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Author: **Frederick A. Miller**

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ACTIVITIES OF ALIPHATIC ACIDS AND ALCOHOLS IN BINARY AQUEOUS SOLUTIONS

by

Frederick A. Miller

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

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Dean of Graduate College

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DEDICATION

To Elaine

I. INTRODUCTION

During the development of classical thermodynamics and subsequent applications of this theoretical tool to chemistry, one of the most perplexing and misunderstood concepts was the calculation of the difference in partial molal free energy of a dissolved substance at two concentrations. This misunderstanding led G. N. Lewis (1,2) to define a quantity which he called the activity.

In any multiphase equilibrium, the chemical potential of any component must be the same in each phase. For the special case of a two-phase equilibrium, in this case liquid and vapor phases,

$$\mu_{i(l)} = \mu_{i(v)} , \qquad (1)$$

so that a measurement of the chemical potential in one phase determines it in the other. The chemical potential is dependent on the partial pressure p_i in the vapor phase by the relation

$$\mu_{i(v)} = \mu^{o}_{i(v)} + RT \ln p_i , \qquad (2)^{1}$$

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[1] If the vapors deviate from ideality, the fugacity of the i th component should be substituted for the partial pressure (3).

where $\overset{\circ}{\mu}_{i(v)}$ is the chemical potential of the pure component i in the vapor state at the temperature of interest. By combining Equations 1 and 2, the resulting equation becomes

$$\mu_{i(l)} = \overset{\circ}{\mu}_{i(l)} + RT \ln \left(\frac{p_i}{\overset{\circ}{p}_i} \right) \quad , \qquad (3)$$

where,

$$\overset{\circ}{\mu}_{i(l)} = \overset{\circ}{\mu}_{i(v)} + RT \ln \overset{\circ}{p}_i$$

is the chemical potential of pure component i in the liquid state. Standard states other than the pure liquid state can be chosen; this being the standard state usually chosen for volatile components in binary non-electrolytic solutions. The ratio of the partial pressures of Equation 3, or more accurately the ratio of the fugacities, is what Lewis defined as the activity, that is,

$$a_i = \frac{p_i}{\overset{\circ}{p}_i} \quad . \qquad (4)$$

Since this research was performed with volatile non-electrolytes, only the theory and previous work performed on these systems will be considered. The activities of electrolytes have been treated fairly extensively and comprise quite a study of their own.

For the ideal solution, the activity and mole fraction of a constituent in solution are identical. Equation 3 then becomes

$$\mu_{1(l)} - \mu^{0}_{1(l)} = RT \ln X_{1(l)} \ . \qquad (5)$$

Just as the ideal gas is of theoretical interest and never realized in practice, the ideal solution is never actually found. Thus the activity coefficient γ_1 was introduced so as to make

$$\mu_{1(l)} - \mu^{0}_{1(l)} = RT \ln \gamma_1 X_{1(l)} \ ,$$

or from Equations 3 and 4,

$$\gamma_1 = \frac{a_1}{X_{1(l)}} \ .$$

The activity coefficient reflects the amount to which a constituent deviates from ideal behavior, since the coefficient is unity in an ideal solution.

Equation 5 is a thermodynamic statement of the well known Raoult's law of solutions (4,5). From his significant work, he concluded that the vapor pressure lowering was proportional to the concentration of the solution. Thus the vapor pressure of the solvent in a solution obeying Raoult's law is directly proportional to the mole fraction of the solvent, or as commonly expressed,

$$p_1 = X_1 \, p^{0}_1 \ . \qquad (6)$$

For a solution to obey Raoult's law, it is generally believed that the interaction energy between two types of molecules, say A and B, is no different from the interaction energy in A-A and B-B contacts. Guggenheim (6) has shown that the interaction energy of an A-B pair must be equal to the arithmetic mean of the interaction energies of A-A and B-B pairs. Thus the assumption of equal interaction energies is a special case of the Guggenheim conditions.

Most systems which have been found to agree quite closely with Raoult's law involve pairs of liquids of nearly equal molar volumes and chemical construction, such as the system benzene - toluene. Several pairs of liquids of unequal properties, such as chlorobenzene - napthalene and chlorine - carbon tetrachloride, are also known to behave nearly ideally.

Another fundamental law of solution, of which Raoult's law is a special case, is Henry's law. This law in practice is applicable mainly to the solute in dilute solution. In sufficiently dilute solution, the solute molecules are surrounded by solvent molecules only, thus producing a constant effect upon the solute molecules, although the effect may differ markedly from that produced when the solute molecule is surrounded by its own species. Their tendency to escape is thus proportional to their concentration, or more briefly, $p_1 = K_1X_1$.

By setting p_1 equal to $\overset{o}{p}_1$, the vapor pressure of the pure liquid 1 when X_1 is unity, the proportionality constant becomes $\overset{o}{p}_1$, and one obtains Equation 6. It can be shown (7) that if one component obeys Raoult's law over a portion of the concentration range, the other must of necessity obey Henry's law.

Again idealized empirical relations are found to agree with experiment in only a few cases. As a consequence, in order to obtain reliable data for a system it is necessary to determine the activity from a colligative property of the solution. In the past, much work has been done in studying various binary systems. However, there are so many possible combinations of systems to be studied, and all of these at varied temperatures, that as yet relatively few have been extensively investigated.

The activity coefficients are important because they shed some light on the conditions within a solution. Of all the binary systems studied, most deviate positively from ideal behavior, a few deviate negatively, and still fewer approach an ideal behavior. The classic example of a system which deviates negatively is acetone - chloroform at 35.17°C. which was discovered in the pioneering work of Zawidzki (8). From the same work an example of a system which deviates positively is carbon disulfide - acetone at the same temperature. The activity coefficient is a measure of what has been commonly called the "escaping tendency". If the components of a binary system deviate positively from Raoult's law the conclusion can be drawn that the two types of molecules are not mutually compatible. Thus, the molecules will be in an environment in solution which is not as satisfactory as that found when surrounded only by molecules of its own kind. The result is that the system will attempt to readjust itself to a more favorable situation. This readjustment can take place in a number of different ways. The composition and amount of vapors may be altered from the expected behavior, this forming a basis for fractional distillation. In addition, the component present in the least amount on a mole fraction basis, which will be referred to as the solute, will tend to concentrate at the air - liquid interface thus altering the surface tension abnormally. Along a similar line, the principle of selective adsorption is based somewhat upon the activities, although not wholly, because the nature of the adsorbent alters the selectivity also. As in the case of the surface tension alteration, the solute molecules will tend to concentrate at the liquid - solid interface. It has been demonstrated (9), that the adsorption of aqueous solutions of the normal fatty acids on a number of non-porous carbon blacks are congruent functions of the activity of the acids.

The same was found to be nearly true for aqueous solutions of the normal alcohols on the same carbon blacks.

The extraction of a solute by an immiscible solvent is based upon the difference in the activity coefficients of the solute in the two solvents. Since the chemical potential of the solute must be the same in each phase, it follows that the activities of the solute in each phase must be equal at equilibrium. This requires for two phases, A and B, that

$$\gamma_1^A X_1^A = \gamma_1^B X_1^B \quad .$$

If the activity coefficient of the solute in the original solution is higher than that in the extracting solution, the extracting solution will become richer in solute than the extracted solution.

The use of activities places equilibrium constants on a sound thermodynamic basis. Consider the reaction,

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D \quad .$$

The true equilibrium constant becomes,

$$K_a = \left(\frac{\gamma_C^c\, X_C^c}{\gamma_A^a\, X_A^a}\right)\left(\frac{\gamma_D^d\, X_D^d}{\gamma_B^b\, X_B^b}\right) .$$

To determine all the activity coefficients in a case like this would be very difficult, as one would have at best a four-component system. However, by knowing the activities in a binary system, an intelligent estimate could be made of the activity of a component in a multi-component system.

The entire subject of solubility is related to the activity coefficient and vice versa. This topic is so excellently discussed by Hildebrand and Scott (10) that a review of the subject would be redundant.

Many attempts have been made to account both qualitatively and quantitatively for the deviations of solutions from ideal behavior. Studies of gases are simplified by the fact that very little of the total volume occupied by a gas is actually occupied by the molecules, meaning that inter-molecular interactions are due mainly to collisions. In most solids, the molecules or ions are in close proximity but in an ordered array. Liquid structure is still more complicated since besides having the molecules separated only be molecular distances, they are free to move almost at will, leaving the "instantaneous structure" somewhere between a completely random distribution of molecules and a completely ordered array.

The forces existing between molecules in solution are numerous and become more complicated as the complexities of the molecules are increased. The van der Waals or short range forces between molecules fall into three general classes:

1. The interaction between permanent dipoles with the resulting force varying as r^{-7}.
2. The interaction between a permanent dipole and an induced dipole, this force varying as r^{-7}.
3. The London dispersion forces between neutral molecules arising from instantaneous changes of charge, giving rise to r^{-7} to r^{-13} forces.

In some instances, when two components are mixed there is a chemical combination to form an addition compound. This being true, the number of uncombined molecules of each species will be greatly reduced and the resulting escaping tendencies diminished. This model was successfully used by Dolezalek (11) to explain the negative deviations of the acetone - chloroform system. Hildebrand and Scott (10, p.183) state,

> We may feel reasonably certain that the intermolecular attraction which yields solid 'addition compounds' operates also in the liquid state to cause negative deviations from Raoult's law, so that the abundant existing evidence of the sort above cited justifies the statement that negative deviations from Raoult's law and abnormally great solubilities occur most frequently when the components are highly polar.

A particular type of association which is limited to compounds in which hydrogen is linked to the highly electronegative elements; nitrogen, oxygen, and fluorine, is commonly called hydrogen bonding. The small size of the hydrogen atom is believed responsible for the close approach to form the bond. Common examples of substances highly polymerized by this type of bonding are water, the alcohols, carboxylic acids, ketones, aldehydes, ethers, and amines.

A theoretical treatment of a solution in which either one or both of the components polymerizes is a difficult chore. The actual liquids consist of an equilibrium mixture of polymers of all degrees of polymerization. In addition, the type of polymer formed depends upon the number of hydrogen bonds which a molecule is able to form. Water, which can form four tetrahedral bonds per molecule (ice structure) forms a three dimensional polymer network. Molecules which can form only two bonds, such as alcohols and amines, exist in linear or cyclic polymers. Two noteworthy attempts to treat solutions of a non-associated liquid in an associated liquid by means of high polymer equations have been made (12,13). Redlich and Kister (14) have also obtained an expression for the activity coefficient of the non-associating component and have fitted the data in several systems in which methanol is the associating component. The more exact theoretical treatment of solutions which polymerize, awaits a determination of the structure and number of polymers in solution.

It should not be assumed that association always leads to negative deviations. Actually the introduction of solute molecules into an associated liquid tends to break up the association, producing more and smaller polymers and thus increasing the escaping tendency. In a like manner, the solute will be effectively "squeezed out" of solution by the associating liquid as it tries to attain its polymerized structure. This is the cause of positive deviation in many systems.

The determination of the activities, as previously stated, depends upon the measurement of a colligative property of the solution. The more common methods employ vapor pressure or freezing point depression measurements, although osmotic pressure and boiling point elevation measurements can also be used.

The freezing point depression method suffers from the fact that much work and care is required to get good results. The direct measurement gives the activity of the solvent at the freezing point. If the activity is desired at one temperature, the activities must be corrected from the freezing point to the temperature of interest. This procedure requires a knowledge of the partial molal heat capacities of the components as functions of temperature. The activity of the solute is inferred from that of the solvent by use of the Gibbs - Duhem equation (3), this process usually involving a graphical integration. A very small portion of solvent must be frozen or else the concentration of the solution will be changed considerably.

In addition, great care must be exerted to prevent supercooling. Some of the apparatuses used for freezing point depression measurements are outlined by Glasstone (7) and by Skau and Wakeham (15). The freezing point depressions of aqueous solutions of various organic solutes have been measured by Abegg (16), Loomis (17), and Jones and Bury (18).

The methods of measuring the partial pressures of a solution can be divided roughly into two classes, the static and dynamic methods. An interesting review of many of the early methods of measurement has been outlined by Pearce and Snow (19). A review of the various apparatuses used is given by Thompson and Partington (21).

By the static method, a mixture of known composition is vaporized into an evacuated space, the total pressure measured, and a portion of the vapors removed and analyzed. The calculations are straightforward (7). The greatest sources of error are the dissolved air in the solution which causes the total pressure to be too high, and the inability to attain an equilibrium composition of vapors over the solution. All isotenoscopes use this principle of measurement.

With one type of dynamic method, the external pressure above a solution is adjusted until the solution just boils. At this point the vapor pressure and external pressure are equal. A portion of the vapors is collected, analyzed, and this together with the total pressure enables the partial pressures to be readily calculated. This method was used by Zawidzki (8) and Wrewsky (22) in their work on binary solutions, and by Young (23) on the vapor pressures of pure liquids. Superheating of the liquid is the biggest source of error. This method is little used at present.

The transpiration or gas saturation method has been used frequently of late years. By it, a measured volume of an inert gas is passed through or over the solution of interest until saturated with mixed vapor. The vapors are condensed from the gas stream, weighed, and analyzed. By simple calculations, assuming ideal gaseous behavior, the partial pressure of each component can be found (20). This experimental procedure was used for aqueous methanol solutions at 0°C. by Brown (24), for aqueous ethanol at 25°C. by Dobson (25), for aqueous methanol, propanol-1, and butanol-1 at 25°C. by Butler, Thomson, and Maclennan (26), and for aqueous butanol-1 at 30°C. by Randall and Weber (27). The method is simple in principle but very time consuming. It is difficult to attain a gas stream saturated with vapor. If the flow rate is too rapid, the gas stream may not be completely saturated or else a spray may be carried along. If too slow, it takes a very long time to collect enough sample for analysis .

The method of Hill (28) is based on the principle of the wet bulb thermometer. At each thermometer site is located a sensitive thermoelectric couple for temperature measurements. The entire assembly is placed in a thermostatted tube containing soaked filter paper which serves as a moisture chamber. On one thermoelement is placed a reference liquid, usually the pure liquid solvent, and on the other the solution of interest. The difference in temperature due to the distillation of solvent into the solution, causes a galvanometer deflection. By calibrating this arrangement with a solution of known partial vapor pressure for the solvent, the galvanometer scale readings canbe used directly as a measure of the partial pressure of the solvent in the unknown solution. Giacalone, Accascina, and Carnesi (29) used the method for aqueous solutions of formic, acetic, proponic, and n- butyric acids at 34.45°C. This method is of limited value because such a small quantity of solution is used. Consequently, the concentration is continually changing because of the distillation of solvent into the solution.

