently in internal pressure to form an azeotrope. In addition, ethylacetate differs in polarity from $CCl_4$; another factor contributing to the formation of the azeotrope. Since the system deviates positively from ideality, the azeotrope will have a minimum boiling point.

Alcohols in solution with non-polar components show large positive deviations from ideality, sufficient in some cases to give phase separation. Solutions of alcohols with non-polar components have been the object of a large number of investigations. Scatchard, Wood and Mochel[22] made an intensive study of methanol with $C_6H_6$ and $CCl_4$ in which they determined the total pressure and partial pressure curves as a function of the concentration. From these data, they calculated the various thermodynamic quantities like excess heats of mixing. From the behavior of these thermodynamic quantities, the authors concluded that there was a strong interaction between molecules of the two components corresponding to association of the alcohol molecules. Redlich and Kister[23] considered the influence of continuous association of one component on the free energy of a non-electrolyte solution. On the basis of a number of assumptions about the associating species, they were able to calculate the thermodynamic properties of a series of alcohol-hydrocarbon mixtures and found their results in accordance with experimental data for these systems. They also discuss briefly systems of two associating components and give a general interpretation of the free energy of non-electrolyte solutions.

The system $C_6H_6$-methanol has also been extensively investigated. Williams, Rosenberg and Rothenberg[24] determined the liquid-vapor equilibrium curve at atmospheric

pressure along with the excess thermodynamic quantities. The system forms an azeotrope at about 40 mole % $C_6H_6$ with a boiling point of 57 °C. In the present work, a maximum was found in the total pressure indicating the existence of an azeotrope. In addition, the system $C_6H_6$-ethanol also shows an azeotrope as was determined by Brown and Smith[25] in their study of the system at 45 °C. They also determined the liquid-vapor equilibrium curve for this system. A maximum in the vapor pressure for this system was found in this work also.

$CCl_4$ and the alcohols have also been the subject of a number of important investigations. Haywood,[26] as early as 1899, determined the liquid-vapor equilibrium curve for the system $CCl_4$-ethanol at atmospheric pressure and noted the existence of an azeotrope. A more recent investigation of the system has been carried out by Barker, Brown and Smith.[27] The authors determined the liquid-vapor equilibrium curve at 45 and 65 °C using an equilibrium still. In addition, they also investigated the system $CCl_4$-methanol at these same two temperatures. The authors chose values for the interaction energies of each pair of components and used these energies to calculate the excess thermodynamic functions. Comparison is made with the values determined experimentally and agreement is reasonably good over the entire concentration range. In view of the very complicated unsymmetrical behavior of the thermodynamic functions for

these systems, the agreement is very satisfactory. However, they point out that both alcohol systems cannot be fitted well with a single set of interaction energies and consider that the geometrical models used for the solutions or the insufficient details in the interaction energies may account for this deficiency. They further add that the interaction energies may indeed be different for the two alcohols.

Hipkin and Myers[28] have studied the system $CCl_4$-methanol to determine the liquid-vapor equilibrium curve at atmospheric pressure. The system formed an azeotrope at 55.1 mole % methanol boiling at 55.7 °C. They also calculated the limiting values of the activity coefficients. For methanol, the value was 23 while for $CCl_4$ it was 7.25. The authors attempted to fit the activity coefficients as a function of the liquid composition with a number of equations, but were unable to get satisfactory agreement over the entire concentration range.

Barker[29] has recently undertaken a study of alcohol solutions in which he considers the general theoretical method involving the molecular interaction of the species in solution. The model is based on the assumption that the interaction energies of neighbouring molecules depend upon the relative orientation of the molecules. The interaction energies are supposed to depend upon which parts of the molecule are in contact with another. He gives a method for calculating the configurational contribution to the

thermodynamic functions of solutions of associated liquids provided that the molecules of the liquids can be considered to be represented by certain models. The approach will be useful if the configurational contribution to the thermodynamic functions is important. The author sets up a series of models for the systems $C_6H_6$-methanol and $CCl_4$-methanol and finds that there is good agreement between experimental thermodynamic quantities and those calculated from the model, for for the system $CHCl_3$-ethanol, the agreement is only qualitative. The author further points out that the models set up in some cases are certainly artificial, but they do give some representation of the volume and surface relationships of the molecules. Since this is the only model for which simple and general theoretical results can be found, it is a good choice for the preliminary investigations in the field.

The systems $C_6H_6$-methanol, $C_6H_6$-ethanol, $CCl_4$-methanol and $CCl_4$-ethanol all show marked positive deviation from ideality. All systems show maxima in the total pressures indicating azeotrope formation. No attempt was made to determine the composition of the azeotrope for each system. The plots of the experimental activities $a_1$ vs. $a_2$ show that the majority of the data points fall within the middle portion of the curve with few points at either end. During the experimental work, it was not fully realized that the points would fall so closely together in one region of

the plot. The addition of even a small amount of one component to the other in the solution vessel caused a sharp rise in the total pressure. In future investigations, it would be necessary to add smaller increments at the beginning of the run to evaluate more precisely the limiting regions of the activity curve. In the present work, the behavior of the activity curve at either end cannot be determined too accurately due to the lack of experimental points in these regions.

For the system $CCl_4$-methanol, comparison of the activity data with values calculated from a smooth extrapolation of the data of Scatchard et al.[22] taken at temperatures from 25 to 55 °C shows reasonable agreement. The data of Scatchard are more precise and are taken over a regular concentration interval, whereas the data in this work are clustered in one region of the curve. Thus a rigorous comparison of the data over the entire concentration could not be made. Hipkin and Myers[28] report limiting values of the activity coefficients for methanol of 23 and for $CCl_4$ of 7.25 for the liquid-vapor equilibrium at atmospheric pressure. In this work, the values found were 23.8 and 3.95 respectively. The agreement is quite close for methanol, but for $CCl_4$, there is a difference of a factor of two. The data of Barker et al.[27] on the system $CCl_4$-ethanol, taken at 45 and 55 °C were extrapolated and compared with the activities obtained here. Again, agreement

is reasonable, but a true comparison between the two sets of data cannot be made because of the lack of data points in the limiting regions of the activity curves in this work.

For the systems investigated here, the activity data were grouped in the central portion of the activity curve. The curve fitting program used experimental points as the input and because the data lie so closely together, the calculated curve would be weighted in this direction. This would show up in the values of the constants used in equation (15). The limiting values of the activity coefficients, evaluated from the constants, would show the effect of the data being so closely grouped. The fact that one of the limiting values of the activity coefficients does not agree with that of Hipkin and Myers[28] may be partially explained by this. For a more exact curve fit, data points would be needed over the entire concentration range. The limiting values of the activity coefficients could then be calculated more precisely and a better comparison could be made with existing data.

The vapor density method for the determination of activity coefficients has a number of important advantages. It is an extremely rapid method making it possible to determine activities and activity coefficients of both components in a binary mixture over the entire concentration range in a period of a day. The analysis of the vapor is accomplished directly by the buoyancy bulb and there is no need of

removing vapor samples for analysis. Equilibrium is attained rapidly in the system. About five minutes were required for the system to achieve equilibrium after the addition of an increment of one component to the solution. Any shift in the equilibrium could be detected by a change in the position of the pointer on the buoyancy bulb.

The vapor density balance can also be used for the study of components which may react with water vapor or air. Once the components are introduced into the system, no air. is admitted until the completion of the run. Contamination of the components is reduced to a minimum and the problem of analysis of the vapor is considerably simplified. The apparatus could also be used to determine vapor densities and hence, association constants. Corrections could then be applied to the associated species to account for their deviation from ideality.