II. OBJECTIVES

The primary objective underlying this research was to develop a method for determining the activities of volatile components in solution in a convenient and rapid manner. The various methods as outlined in the above section require either extensive calculations (freezing point depression method) or are time consuming.

Activity coefficients of the three lower straight chain aliphatic alcohols in aqueous solution were determined previously at 25°C. (25,26), but the activity coefficients of aqueous solutions of acetic, propionic, and n- butyric acids have never been reported at this temperature.

The systems chosen were known to be non-ideal so a knowledge of the deviations from ideality (activity coefficients) provides a key to the interaction energy between components in solution. The theoretical formulae derived for the behavior of components in solution can be compared with experimental results.

The properties in solution of members in a homologous series can be compared. Differences in solution behavior between the alcohols and acids can be determined.

III. MATERIALS

A. Water

All water was redistilled from alkaline permanganate solution through an all glass system and stored in glass stoppered bottles.

B. Methanol

Baker and Adamson reagent grade methanol was distilled directly through an Oldershaw column at a 10 - 1 reflux ratio. No separate precautions were taken to remove water from the alcohol as the two do not azeotrope at atmospheric pressures. About half the original sample, the middle fraction, was retained. The boiling point range corrected to 760 mm. pressure was 64.51 - 64.59° ± 0.02°C.[1]

C. Ethanol

Absolute ethanol obtained from Commercial Solvents Corp. was purified by a modification of the method of Lund

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[1] The boiling points were all corrected to 760 mm. pressure by use of the Sydney Young equation, known as the A.S.T.M. method (30). By this equation, the corrections C_c to be made to the observed temperatures t_c at a barometric pressure P are; for the alcohols,

$$C_c = 0.000100\ (760 - P)(273 + t_c),$$

and for the acids,

$$C_c = 0.00012\ (760 - P)(273 + t_c).$$

and Bjerrum (31). In order to remove acetaldehyde, which boils at about the same temperature as the alcohol, a colloidal suspension of Ag_2O was prepared by mixing 10 grams of $AgNO_3$ and 3 grams of NaOH per liter of alcohol, and refluxing this mixture for 12 hours. This resulted in the deposition of a silver mirror which indicated the presence of easily oxidazable materials, as alcohols are not affected by this procedure. This mixture was then filtered and the method of Lund and Bjerrum applied to the filtrate to remove water. After refluxing for 4 hours with the magnesium ethylate formed, the alcohol was distilled through the Oldershaw column at a 10 - 1 reflux ratio. The corrected boiling point range was 78.50 - 78.52° + 0.02°C. for the middle fraction collected.

D. Propanol-1

Fisher Scientific Co. propanol-1 was chosen for purification; as a rough test involving the decoloration of bromine showed it to contain less unsaturated compounds. To facilitate the removal of allyl alcohol, a common impurity of propanol-1, the stock alcohol was first treated with bromine until a discoloration resulted. The excess bromine was removed by adding enough Na_2SO_3 to decolor and then a small excess. The method of Lund a Bjerrum was again used to remove water. A subsequent distillation at a 10 - 1 reflux ratio in the Oldershaw column resulted in a boiling range of 97.43 - 97.51° ± 0.02°C. for the central fraction.

E. Acetic Acid

Baker and Adamson reagent grade acetic acid was distilled directly in the Oldershaw column at a 10 - 1 reflux ratio. Acetic acid does not azeotrope with water so no special precautions were taken for its removal. The retained fraction boiled over the range 118.20 - 118.33° ± 0.02°C.

F. Propionic Acid

Since water and propionic acid azeotrope, but at a concentration of 17.7 weight per cent acid, a straight distillation through the Oldershaw column was sufficient to remove the water. Eastman Kodak white label acid was used, the corrected boiling range being 141.44 - 141.61 ± 0.02°C.

G. n- Butyric Acid

The n- butyric acid used was derived from two sources. Two-thirds was Eastman Kodak white label, the remainder being Matheson c.p. grade. The Matheson acid was partially purified by fractional melting in an apparatus similar to that described by Aston and Mastrangelo (32). This treatment lowered the mole per cent impurity to less than one per cent. This fraction was then mixed with the Eastman Kodak acid and distilled in the Oldershaw column at a reflux ratio of 10 - 1. This produced an acceptable product boiling at 164.0 - 164.2 ± 0.05°C. when corrected to standard conditions.

All the organic liquids were stored in glass stoppered flasks and were only allowed to be opened to dry air when liquid was being removed.

IV. EXPERIMENTAL INVESTIGATION

A. General Method

As stated previously, when activities are determined from vapor pressure measurements it is necessary to know the partial pressures, or more exactly the fugacities, of at least one of the components over the solution of interest. In addition, for the choice of standard states as made in this research, the vapor pressures of the pure liquid components must be known at the same temperature. To calculate the activity coefficient, the composition of the solution of interest must be known.

The method employed in this research was different from any previously reported. An equilibrium composition of vapors was taken from above the solution and stored in a previously evacuated flask. When total pressure equilibrium was established, the pressure was read, the vapors were removed by a liquid nitrogen trap, and the original solution as well as the condensed vapors were analyzed interferometrically.

B. Apparatus

1. <u>Oldershaw distilling column</u>

The column was the D-1 model manufactured by Glass

Engineering Laboratories. It contained 30 plates, was vacuum jacketed, and was fitted with a liquid dividing head. The performance of this column has been studied and reported in detail by Collins and Lantz (33).

2. Refractometer

An Abbe - 56 refractometer was used, being operated at 25°C.

3. Interferometer

A Rayleigh Interference Refractometer for liquids manufactured by Adam Hilger, Ltd. of London was used. The entire apparatus was enclosed in an uninsulated masonite box where it was air thermostatted by means of a Precision Scientific Co. "Merc-to-Merc" thermoregulator to 25.0 ± 0.1°C.

4. Interferometer cells

One centimeter path length cells were used throughout this research. The cells were precision made of pure quartz by the Hilger Laboratories. Cell covers were made of sheet teflon to prevent evaporation from the solutions to be analyzed. All the covers were sealed to the top of the cells by mercury seals. A small hole was drilled in the cover above the liquid wells of the cell for insertion of solution. After the well was filled, the hole was covered by mercury.

5. Activity apparatus

The apparatus designed and used in this research is illustrated in Figure 1 (front view) and Figure 2 (the central portion of the apparatus from side view). In these figures, A is a 1-liter pyrex flask fitted with a $\overline{\$}$ 29/42 top joint and a $\overline{\$}$ 10/30 side joint. A flat bottomed flask was used to enable the use of a teflon covered stirring bar H, activated by a Precision Scientific Co. "Mag-Mix" magnetic stirrer H'. Flask A is immersed in a water bath B thermostatted to 25.00 ± 0.02°C. by a Precision Scientific Co. "tungsten-to-mercury" thermoregulator. D is a 22-liter flask connected directly to the generating flask A by a $\overline{\$}$ 71/60 joint, through stopcock S2 (10 mm. bore), and also through the stopcock S6 (2 mm. bore) and the intermittent bleeder C. Flask D is also connected to a mercury manometer E, through stopcock S4 to a liquid nitrogen trap (F, G), and through stopcock S3 (two-way) to both atmosphere and vacuum line. S5 is a stopcock (two-way) which connects to vacuum line and to the atmosphere. Stopcock S1 leads to the atmosphere.

The intermittent bleeder C is a solenoid operated valve. The outside portion was constructed from 15 mm.

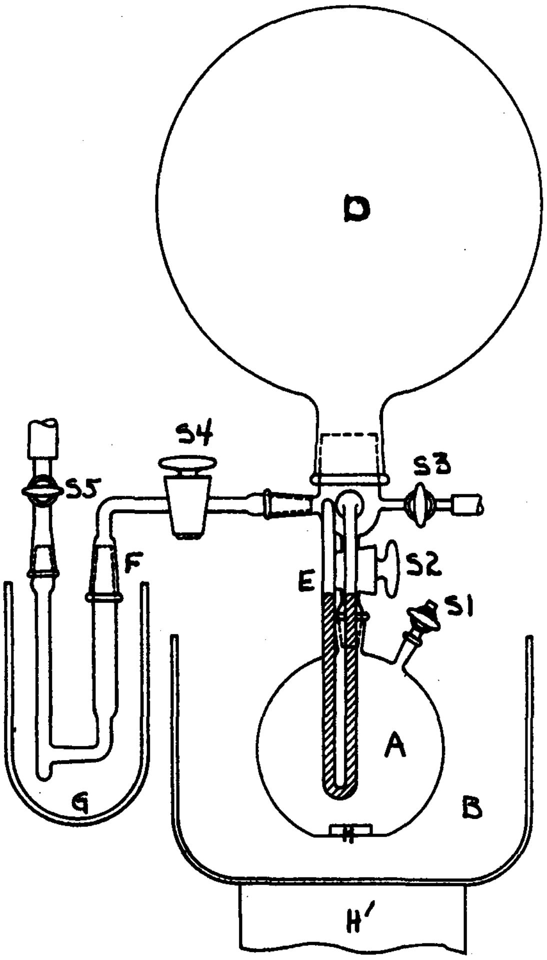

Figure 1. Apparatus for Determination of Activities of Components of Volatile Binary Solutions (Front View)

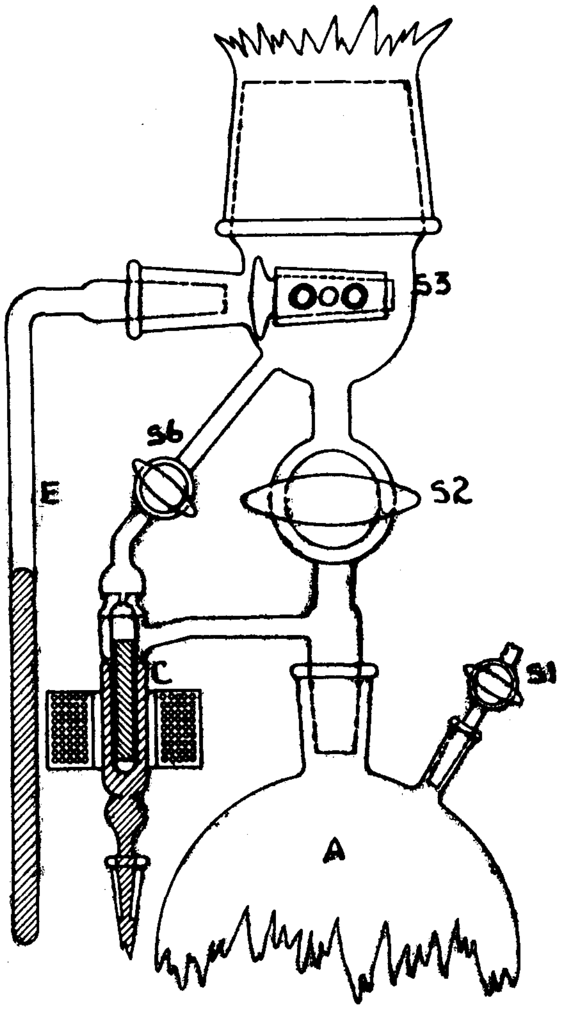

Figure 2. Central Section of Apparatus for Determination of Activities of Components of Volatile Binary Solutions (Side View)

inside diameter pyrex tubing. A constriction was turned (on a glass lathe) near one end of the tube such that an opening of about 4 mm. remained. The end of a piece of 8 mm. inside diameter tubing was sealed off in the shape of a hemisphere. At this point, the hemispherical portion was lapped into the constriction with the aid of carborundum grinding powder, the lapped surface being about 3 mm. in length. Upon completion of the grinding operation, a soft iron core of 8 mm. diameter was sealed into the smaller tube. This cartridge containing the iron core was floated on a pool of mercury of sufficient depth so the lapped joints would be closed tightly. Small indentations were made in the outer tube to guide the cartridge into position, one set near the top of the cartridge when in position and the other near the bottom. The solenoid surrounding the outer tube was activated through an Eagle Signal Corp. Flexapulse timer. When the solenoid was activated, the joint was broken as the cartridge was drawn into the mercury pool. With the current off, the cartridge was again buoyed into place. The joint formed was found to be nearly vacuum tight to pressure differences of at least 200 mm. Hg.

The manometer E is of the differential type. Pyrex tubing of 9 mm. inside diameter was used for its construction. It is connected to the central portion of the apparatus through a $\$$19/38 joint. The closed end of the manometer was evacuated to less than 10^{-5} mm. Hg. with a mercury diffusion pump and then sealed off, after degassing the mercury by boiling.

The entire apparatus was enclosed in a masonite box and air thermostatted to 27.0° ± 0.1°C. to prevent condensation in the reservoir flask D.

6. Cathetometer

A Gaertner M-901 cathetometer was used, permitting pressure readings to 0.05 mm. Hg.

7. Thermometers

All thermometers used with the distilling column were of very good quality, although not calibrated. They were purchased from Emil Greiner Co. The thermometer used in the water bath B, was calibrated by the National Physical Laboratory of Teddington, England. No correction was needed at 25.00 ± 0.02°C.

C. Method of Procedure

1. Interferometer calibration

The interferometer is a comparison instrument, by means of which the refractive index of a solution of known composition may be compared with that of the unknown.

For this reason, it is necessary to calibrate the instrument for each system of interest. The interferometer scale reading obtained with two different solutions in the cell, minus the zero reading obtained with pure solvent in both sides of the cell, gives a value ΔR which is proportional to the difference in refractive index between the two solutions. This quantity divided by the difference in concentration between the solutions, gives $\Delta R/\Delta C$, which is proportional to the change in refractive index per unit difference of concentration. By plotting this quantity against the mean concentration of the solutions a calibration curve can be drawn for analytical use. Most of the calibration curves used in this research were taken from the work of Dr. R. P. Craig (34). Some were redetermined where point scattering was bad, and all were spot checked. All solutions were transferred to the interferometer cells with a hypodermic syringe, to prevent any minor changes in concentration due to evaporation.

2. Preparation of standard solutions

The standard solutions were prepared directly on a weight per cent basis. The calibration curves used were also in weight per cent units. Weight per cent, because it is a more linear function of the amount of solute added, was chosen rather than mole per cent, the two being quite readily interconvertible.

The number of standard solutions prepared depended upon the shape of the calibration curve. Enough solutions were made so the entire usable range of the calibration curve could be covered without having interferometer readings which were very large. All solutions were stored in 25 ml. lightly greased glass stoppered volumetric flasks.

3. Refractive index curves

For each system, the refractive index of all standard solutions was taken with the Abbe refractometer. A plot was made of the refractive index against weight per cent, the resulting curve serving as a rough analytical curve for the system.

4. Collection of vapor samples

The temperature of the water bath B and of the air bath surrounding the entire apparatus were maintained constant for at least 30 minutes before any vapors were collected. At the same time the magnetic stirrer H was turned on. (The stirrer generated quite a bit of heat, and unless it was turned on for some time to warm up, the temperature of the water bath could not readily be maintained constant.) For high water concentrations, about 300 ml. of water was introduced into the flask through the opening at S1.

Sufficient solute was then added to make the solution of desired concentration. After samples from one solution had been taken, more solute was added to prepare the next solution. This process was continued until a mole fraction of about 0.20 was attained. At this point, things were reversed, and water was added to the organic solvents similarly. The magnetic stirrer bar was set in motion to stir the solution after the addition of solute. Before each run, a small sample of solution was removed and roughly analyzed in the refractometer. This measurement permitted estimation of the concentration in the flask. If the solution was of the proper concentration, a hypodermic syringe fitted with a long needle was used to remove about 3 ml. of the solution for later analysis. (The long needles were made by pulling glass tubing into long capillaries. They were then cut off and cemented to a size 19 hypodermic needle with glyptal. The assembled needles were baked in an oven until dry. This made a needle of about 9 inches total length.) All the collected samples were stored in small tubes of about 6 ml. capacity. The tubes were closed by ₷ 10/30 slightly greased joints.

With the solution prepared, stopcocks S1, S2, S4, S5, and S6 were closed and the reservoir flask D evacuated through S3. (Actually, the evacuation was proceeding as the solution was prepared.) The magnetic stirrer was set in in rapid motion, S3 was closed and S2 was opened slightly; the opening was such that the solution boiled vigorously, but not turbulently. When the solution stopped boiling, S2 was closed, and the large flask evacuated through S3. This procedure was believed sufficient to outgas the generating flask, as consecutive readings of the vapor pressure of pure liquids showed very little change from the first to second readings. The boiling action appeared sufficient to sweep the air into the reservoir flask.

All stopcocks were now closed except S6, and the intermittent bleeder was turned on through the timer until the change in pressure per opening of the shut-off valve was small, i.e., 0.05 mm. or less, usually requiring about 20 minutes. S2 was then opened for 10 minutes to permit total pressure equilibration. The total pressure was read from the manometer by means of the cathetometer.

During the collection of vapors the condenser F was evacuated through stopcock S5. Stopcocks S2, S5, and S6 were closed and S4 was opened; the vapors condensing in the trap. The condensing process was greatly accelerated, without loss of material, by opening S5 to the vacuum line very slightly. This procedure required about 3 minutes, the total pressure in the reservoir flask was zero at the completion of the operation. After condensation, S4 and S5 were closed.

If more than one vaporization was necessary in order to obtain a large enough sample for analysis (at least 1.5 ml.), as was usually the case except for those systems where the vapor pressure was quite high, the procedure as outlined was repeated. When sufficient sample was collected, the liquid nitrogen bath was removed from the trap, the trap allowed to warm slightly, and S5 turned to the atmosphere side where dry (anhydrone), CO_2 free (ascarite) air was admitted. The trap was allowed to warm to room temperature as the melt flowed into the small well at the extreme bottom of the condenser. It was necessary to have the condenser drain clean in order to insure obtaining a homogeneous sample. One of the long needles previously described was used with a hypodermic syringe to remove the condensate and to place it into a storage tube.

An aliquot of the solution in the generating flask was removed by syringe after S1 was opened to the atmosphere. Analysis of this sample gave the final solution composition.

The crucial feature of this apparatus was the intermittent bleeder C. In principle, it may appear that a small-bore stopcock would perform the same function as the bleeder, but in practice it was found not to. With a small bore stopcock opened very slightly so vapors were collected slowly, the results were always characterized by high partial pressures for water as compared to best literature values. Calculations by Dr. R. S. Hansen (35) showed that equilibration between vapors and solution in the generating flask should be made within 10 seconds. As a result of this, the intermittent bleeder was operated on a cycle of 1/2 second on - 15 seconds off. In this way, the vapors would have time to equilibrate with the solution between each valve opening. The time of the opening was made as short as possible. Under operating conditions, the initial pressure increment in the reservoir flask per opening was about 1.7 mm. in the case of methanol (vapor pressure = 125.77 mm. Hg.) and 0.5 mm. in the case of water (vapor pressure = 23.65 mm.).

At present, the author is unable to explain quantitatively why the intermittent bleeder gave good results and a small-bore stopcock poor results. From a qualitative standpoint, with a small-bore stopcock an equilibrium condition was never reached in the generating flask because vapors were continually bled out. This led to vapors which were richer in the faster evaporating component; this being water because of its lower molecular weight. In the case of the intermittent bleeder, liquid-vapor equilibrium was established before each opening of the valve.

5. Analysis of samples

To select the proper standard for use in interferometric analysis, the refractive index of each sample was taken and compared with those of the standards. The standard with refractive index nearest to that of the sample was chosen for comparative purposes. From the calibration curve, previously described, the value of $\Delta R/\Delta C$ could be determined at the concentration of the standard solution. Thus by knowing the ΔR between the sample and the standard the first concentration correction ΔC could be calculated. To be consistent with the construction of the calibration curve, the $\Delta R/\Delta C$ value of a concentration midway between that of the standard and the first corrected concentration was taken; the calculation process was repeated to give the final corrected concentration.

D. Method of Calculation

By knowing the mole fraction of each component in the condensate and the total pressure of the vapors, the partial pressure of each component was obtained; assuming no vapor phase association. The activity of each component was obtained as the ratio of its partial pressure to its vapor pressure in the pure liquid. The total pressures as read on the manometer, were all increased by 0.25 mm. when

It was found that the manometer readings were too low by this amount. The meniscus heights in the arms of the manometer were not equal, and in attempting to use a capillary depression correction for each meniscus height, it became apparent that this correction would lead to a vapor pressure much too low for water. The manometer was then checked against another manometer whose meniscus heights were nearly equal, thus cancelling any capillary depression effects. The standardizing manometer was found to give readings which were higher by about 0.25 mm. than the readings of the manometer used in this research. As a result of this comparison, it was felt an additive correction was justified. The total pressure readings were all corrected from 27°C. to 0°C. by multiplying by the ratio of the density of mercury at 27°C. to that at 0°C.; this factor being 0.9951.

The mole fraction used for calculation of the activity coefficient was obtained from the analysis of the solutions collected prior to the degassing operation and that collected at the completion of the run. Since the concentration changed slightly during the course of a run, the concentration chosen was that present at the middle of the actual vapor collection run. Representing the initial mole fraction by X_i, and the final mole fraction by X_f, the middle mole fraction was calculated from,

$$X = \frac{n\,X_i + (n + 2)X_f}{2(n + 1)} \ ,$$

where n represents the number of vaporizations performed.

The method of calculation of partial pressures, which assumed a Daltonian vapor behavior, was not valid for vapors of the carboxylic acids which are known to associate in the vapor state. MacDougall has studied the vapor phase association of acetic acid (36) and propionic acid (37). He reported equilibrium constants for the equilibria

$$2(\text{Acid monomer}) \rightleftharpoons (\text{Acid dimer})$$

and

$$3(\text{Acid monomer}) \rightleftharpoons (\text{Acid trimer})$$

at various temperatures and partial pressures. The constants used in this research for acetic acid were calculated from his data by fitting a least squares straight line to the linear portion of his data at 25°C. and extrapolating to zero pressure. The results were:

$$K_2 = \frac{p_D}{p_M^2} = 1.63 \text{ mm.}^{-1} \quad \text{and} \quad K_3 = \frac{p_T}{p_M^3} = 0.0015 \text{ mm.}^{-2} .$$

For propionic acid, the constants were extrapolated from his data at elevated temperatures by use of the vant Hoff equation. Again, a least squares straight line was fitted to the experimental points and the extrapolation to 25°C. was made from it. The results were:

$$K_2 = 3.92 \text{ mm.}^{-1} \text{ and } K_3 = 0.074 \text{ mm.}^{-2} .$$

The association constants for n- butyric acid were not available in the literature. Vapor density data of sufficient accuracy were not available, so the constants could not be calculated. The possibility of determining the equilibrium constants at 25°C. was investigated and it was concluded that, because of the low vapor pressure of n- butyric acid at 25°C, satisfactory determination would require construction of fairly involved apparatus, and probably extrapolation of values obtained at temperatures above 60°C. The constant used in this research was therefore estimated from the constants for the three lower acids. The association constant for formic acid was determined by Coolidge (38). He reported only a value for dimerization, that being;

$$K_2 = 0.429 \text{ mm.}^{-1} .$$

Since it was believed that the free energies of dimerization should vary in a fairly uniform manner, a plot was made of log K_2 against the number of carbon atoms in the molecule. This curve is shown in Figure 3. The value 7.5 mm.^{-1} chosen was the mean between the two extremes of possible extrapolated values. Only a dimerization constant was considered, as the uncertainty in any trimerization constant would be much too great for it to be of any practical value. The effect of ignoring the trimer will be discussed with the experimental results.

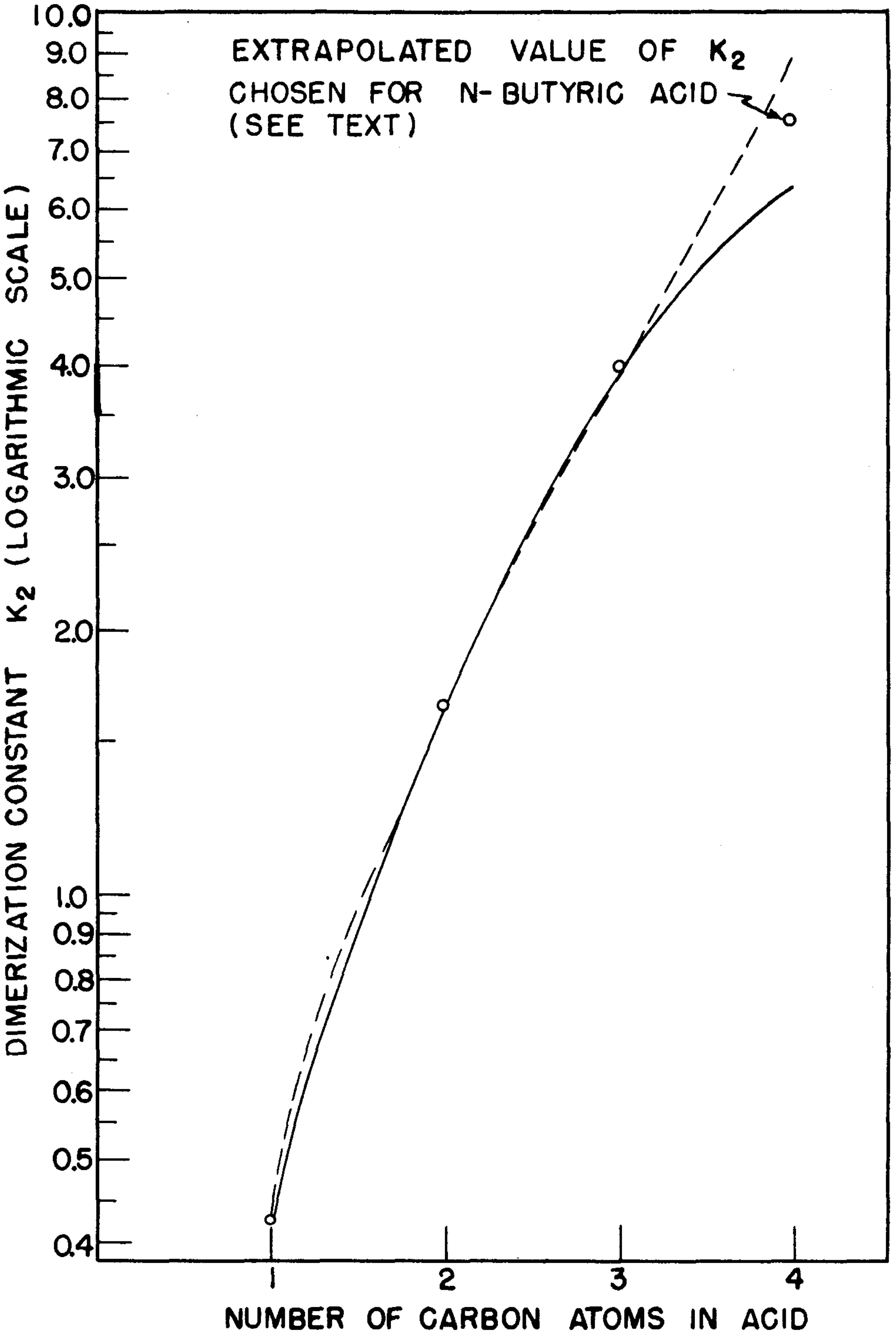

Figure 3. Extrapolation for K_2 of n- Butryic Acid

The corrections to be applied to the acid vapors to calculate activities are derived from the equilibrium relations. Assuming ideal behavior of individual entities, i.e., considering dimers and trimers as one entity, one gets for the total pressure as measured,

$$P_{(total)} = P_{water} + P_{monomer} + P_{dimer} + P_{trimer},$$

or from the equilibrium constants,

$$P_{(total)} = P_{water} + P_{monomer} + K_2 P^2_{monomer} + K_3 P^3_{monomer} \qquad (7)$$

In a similar manner, the mole fraction of total acid present in the vapor can be expressed in terms of partial pressure, the resulting equation being;

$$X_A = \frac{P_{monomer} + 2\,P_{dimer} + 3\,P_{trimer}}{P_{(total)} + P_{dimer} + 2\,P_{trimer}}\,, \qquad (8)$$

since the dimer and trimer contribute two and three molecules respectively, to the total number of molecules. Substitution for the partial pressures of the dimer and trimer in terms of the equilibrium constants and the partial pressure of the monomer in Equation 8, and rearranging, the following cubic equation was obtained in terms of the monomer partial pressure.

$$K_3(3-2X_A)p_M^3 + K_2(2-X_A)p_M^2 + p_M - X_A\,P_{total} = 0 \ .$$

Analysis of the condensed sample gave X_A, the K's were known, and P_{total} was measured, so the monomer partial pressure was readily calculated. This led directly to the true partial pressure of water from Equation 7, and the resulting activity.