The accuracy of the method will depend upon the sensitivity of the balance. In theory, a balance could be constructed with almost any desired sensitivity, but such a balance would be applicable to a few systems only. A very sensitive balance would give accurate results, but would be limited in its application to systems falling within a narrow range of pressure and molecular weight. In actual practice, a balance is constructed that can be used for a number of systems and still give the desired accuracy. Thus it is of value to decide beforehand what systems are

to be studied and the range of pressure to be investigated. From this knowledge, a suitable balance can be constructed with the desired sensitivity.

There are a few limitations on the types of components that can be profitably studied by the vapor density balance. Both components should be quite volatile. If one component is relatively involatile compared to the other, then the method is not accurate. It is desirable to choose components which differ widely in their molecular weights since this will give a wide scale spread between the pointer readings of the two pure components. In addition, the error in the partial pressure calculation will be reduced since it involves the difference in the average molecular weight of the vapors and that of one of the pure components. The vapor density balance can also be used for systems in which one of the components associates in the vapor phase, provided that the necessary association data are available and that the associated species has a comparable vapor pressure to the second component. Similarly, two components associating in the vapor phase can be treated in an analogous manner.

There are a number of improvements that could be made to the present apparatus. To prevent diffusion from controlling the equilibrium vapor reaching the balance case, it would be desirable to suspend the buoyancy bulb more directly over the solution itself. In this way, the problem

of diffusion of the vapor into the balance case would be avoided entirely or at least, reduced to a minimum. Consequently, the time interval between additions of a component could be reduced even more. The two way stopcock could be moved from its present position above the balance case to a position on the vacuum rack itself. In this way, there would be even less chance for the vapors to be absorbed by the stopcock lubricant. The temperature of the vapor could be followed more rapidly by incorporating a thermometer well into the balance case itself. This would allow a more direct contact of the vapor with the thermometer enabling the temperature of the vapor to be registered more accurately.

## C. DISCUSSION OF ERRORS

### 1. Total Pressure Method

There are a number of errors in the total pressure technique for the determination of activity coefficients. It was assumed that all species in the vapor phase obeyed the ideal gas laws. Furthermore, in all the calculations, the partial pressures were used in place of the fugacities. The error involved in this assumption should be insignificant, because the total pressure was always well below one atmosphere. Concentration errors will also be quite small, since all the weighings in the analyses were made with as large samples as convenient to minimize weighing errors. Concentration errors should not have been greater than 0.001

mole fraction. The variations in the temperature of the thermostated bath should not have been greater than ± 0.05 degrees, which would not have an important effect on the total pressure. The manometer was read with a cathetometer accurate to within ± 0.01 mm. It is estimated that the overall error in the experimental determination of the total pressure should not have exceeded one half per cent.

The data were fitted with a three constant equation and agreement between calculated and experimental points was good in almost all cases. The only places where significant differences occurred in the calculated and experimental values was for the systems which showed extreme deviation from ideality. Even in these cases, the only discrepancy occurred at the places where the total pressure curve had a very steep slope. Otherwise, the agreement was well within experimental error. The curve fitting could be improved by using additional constants in the equations of the program. This would then allow the data to be fitted even more closely over the entire concentration range. The error in the curve fitting program is estimated to be not more than 2 % at the maximum.

2. Vapor Density Balance Method Errors

In the determination of activity coefficients by the vapor density balance, there are a number of sources of error. In all the calculations, the vapor was assumed to behave ideally and the partial pressures were used in place

of the fugacities. These assumptions should lead to a small error over the range of temperature and pressure used in this work. The variations in the temperature of the thermostated bath should not have exceeded 0.05 degrees. Such a variation in the temperature would affect the pressure to a very small extent as can be verified by a simple calculation. The temperature of the vapor, read by a thermometer suspended directly to one side and in contact with the balance case, did not vary by more than 0.05 degrees also. Such a variation would not affect the average molecular weight significantly. The position of the pointer on the balance was read with a precision cathetometer accurate to within 0.005 mm. The manometer was read with a cathetometer accurate to 0.01 mm.