To calculate the activities of the acids, one must first calculate the fugacities of the acid vapor. In the case of the alcohols where no association in the vapor occurs, the partial pressures were assumed equal to the fugacities, but because of association this assumption is not valid for the acids. To determine the fugacity of a gas at any pressure and at any constant temperature, the relation

$$RT \ d \ln f = \overline{V} \ dP$$

or

$$RT \ d \ln f - RT \ d \ln P = \overline{V} \ dP - RT \ d \ln P$$

can be written. This leads directly for the acid to

$$d \ln \left(\frac{f_{acid}}{P_{acid}} \right) = \left\{ \frac{\overline{V}_A}{RT} - \frac{1}{P_A} \right\} dP_A \quad . \qquad (9)$$

The effective number of "moles of acid entities" for each actual mole of acid present is given by,

$$\bar{n}_e = \frac{n_M + n_D + n_T}{n_M + 2 \ n_D + 3 \ n_T} \quad ,$$

or by use of equilibrium constants,

$$\bar{n}_e = \frac{p_M + K_2 p_M^2 + K_3 p_M^3}{p_M + 2K_2 p_M^2 + 3K_3 p_M^3} \quad . \qquad (10)$$

Thus, $$\frac{\bar{V}_A}{RT} = \frac{\bar{n}_e}{\Sigma p_{acid}} = \frac{\bar{n}_e}{p_M + K_2 p_M^2 + K_3 p_M^3} \quad .$$

Substitution for $\bar{n}_e$ from Equation 10 and cancellation gives,

$$\frac{\bar{V}_A}{RT} = \frac{1}{p_M + 2K_2 p_M^2 + 3K_3 p_M^3} = \frac{1}{p_M \left(\frac{d \, \Sigma p_{acid}}{d \, p_M} \right)} \quad .$$

Therefore, letting $\Sigma p_{acid} = P_A$, substitution in Equation 9 gives

$$d \ln \left(\frac{f_A}{P_A} \right) = \left\{ \frac{d \ln p_M}{dP_A} - \frac{1}{P_A} \right\} dP_A \quad ,$$

or

$$d \ln \left(\frac{f_A}{P_A} \right) = d \ln p_M - d \ln P_A \quad ,$$

and by integration

$$\ln \left(\frac{f_A}{P_A} \right) = \ln \left(\frac{p_M}{P_A} \right) \quad .$$

Since as $P_A \rightarrow 0$, $f_A \rightarrow P_A$ and $p_M \rightarrow P_A$,

the relation $\frac{f_A}{P_A} = \frac{p_M}{P_A}$ must hold , so that $f_A = p_M$.

Thus the true activity of the acid is the ratio of the monomer partial pressure over a solution to the monomer partial pressure over the pure acid, assuming the monomer, dimer, and trimer individually to behave ideally.

V. EXPERIMENTAL RESULTS

The experimental data for the aqueous alcohol solutions are given in Tables 1 - 3 and for the aqueous acid solutions in Tables 4 - 6. The calculated activity coefficients are based on a standard state of the pure liquid component at 25.00 ± 0.02°C.

All the results were measured directly except for the partial pressure of the monomer and total vapor pressure in pure n- butyric acid. The measured vapor pressure (2.34 mm. Hg.) and the resulting value of the monomer partial pressure were too high to give a Raoult's law behavior for the acid at high acid concentrations, which was characteristic of the other two acids. Since the total vapor pressure of the aqueous n- butyric acid systems changed rapidly as the acid was diluted, a small amount of water in the original acid could have been responsible for the higher value measured. This point is strengthened because at high acid concentrations a small amount of water changes the mole fraction of acid a great deal. To get a Raoult's law behavior for the acid, a straight line was drawn from the origin through the monomer partial pressure points at the two highest acid concentrations measured and extrapolated to pure acid. This gave the monomer partial pressure and total vapor pressure of the pure acid as shown in Table 6.

Table 1

Experimental Data for Methanol - Water System at 25°C.

Mole Fraction MeOH in Solution	Mole Fraction MeOH in Vapor	Total Pressure mm. Hg.	Activity Coefficient MeOH	Activity Coefficient H_2O
0.0000	0.0000	23.65	—	1.0000
.0263	.1793	28.36	1.54	1.011
.0608	.3373	33.87	1.49	1.011
.0894	.4285	38.69	1.47	1.027
.1210	.5105	43.74	1.467	1.030
.1510	.5666	48.40	1.444	1.045
.1926	.6216	53.67	1.377	1.064
.2236	.6609	57.84	1.360	1.068
.2737	.7110	63.74	1.316	1.072
.2999	.7260	66.77	1.285	1.104
.3366	.7496	70.05	1.240	1.118
.3700	.7613	73.08	1.196	1.170
.4057	.7781	75.61	1.153	1.194
.4450	.7997	78.93	1.128	1.204
.4884	.8185	82.36	1.097	1.235
.5382	.8379	86.63	1.072	1.285
.5890	.8607	90.11	1.047	1.291
.6421	.8789	94.13	1.024	1.847
.6933	.8989	98.54	1.016	1.373
.7398	.9136	102.32	1.005	1.437
.7809	.9273	105.94	1.000	1.486
.8347	.9489	110.80	1.002	1.448
.8905	.9667	116.18	1.003	1.494
.9345	.9801	119.81	0.9991	1.54
1.0000	1.0000	125.77	1.0000	—

Table 2

Experimental Data for Ethanol - Water System at 25°C.

Mole Fraction EtOH in Solution	Mole Fraction EtOH in Vapor	Total Pressure mm. Hg.	Activity Coefficient EtOH	Activity Coefficient H_2O
0.0000	0.0000	23.65	——	1.000
.0243	.1754	28.21	3.47	1.008
.0482	.2879	31.98	3.25	1.011
.0709	.3814	35.92	3.29	1.011
.1040	.4543	39.82	2.962	1.025
.1513	.5252	43.96	2.599	1.040
.2020	.5679	46.75	2.238	1.070
.2986	.6125	49.96	1.745	1.167
.3837	.6428	51.78	1.477	1.269
.4691	.6680	53.20	1.290	1.406
.5664	.7057	54.84	1.164	1.574
.6649	.7546	56.18	1.086	1.740
.7711	.8089	57.38	1.025	2.026
.8412	.8597	57.89	1.008	2.16
.8951	.9057	58.32	1.005	2.22
.9469	.9509	58.42	0.990	2.28
1.0000	1.0000	58.71	1.000	——

Table 3

Experimental Data for Propanol-1 - Water System at 25°C.

Mole Fraction P_rOH in Solution	Mole Fraction P_rOH in Vapor	Total Pressure mm. Hg.	Activity Coefficient P_rOH	Activity Coefficient H_2O
0.0000	0.0000	23.65	——	1.000
.0230	.1904	28.66	11.2	1.004
.0452	.2904	32.29	9.81	1.014
.0661	.3357	33.96	8.15	1.021
.0876	.3498	34.50	6.51	1.039
.1216	.3596	34.79	4.864	1.072
.1517	.3634	34.86	3.948	1.106
.2406	.3728	34.90	2.557	1.219
.2958	.3774	35.04	2.113	1.310
.4049	.3909	35.11	1.602	1.520
.4970	.4070	34.93	1.352	1.742
.5833	.4290	34.60	1.203	2.005
.6812	.4749	33.56	1.106	2.337
.8015	.5630	31.01	1.030	2.886
.8581	.6328	29.01	1.012	3.178
.9070	.7181	26.67	0.998	3.42
.9522	.8322	24.11	0.996	3.58
1.0000	1.0000	21.15	1.000	——

Table 4

Experimental Data for Acetic Acid - Water System at 25°C.

Mole Fraction HOA_c in Solution	Mole Fraction HOA_c in Vapor	Total Pressure mm. Hg.	Partial Pressure HOA_c monomer mm. Hg.	γHOA_c	γH_2O
0.0000	0.0000	23.65	0.000	—	1.0000
.0216	.0115	23.24	.171	2.83	0.9948
.0426	.0264	23.09	.306	2.56	0.9994
.0645	.0428	22.79	.417	2.31	0.9984
.0861	.0615	22.71	.524	2.17	1.006
.1196	.0910	22.55	.667	1.99	1.016
.1564	.1187	22.40	.782	1.78	1.033
.1986	.1543	22.21	.914	1.64	1.052
.2586	.2015	22.00	1.07	1.48	1.087
.3060	.2474	21.73	1.21	1.41	1.106
.3560	.2889	21.50	1.32	1.32	1.138
.4164	.3489	21.16	1.47	1.26	1.172
.5035	.4305	20.84	1.69	1.20	1.233
.5464	.4743	20.58	1.79	1.17	1.264
.5989	.5320	20.36	1.91	1.14	1.317
.6558	.5818	20.10	2.04	1.11	1.384
.7164	.6437	19.75	2.18	1.09	1.46
.7730	.6998	19.27	2.30	1.06	1.55
.8407	.7706	18.77	2.45	1.04	1.73
.8914	.8284	18.00	2.54	1.02	1.92
.9484	.9031	17.08	2.65	0.997	2.42
1.0000	1.0000	15.61	2.80	1.000	—

Table 5

Experimental Data for Propionic Acid - Water System at 25°C.

Mole Fraction HOP_r in Solution	Mole Fraction HOP_r in Vapor	Total Pressure mm. Hg.	Partial Pressure HOP_r Monomer mm. Hg.	γHOP_r	γH_2O
0.0000	0.0000	23.65	0.000	——	1.0000
.0246	.0205	23.41	.192	9.43	1.001
.0492	.0396	23.39	.288	7.05	1.012
.0729	.0529	23.33	.342	5.67	1.027
.1005	.0638	23.23	.381	4.58	1.047
.1423	.0750	23.10	.415	3.51	1.084
.1813	.0830	22.93	.439	2.92	1.123
.2196	.0916	22.66	.462	2.54	1.157
.2826	.1111	22.39	.513	2.19	1.228
.3499	.1266	21.82	.545	1.88	1.307
.4069	.1418	21.34	.576	1.71	1.386
.5055	.1671	20.29	.616	1.47	1.553
.5657	.1905	19.67	.655	1.39	1.685
.6182	.2064	18.85	.671	1.31	1.815
.6948	.2341	17.67	.698	1.21	2.081
.7623	.2633	16.44	.721	1.14	2.419
.8314	.3047	14.88	.748	1.08	2.983
.8753	.3479	13.18	.761	1.05	3.432
.9534	.5010	9.10	.798	1.01	5.236
1.0000	1.0000	3.58	.830	1.00	——

Table 6

Experimental Data for n- Butyric Acid - Water System at 25°C.

Mole Fraction HOBu in Solution	Mole Fraction HOBu in Vapor	Total Pressure mm. Hg.	Partial Pressure HOBu monomer mm. Hg.	γ_{HOBu}	γ_{H_2O}
0.0000	0.0000	23.65	0.000	——	1.000
.0238	.0195	23.43	.145	24.2	1.002
.0462	.0248	23.53	.168	14.4	1.026
.0703	.0257	23.38	.171	9.65	1.046
.0995	.0263	23.38	.173	6.90	1.079
.2061	.0276	23.40	.175	3.37	1.225
.2815	.0287	23.30	.181	2.56	1.346
.3910	.0307	22.78	.186	1.89	1.551
.4791	.0340	22.44	.196	1.62	1.782
.5836	.0385	21.20	.204	1.39	1.998
.6534	.0429	20.19	.211	1.28	2.397
.7281	.0471	19.16	.216	1.17	2.891
.8215	.0565	16.65	.222	1.07	3.804
.8854	.0728	13.58	.229	1.03	4.782
.9387	.1095	9.90	.243	1.02	6.35
1.0000	1.0000	.728	.252	1.00	——[1]

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[1] Partial pressure of monomer in pure acid and total vapor pressure obtained from extrapolation as explained in text.

Figures 4 - 6 are the total pressure and partial pressure curves for the aqueous alcohol systems while the aqueous acid results are shown in Figures 7 - 9. For comparison with best literature values, the data of Dobson (25) on the aqueous ethanol system and Butler, Thomson, and Maclennan (26) on the aqueous methanol and propanol-1 systems are included on the respective figures.

The vapor pressures of the pure components as measured in this research are compared in Table 7 with values obtained by previous investigators. For the most part, the agreement between the values obtained in this research and those previously reported is excellent, except for the measured vapor pressure of n- butyric acid. The extrapolated value, obtained as described above, agrees very well with the reported values. The vapor pressures of the acids, attributed to Schmidt and Kahlbaum, were obtained by extrapolation from their data at temperatures above 25°C.

The activity data as collected can be checked for self-consistency by use of a form of the Duhem - Margules equation; namely,

$$X_1 \left(\frac{\partial \log \gamma_1}{\partial X_1}\right)_{T,P} = X_2 \left(\frac{\partial \log \gamma_2}{\partial X_2}\right)_{T,P} , \quad (11)$$

where the X's represent mole fractions and the γ's,

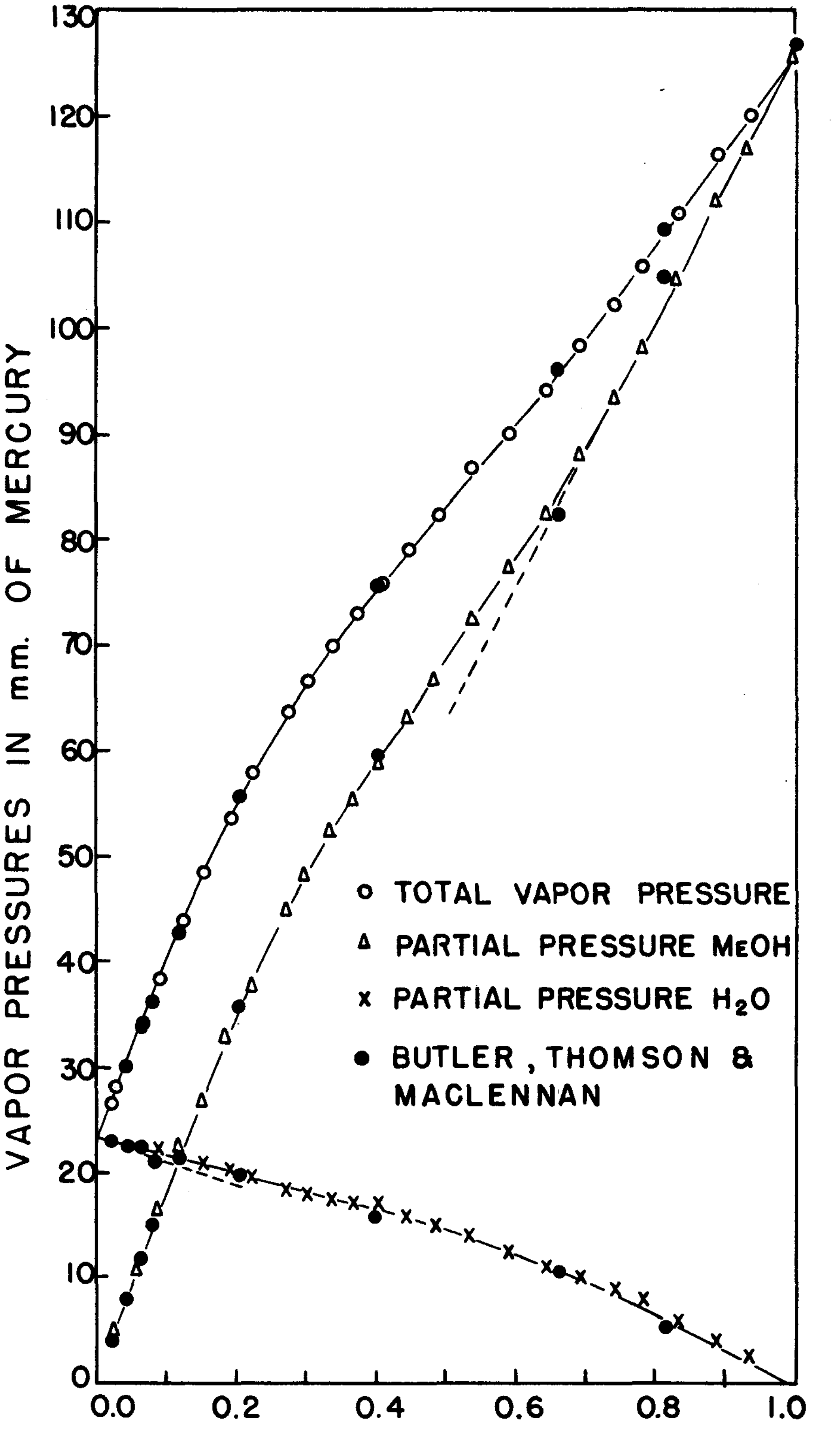

Figure 4. Vapor Pressures of Methanol Solutions

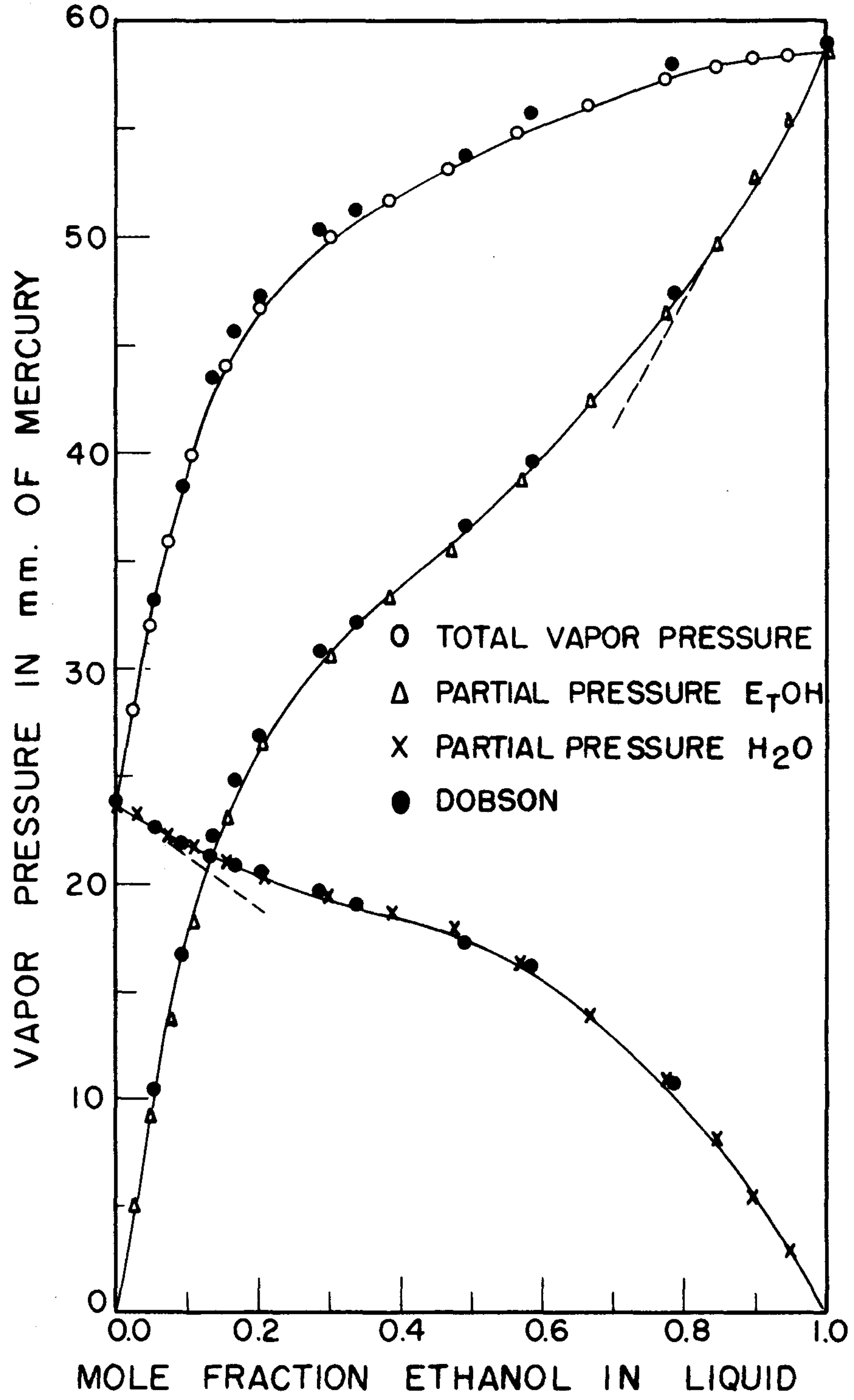

Figure 5. Vapor Pressures of Ethanol Solutions

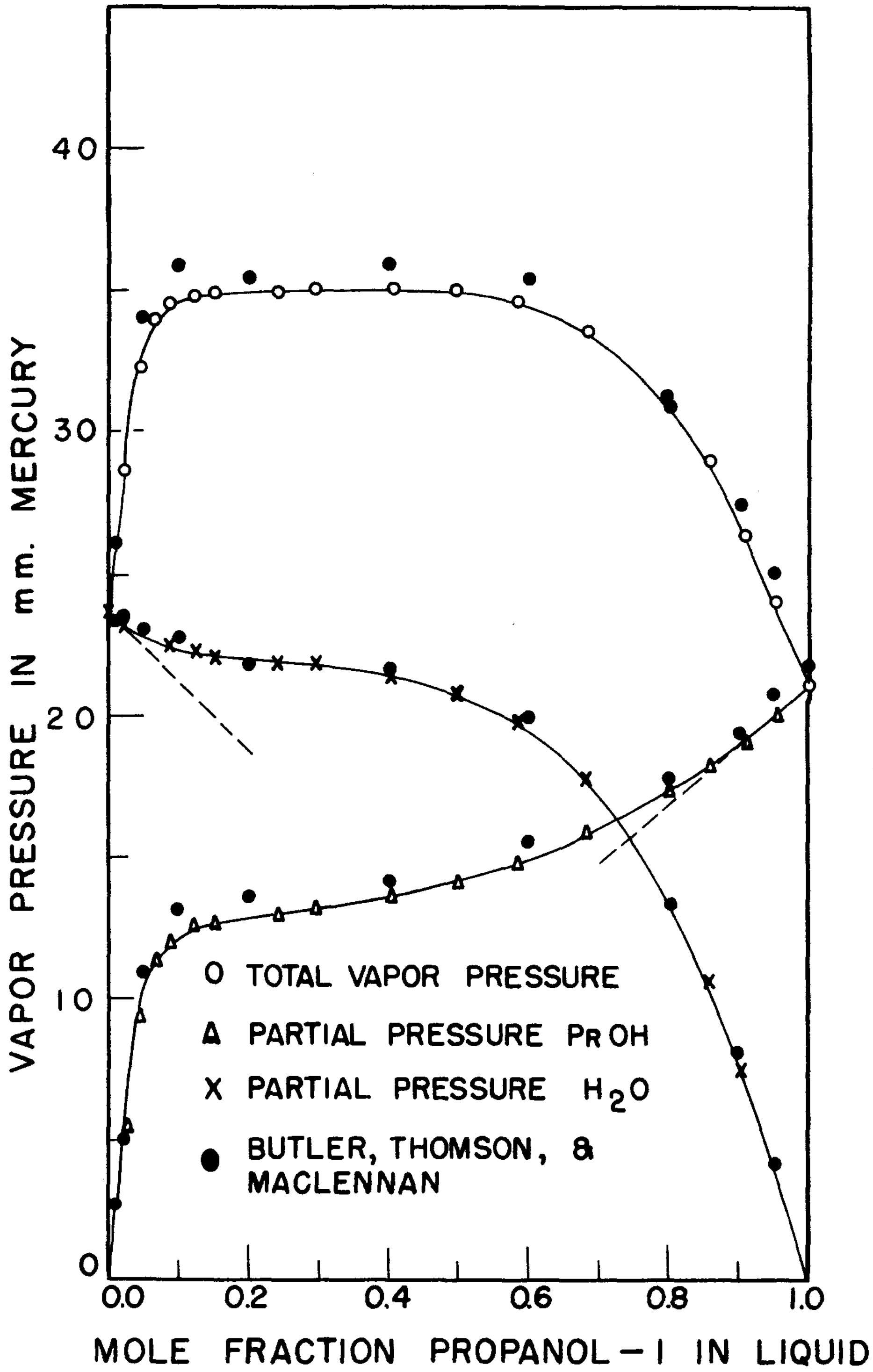

Figure 6. Vapor Pressures of Propanol-1 Solutions

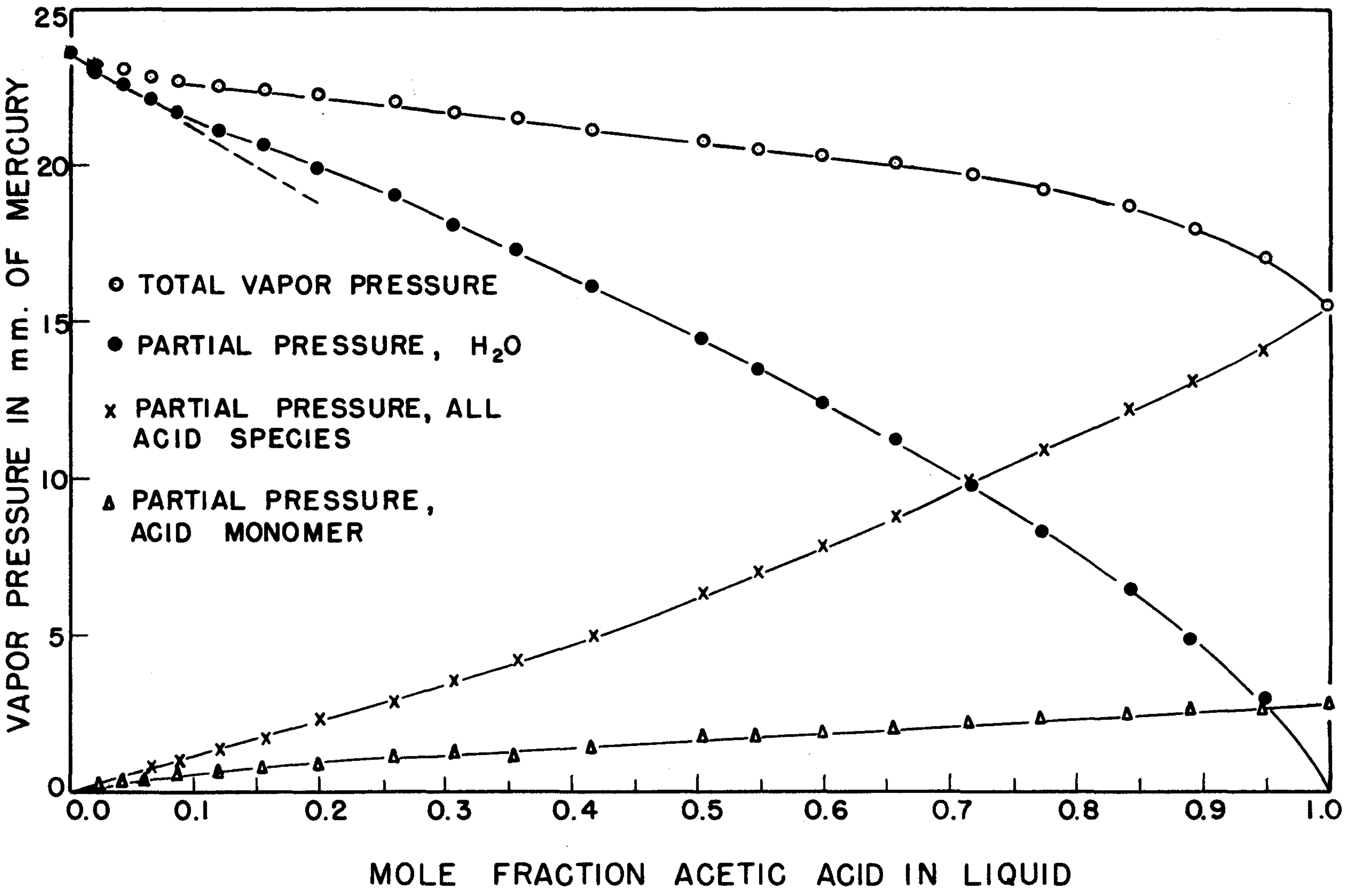

Figure 7. Vapor Pressures of Acetic Acid Solutions

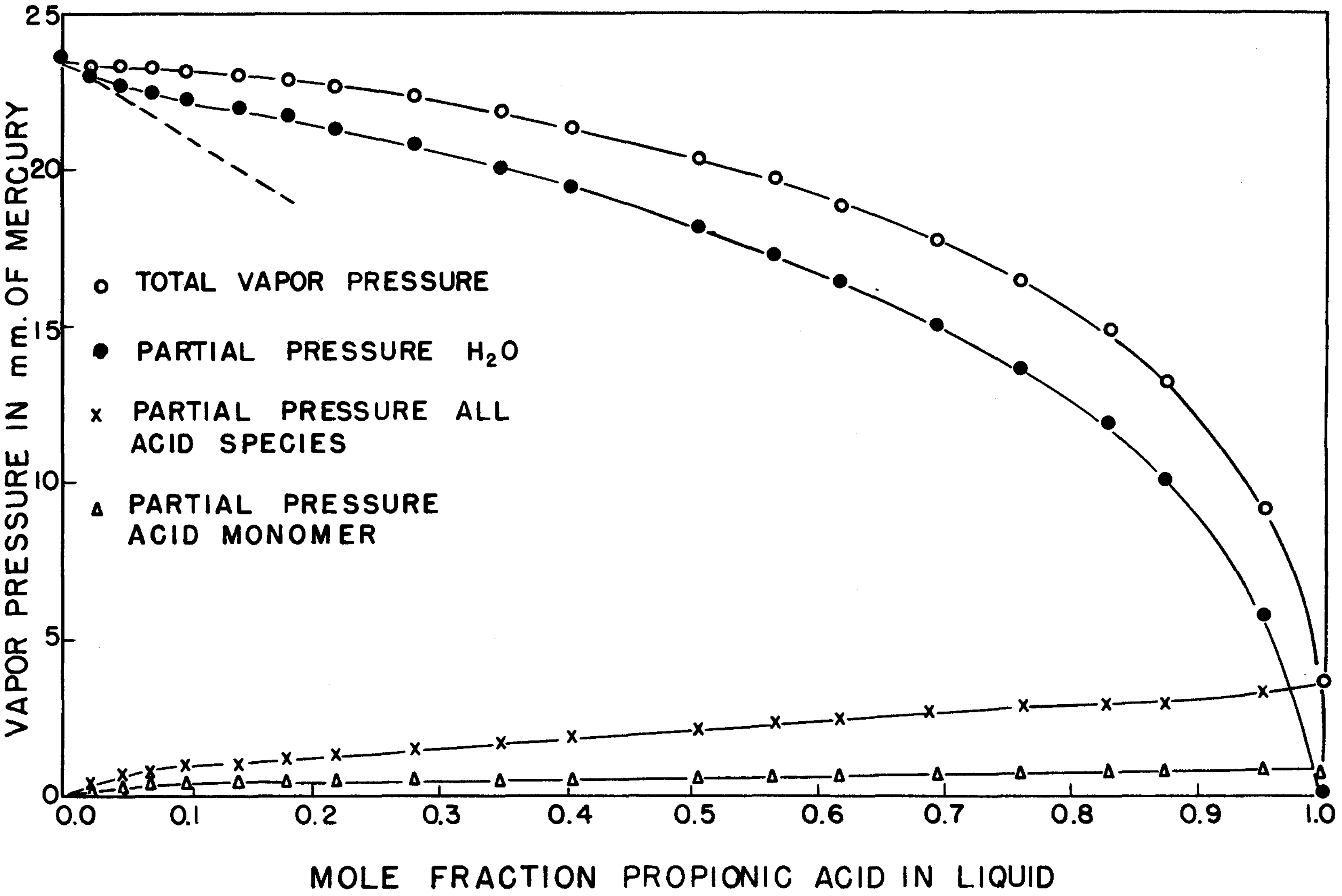

Figure 8. Vapor Pressures of Propionic Acid Solutions

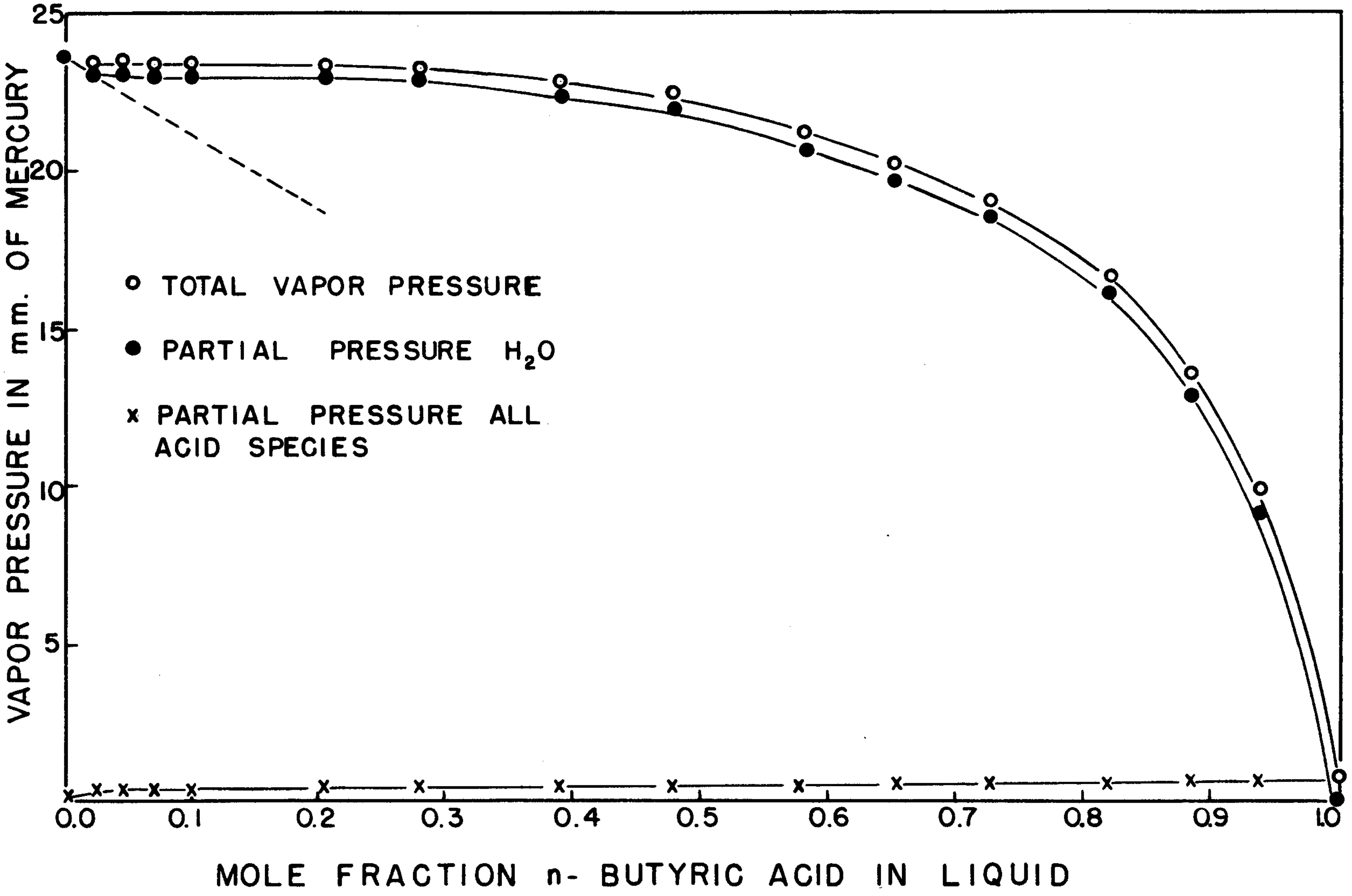

Figure 9. Vapor Pressures of n- Butyric Acid Solutions

Table 7

Reported Vapor Pressures at 25°C.

Component	Vapor Pressure	Literature Reference
Water	23.756 mm. Hg.	International Critical Tables (39)
	23.729	Osborne and Meyers (40)
	23.65	This Research
Methanol	126.6	Butler, Thomson and Maclennan (26)
	125.77	This Research
	124.4	Pesce (41)
	124.07	Young (23)
Ethanol	59.01	Dobson (25)
	58.90	Young (23)
	58.71	This Research
Propanol-1	21.76	Butler, Thomson and Maclennan (26)
	21.15	This Research
	20.53	Young (23)
	20.1	International Critical Tables (39)
Acetic Acid	15.64	Young (23)
	15.61	This Research
	14.6	Schmidt (42)
Propionic Acid	4.2	Schmidt (42)
	3.58	This Research
	3.0	Kahlbaum (43)
n- Butyric Acid	2.34	This Research (Measured)
	1.19	Kahlbaum (43) (Dynamic Method)
	0.93	Schmidt (42)
	0.728	This Research (Extrapolated)
	0.72	Kahlbaum (43) (Static Method)

activity coefficients of the respective components. This equation can be used to check the data for consistency, and can be used along with the experimental data to give the best possible activity curves from the knowledge at hand. When attempting to draw a curve through a set of experimental points which have some scatter, it is generally possible to draw quite a number of slightly different curves, none of which is unique. With the Duhem - Margules equation, it is possible to draw curves through the points which will at the same time be self-consistent and thus be the best curves fitting the data. The Duhem - Margules equation relates the slopes of the two experimental curves of a binary system. Matching slopes at points along two curves leads to much uncertainty, so it is best to have analytic expressions for the activity coefficients in terms of mole fractions to represent the experimental data. This enables the slopes to be calculated directly.

The Margules equation is an empirical equation which purports to represent the variation of vapor pressure with composition of liquid mixtures. To an approximation in which only leading terms are considered, it can be shown (3) that plots of log γ_1 versus X_2^2 and log γ_2 versus X_1^2 should lead to straight lines of equal slopes. For most systems, these straight lines are never found. However, the plots generally lead to quite smooth curves which suggested trying to fit these curves with empirical equations. The equations can be represented by,