The precision of the method will be a function of the sensitivity of the balance. It is possible to construct a balance capable of detecting a change in the vapor density of $10^{-6}$ to $10^{-7}$ gm. $cm^{-3}$, but such a balance would be thrown completely off scale during a run involving components differing widely in molecular weights and vapor pressures. A balance is constructed to be usable in the range of the systems to be studied. The balance used in these determinations was capable of determining molecular weights in the range 50 to 200 at total pressures between 25 and 150 mm. It is estimated that the total error in the pressure determination should not have exceeded 1 %.

For the alcohol systems, plots of the experimental values of $a_1$ vs. $a_2$ show some scatter. Solving equation (5) for $p_1$ gives the result:

$$p_1 = \frac{(\bar{M} - M_2)\ p}{(M_1 - M_2)} \qquad (23)$$

If $M_1$ refers to the molecular weight of $C_6H_6$ (78.11) and $M_2$ of ethanol (46.02), then an error of only 1 in the value of $\bar{M}$ would give an error of 3 % in the value of $p_1$; assuming no error in p. Consequently, the accuracy in the activities will be dependent upon the accuracy with which the average molecular weight $\bar{M}$ can be evaluated. It is thus essential that the error in reading the scale for the pointer deflection be reduced to a minimum, since any error in this reading would be directly reflected in the calculation of $\bar{M}$. Choosing components of widely differing molecular weights would increase the value of the quantity $(M_1 - M_2)$ and so decrease the error in the partial pressures and hence, the activities. Any error incurred in the determination of the activity will be reflected in the calculation of the liquid composition and activity coefficient.

# CHAPTER VII

## SUMMARY

Two new methods have been developed for the determination of activities and activity coefficients of volatile binary mixtures. The first technique consists of measuring the total pressure above the solution and determining the composition of the liquid phase. By means of a suitable computer program, the partial pressures and activity coefficients can be evaluated for the components. In the second method, the total pressure and vapor density are determined, allowing the calculation of the partial pressures, activities, liquid composition and activity coefficients.

The total pressure method has been used in the study of two systems, acetic acid-$CCl_4$ and trifluoroacetic acid-$CCl_4$ at 10, 20 and 25 $^{o}C$. Both systems show positive deviation from ideality, with the latter system forming an azeotrope. The total pressure curves for the systems were curve fitted using an IBM 650 computer. From these curves the partial pressures and activity coefficients were calculated for the components by means of the Gibbs-Duhem equation. From the values of the activity coefficients at the

different temperatures, it appears that the heats of mixing are small for these systems.

The vapor density balance method has been applied to systems showing moderate positive deviation from ideality as in the case $C_6H_6$-$CCl_4$ as well as to systems showing extreme positive deviation as in the cases $C_6H_6$-methanol and $CCl_4$-ethanol. For systems which deviate only moderately from ideality, comparison of the data obtained by the vapor density balance method gives comparable accuracy. The activities were curve fitted by a computer program using a three constant equation involving a power series in the activity of one component, $a_1$. The liquid phase composition and the activity coefficients were calculated as part of the same program using the Gibbs-Duhem equation.

Both the total pressure method and the vapor density balance method have been shown to be applicable to a wide variety of systems. The determination of partial pressures and hence, the activity coefficients from total pressure-liquid composition data is a very useful and accurate means of studying binary systems. Although sampling and analysis of the liquid phase is necessary, a system can be investigated over the whole concentration range in a day. The vapor density balance method has also been successfully applied to a number of systems and proved to be a simple and rapid method for determining activity coefficients of binary mixtures. A system can be studied in a day or less and

there is no need for analysing the liquid phase. The availability of these two techniques should prove to be important to the field of solution chemistry, since they provide accurate and rapid methods for gathering data on binary mixtures. At the present time, more data are needed on a variety of systems to further the development of a general theory of solutions.

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