$$\log \gamma_1 = X_2^2\, f(X_2) \quad \text{and}$$
$$\log \gamma_2 = (1 - X_2)^2\, g(X_2),$$

where $f(X_2)$ and $g(X_2)$ represent functions which are interrelated through the Duhem - Margules equation. Since in a binary system, $X_1 + X_2 = 1$, it follows that, $dX_1 = - dX_2$, so the Duhem-Margules equation, Equation 11, can be put in the form,

$$(1 - X_2)\, \frac{d \log \gamma_1}{dX_2} = - X_2\, \frac{d \log \gamma_2}{dX_2} .$$

From this it follows that

$$(1-X_2)\, [2X_2\, f(X_2) + X_2^2\, f'(X_2)] = - X_2 [-2(1-X_2) g(X_2) + (1-X_2)^2\, g'(X_2)] ,$$

from which by cancellation,

$$2f(X_2) + X_2\, f'(X_2) = 2g(X_2) - (1-X_2) g'(X_2) = G(X_2). \quad (12)$$

If one lets the function $g(X_2)$ be represented by a quadratic equation of the form,

$$g(X_2) = a + bX_2 + cX_2^2 \quad ,$$

it follows from Equation 12 that,

$$G(X_2) = 2a + 2bX_2 + 2cX_2^2 - (1-X_2)b - 2c(1-X_2)X_2 \ . \qquad (13)$$

Since,

$$\frac{d[X_2^2\ f(X_2)]}{dX_2} = 2X_2\ f(X_2) + X_2^2\ f'(X_2) \quad ,$$

if follows from Equation 12 and 13 that,

$$\frac{d[X_2^2\ f(X_2)]}{dX_2} = (2a-b)X_2 + (3b-2c)X_2^2 + 4cX_2^3 \quad ,$$

from which by integration and cancellation

$$f(X_2) = (a-\frac{b}{2}) + (b-\frac{2}{3}c)X_2 + cX_2^2 + \frac{I}{X_2^2} \qquad .$$

From the curves to be fitted, it was apparent that f(0) was finite, so the integration constant I was necessarily zero to avoid an infinite term. Thus the two equations which are related through the constants are,

$$g(X_2) = a + bX_2 + cX_2^2 \qquad \text{and} \qquad (14)$$

$$f(X_2) = (a- \frac{b}{2}) + b- \frac{2}{3}c)X_2 + cX_2^2 \ . \qquad (15)$$

If $g(X_2)$ is chosen as a linear function it can be seen that the lines must be parallel, and the intercepts related through the slope. This treatment can be extended to higher powers in X_2 and to analytic function other than polynomials.

When plots were made with the experimental data of the functions, log γ_1/X_2^2 and log γ_2/X_1^2, against the mole fraction of the organic component X_2, the alcohol systems were found to give near straight lines or else parabolic segments which had a small curvature. Each acid system gave two curves which were nearly parabolic in shape. In Figure 10 is shown the above mentioned plot for the aqueous ethanol system and Figure 11 the same for the aqueous acetic acid system. The straight lines drawn through the points in the ethanol system are believed to be the best fit to the data with the constraint required by the Duhem-Margules equation, thus making the lines self-consistent. For the acetic acid system, two sets of parabolic equations were fitted to the data; one set for the range 0 to 0.65 mole fraction acid the other set for the remainder of the range. (Two sets were used because it was found to be impossible to fit the data with one set of quadratic equations for the entire range.) An estimation of the expected experimental error is shown in each graph. In all cases, the experimental scatter was less for the solute, (component present in amount less than 0.5 mole fraction) so the constants of the functions were determined from these regions.

Table 8 shows the constants obtained for the various systems, where the subscript A refers to either alcohol or

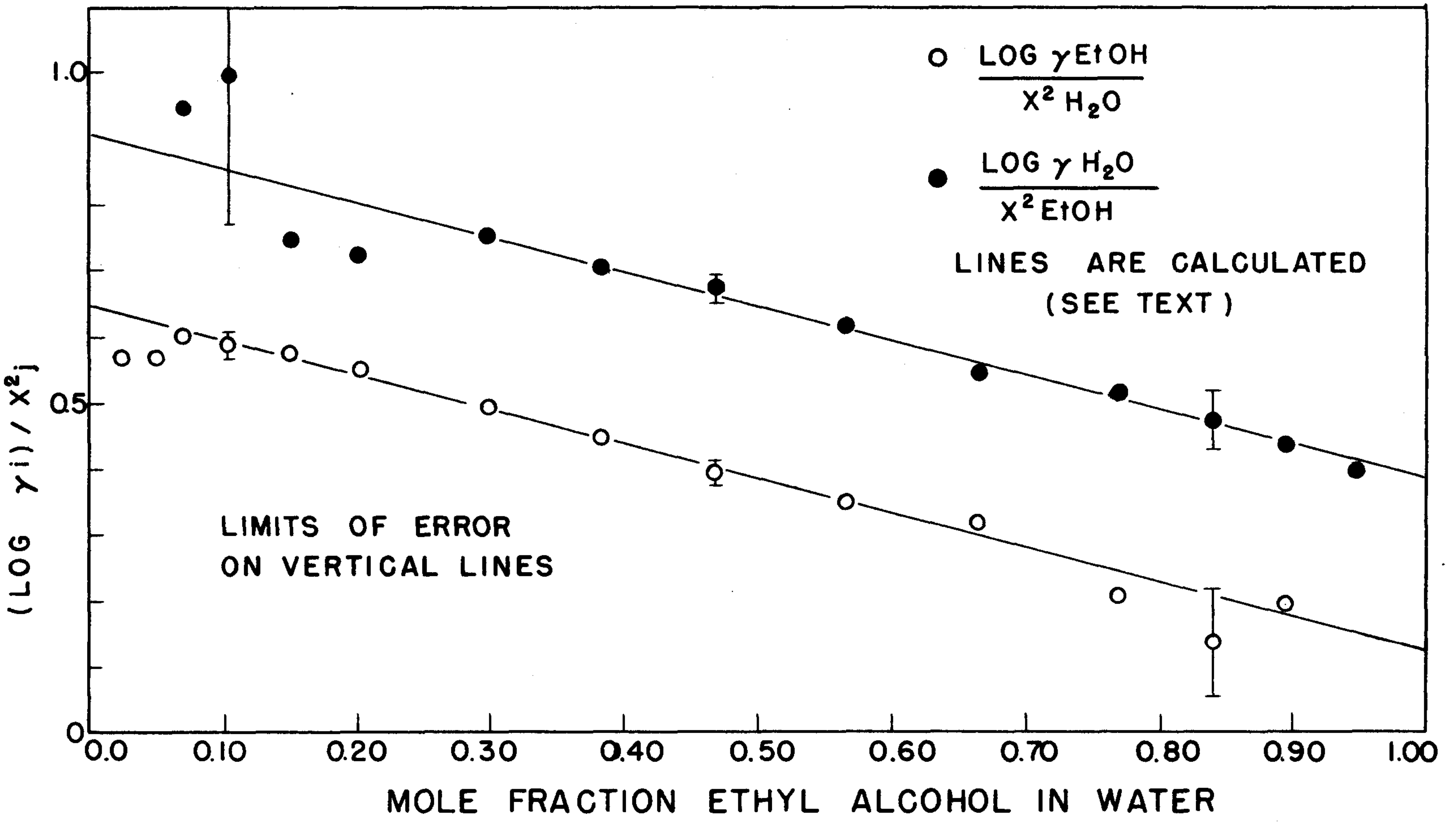

Figure 10. Self-Consistent Functions for Ethyl Alcohol and Water

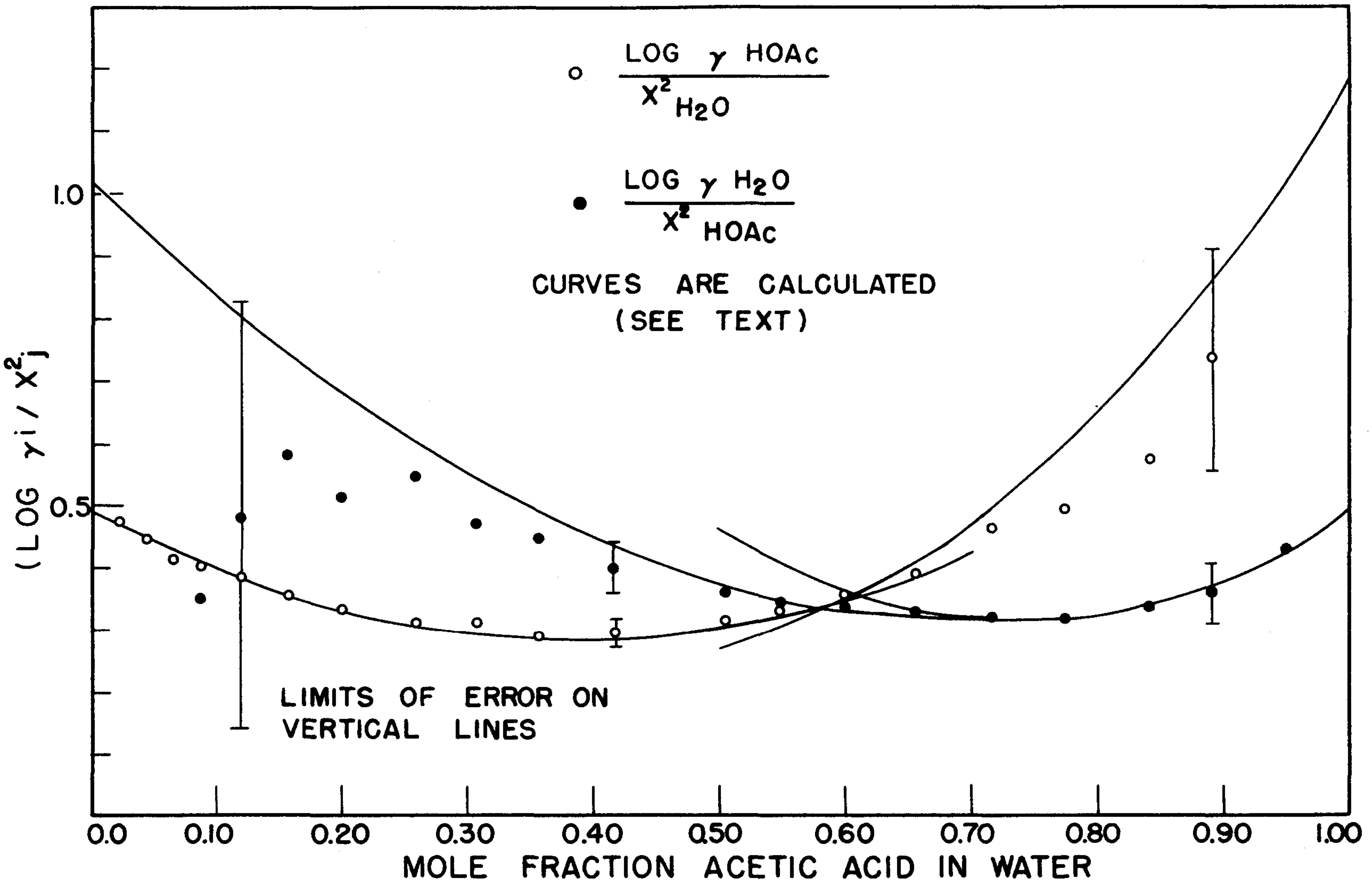

Figure 11. Self-Consistent Functions for Acetic Acid and Water

Table 8

Constants of Analytic Expressions for The Activity Coefficients

$(\log \gamma_A = (1 - X_A)^2 (a + bX_A + cX_A^2))$

Aqueous System	a	b	c	Range of Concentration (Mole Fraction)
Methanol	0.180	0.360	0.737	0.0 - 1.00
Ethanol	0.646	-0.521	0	0.0 - 1.00
Propanol-1	1.200	-2.50	0	0.0 - 0.15
	1.069	-1.76	1.23	0.15 - 0.55
	0.980	-0.860	0	0.55 - 1.00
Acetic Acid	0.492	-1.06	1.37	0.0 - 0.65
	0.680	-2.14	2.64	0.65 - 1.00
Propionic Acid	1.07	-2.81	4.46	0.0 - 0.40
	0.948	-1.75	2.32	0.40 - 1.00
n- Butyric Acid	1.57	-7.33	18.3	0.00 - 0.22
	1.30	-2.79	3.54	0.22 - 0.50
	1.26	-2.20	2.41	0.50 - 1.00

or acid. All the equations have been made self-consistent over the range of concentration indicated in the table. Of course, by knowing the constants for the activity coefficients of the acids or alcohols, those for the water can be readily calculated from Equation 15.

By using these equations, activities can be obtained. Figures 12 and 13 are plots of the activities of the components against the mole fraction of either alcohol or acid. The smoothed curves have been calculated from the equations for the self-consistent curves and the points are experimental from this research. In the case of aqueous methanol solutions, the experimental points of Butler, Thomson, and Maclennan (26) have been included for comparison. The data of Jones and Bury (18) on the activities of the acids in aqueous solution at 0°C. are included for comparison on Figure 13. Their data were obtained by a freezing point depression technique. Their standard state was taken such that the activity of the acid and water were unity in a one molar solution of the acid. Their activities are readily reduced to the standard state used in this research. The chemical potential of a component must be the same at any one concentration, regardless of the standard state chosen. Thus

$$\mu_1^\circ + RT \ln a_1 = \mu_1^{\circ *} + RT \ln a_1^*$$

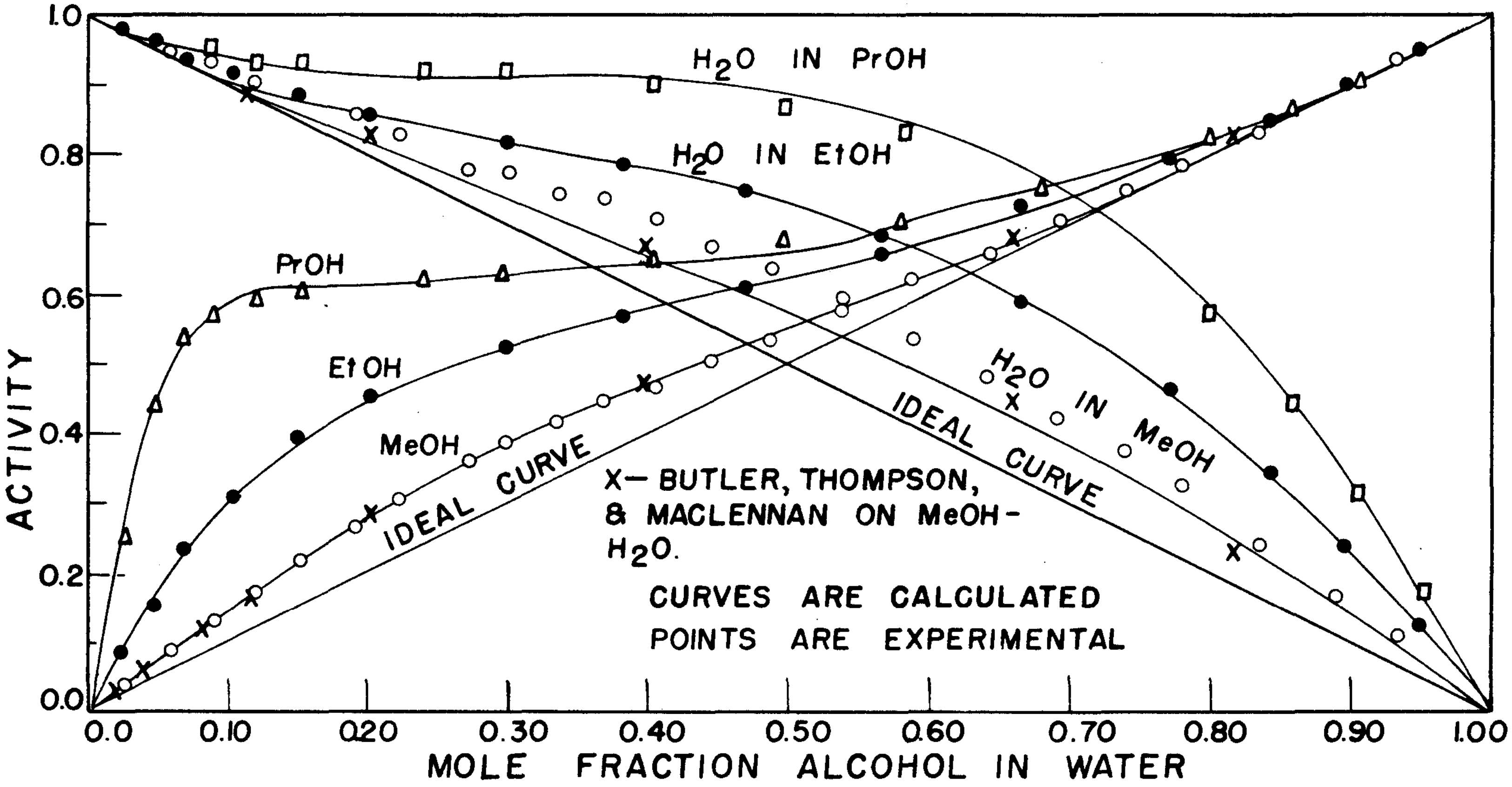

Figure 12. Activity Curves and Experimental Points of the Aqueous Alcohol Solutions

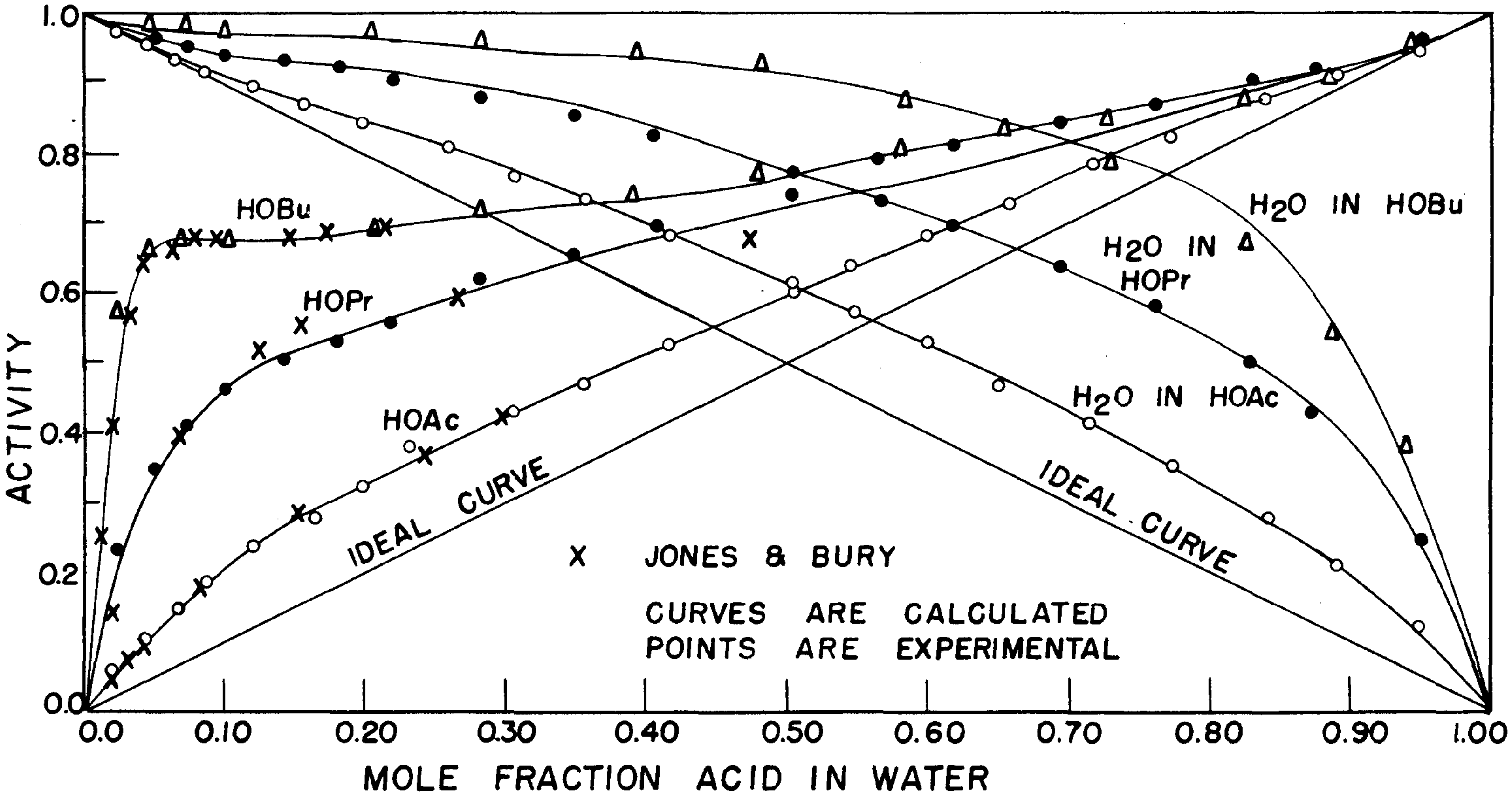

Figure 13. Activity Curves and Experimental Points of the Aqueous Carboxylic Acid Solutions

where the asterisk represents a different choice of standard state. This can be cleared of logarithms and rewritten as,

$$a = a^{*} \exp. \frac{\mu_i^{o*} - \mu_i^{o}}{RT} \quad . \tag{16}$$

Equation 16 shows that the activities differ by a multiplicative constant at any one temperature. By knowing the activity at any one concentration under both choices of standard state, the multiplicative constant can be readily determined. Actually for the comparison of the acids, the difference in temperature at which the two investigations were conducted is ignored. This would tend to make the comparison not strictly justified, but it was the best work available for comparative purposes.

The final results as reported for the aqueous n-butyric acid system would not be altered significantly if the trimer of the acid were included in the calculation of partial pressures. In the first place, its contribution to the total vapor pressure would be immeasurably small under the experimental arrangement. Its inclusion would alter the water partial pressures insignificantly which would leave the water activities unchanged from the values reported in Table 6. By using the trimer, the monomer partial pressure would be less than the values reported. However, both the partial pressure of the monomer above the solution and above the pure acid would be decreased so the ratio in the activity calculation would not be greatly changed.

The data reported for the aqueous methanol system were not consistent under the treatment given. Since it was the first system run, it is possible that the technique was not too well mastered at that time. The methanol - water system is the poorest of the systems run from an analytical standpoint, as the refractive index changes quite slowly with concentration changes.

VI. DISCUSSION

A. Specific Interactions at Infinite Dilution

An ideal solution is one in which all components obey Raoult's law at all concentrations, temperatures, and pressures, i.e., the activity of each component referred to a standard state of pure liquid component, is equal to its mole fraction and its activity coefficient is always one. It follows from straightforward thermodynamic arguments (see, for example, Hildebrand and Scott (10)), that the enthalpy and volume changes in the formation of an ideal solution from its components must be zero. The converse cannot be proven thermodynamically, although it is readily shown that if the enthalpy and volume changes in the formation of an ideal solution from its components are zero, then the activity coefficients are functions of concentrations only and are independent of pressure and temperature if standard states are selected at the same temperature and pressure as the solution of interest. It is also an experimental fact that negligible enthalpy and volume changes on mixing are usually associated with negligible deviations from Raoult's law, and in the case of solutions whose molecules are all of the same size this observation can be explained statistically (6).

Modern statistical theories of solutions are predominately based on lattice models of the liquid state. If in a binary solution component molecules are interchangeable in the lattice, then for the purposes of these theories the molecules are of the same size and the theory simplifies very considerably. Such solutions are called "regular" (6). For the present, it need only be noted that except for specific interaction entropies (Guggenheim formally neglects these, but this neglect is not necessary to his argument), the entropy change in the formation of such a solution from its components is ideal. This permits a straightforward identification of terms in the expression for the chemical potential of component i as follows:

$$\mu_i = \mu_i^o + RT \ln X_i + RT \ln \gamma_i ,$$

where

μ_i^o = chemical potential of pure liquid i at the temperature and pressure of the solution,

$RT \ln X_i$ = contribution to the chemical potential arising from the free energy of mixing of non-interacting components,

and

$RT \ln \gamma_i$ = contribution to the chemical potential arising from specific interactions.

In Guggenheim's treatment, the last term is attributed entirely to specific interaction energies.

No rigorous usable statistical treatment of binary solutions has been achieved for the case where component molecules are not interchangeable in the lattice model, as is the case when the molecules differ appreciably in size. It may be expected that the entropy of mixing is not ideal. Expressions for this quantity have been derived in very special cases by Guggenheim (6) but relevance of model and validity of approximations are questionable. Notwithstanding, an identification of terms in the chemical potential can be made which is identical to that made in the case of regular solutions, except that the term RT ln γ_i must now include a contribution arising from non-ideality in entropy of mixing of molecules differing in size.

In particular, the quantity

$$\lim_{X_i \to 0} \left(RT \ln \gamma_i \right)$$

represents the difference per mole in specific free energy of interaction between a molecule of component i and neighbors consisting wholly of the second component of the binary solution on the one hand; and between a molecule of component i and neighbors consisting wholly of component i on the other hand, plus a contribution due to abnormal partial molar entropy resulting from unequal molecular sizes. This treatment has been followed by Butler, Thomson and Maclennan (26) who tabulated their results for aqueous alcohol solutions in the form

$$(\mu_1^\circ)_j - \mu_1^\circ = RT \ln \gamma_1^\circ \quad . \qquad (16)$$

in which

$$\gamma_1^\circ = \lim_{X_1 \to 0} \gamma_1 \, ,$$

and

$(\mu_1^\circ)_j$ = chemical potential of i in a hypothetical state in which component i has mole fraction of unity, but activity coefficient is the same as at infinite dilution. This form is suggested by treatments of activity coefficients in standard texts on thermodynamics, for example Klotz (44).

From the constants to the equations given in Table 8, these extrapolations are easily made for systems which have been determined. Butler, Thomson, and Maclennan have already reported values for the limiting activity coefficient at infinite dilution and for the specific free energy effect. They determined these quantities for the aqueous systems of methanol, ethanol, propanol-1, and butanol-1 by direct measurement, and for the other normal alcohols through octanol-1 by solubility determinations. They then assumed that the activity coefficient of the immiscible alcohols at infinite dilution was equal to the following ratio;

$$\gamma_1^\circ = \frac{1}{X_1} \, ,$$

where X_1 is the solubility of the alcohol in the water rich phase. This assumption is not valid when one of the components is appreciably soluble in the other. Most of the immiscible alcohols and acids are soluble in water to a very small extent on a mole fraction basis. However, the reverse is not true, as water is quite soluble on a mole fraction basis in many of the organic solvents. The assumption above requires that the activity of the solute be unity in the saturated solution, and this is insufficiently accurate unless both regions of miscibility are very limited.

The activities of a given component in two phases coexisting in equilibrium must be the same. Let X_1 and X_1' be the mole fractions of, for example, a slightly soluble alcohol in the water rich and alcohol rich phases, respectively, and γ_1 and γ_1' the corresponding activity coefficients. Then

$$\gamma_1 X_1 = \gamma_1' X_1'$$

Now if X_1 is sufficiently small, $\gamma_1 \approx \gamma_1^\circ$; data obtained in this work indicate that with the systems studied this approximation is valid to within 2 per cent if $X_1 < 0.02$. If $X_1' \approx 1$, then by definition $\gamma_1 \approx 1$, and so

$$\gamma_1^\circ \approx 1/X_1 \quad .$$

This is the treatment adopted by Butler, Thomson and

Maclennan. For the aqueous solutions of aliphatic alcohols and acids if $X_i' < 1$, then $\gamma_i' > 1$, so that $\gamma_i' X_i'$ will more nearly approximate unity than X_i' alone.

There appears, however, to be a more straightforward way of approximating $\gamma_i' X_i'$ than Butler, Thomson, and Maclennan used. Based on plots of activity as function of mole fraction available for the soluble homologues, it is possible to estimate activities at given mole fractions for the higher homologues, and in particular to estimate the activity at the mole fraction X_i'. For example, in the case of n- valeric acid, $X_i' = 0.505$. At this mole fraction, activities of acetic acid, propionic acid, and n- butyric acid in aqueous solution are 0.60, 0.72, and 0.78 respectively. The activity of n- valeric acid was estimated as 0.82 by graphical extrapolation, which appeared reliable to within 2 per cent.

Estimation of the activity coefficient of water in the limit as its mole fraction approached zero, in the slightly soluble systems, was rendered difficult by the fact that in none of the systems was X_W' sufficiently small to permit the assumption that $\gamma_W' \approx \gamma_W^\circ$. On the other hand, the approximation $\gamma_W' X_W' \approx 1$ was satisfactory to within 2 per cent for all of the slightly soluble systems. Knowledge of X_W' therefore sufficed to establish γ_W' and a_W' at one mole fraction, namely X_W'. A curve through this point similar to the activity diagrams of the lower homologues could then be drawn and γ_W^o estimated from this curve. The objectivity of this method was rather unsatisfactory, and comparison with results obtained by other extrapolation methods indicates that values of γ_W^o tabulated for slightly soluble systems should be considered uncertain to about 20 per cent. The value of γ_W^o in the butanol-1 - water system, however, is available from data of Butler, Thomson and Maclennan, and is considerably more certain.

Table 9 shows the solubilities of the various organic solutes in water and of water in the organic solvents as determined by Craig (9) and Hansen (45). The solubilities shown in the table agree very well with those determined by Butler, Thomson and Maclennan.

Table 10 shows the extrapolated values of the activity coefficients of the various components at infinite dilution, the difference in specific free energy effect as calculated from Equation 16, and the increase in this specific free energy effect Δ between successive members of each homologous series.

The increase Δ is a measure of the change an additional methylene group makes on the specific free energy effect. The average value of the quantity Δ for the alcohols in water is 760 calories and for the acids in water 790 calories. This would tend to show a relatively constant contribution for each methylene group in each system, as the estimation error for the activities of the higher homologues could account for the slight difference in average values.

Table 9

Solubilities of Alcohols and Acids in Water and Water in Alcohols and Acids at 25°C.

Organic Component	Mole Fraction Organic Component in Water-Rich Phase	Mole Fraction Water in Organic-Rich Phase
Butanol-1	0.0188	0.513
Pentanol-1	0.00498	0.371
Hexanol-1	0.00107	0.311
Heptanol-1	0.000268	0.263
n- Valeric Acid	0.006915	0.495
n- Caproic Acid	0.001593	0.282
n- Heptylic Acid	0.0003899	0.171

The value of Δ for water is much higher between methanol and ethanol than between ethanol and propanol-1. Similarly, the value of Δ is much higher between acetic acid and propionic acid than between propionic acid and n- butyric acid. Values of Δ between higher successive homologues appear to be about 200 in both acid and alcohol systems, but as previously explained, uncertainties in γ_W^{o} for the immiscible systems are such that inference of a

Table 10

Activity Coefficients and Standard Free Energies of Alcohols and Acids in Water, and of Water in Alcohols and Acids, at Infinite Dilution

System	γ_i°	$(\mu_i^\circ)_j - \mu_i^\circ$	Δ
Methanol in Water	1.48	232 cal.	—
Ethanol in Water	4.43	884	652 cal.
Propanol-1 in Water	15.9	1640	756
Butanol-1 in Water	42	2200	560
Pentanol-1 in Water	161	3020	820
Hexanol-1 in Water	795	3960	940
Heptanol-1 in Water	3260	4800	840
Water in Methanol	1.30	156	—
Water in Ethanol	2.43	526	370
Water in Propanol-1	3.55	752	226
Water in Butanol-1	4.80	930	178
Water in Pentanol-1	6.60	1120	210
Water in Hexanol-1	9.20	1320	200
Water in Heptanol-1	13.00	1540	220
Acetic Acid in Water	3.11	672	—
Propionic Acid in Water	11.8	1460	790
n- Butyric Acid in Water	37.2	2150	690
n- Valeric Acid in Water	120	2840	700
n- Caproic Acid	565	3760	920
n- Heptylic Acid	2400	4620	860
Water in Acetic Acid	3.09	670	—
Water in Propionic Acid	6.93	1150	480
Water in n- Butyric Acid	9.13	1310	160
Water in n- Valeric Acid	12.2	1480	170
Water in n- Caproic Acid	17.0	1680	200
Water in n- Heptylic Acid	24.0	1890	210

limiting increment is not justified.

The specific free energy effect tabulated in Table 10 as $(\mu_i^\circ)j-\mu_i^\circ$ is a measure of change in free energy of contacts when a molecule of i is removed from neighbors of its own kind and surrounded with molecules of the second component in the binary solution. The progression of this quantity along a homologous series has already been discussed. Comparison of values for acids and alcohols may be of some interest.

The specific free energy effect for an acid was in general approximately 200 calories less than for the alcohol containing the same number of carbon atoms. This appears most simply explained by assuming a stronger interaction between water and the $-COOH$ group than between water and the $-CH_2OH$ group, which is consistent with reasonable hydrogen bonding. The nearly constant difference in interaction energy would then be expected.

The specific free energy effect for water is considerably larger in acids than in the corresponding alcohols. The effect in acetic acid is 144 cal greater than in ethanol, and in higher acids the effect is 350 - 400 cal greater than in the corresponding alcohols. It is probable that these differences reflect the different manners of association of alcohols and acids. Work on the structure of alcohols has been summarized by Glasstone (7); each alcohol molecule tends to coordinate through hydrogen bonding to two neighboring alcohol molecules to form a net (distorted two dimensional lattice). On the other hand, the fatty acids are extensively dimerized (7), and the dimers tend to cluster in approximately parallel chains. In evaluating the specific free energy effect for water in systems of this sort, factors to be considered are 1) the extent to which the water tends to break up the structure

2) the extent to which water is compelled to coordinate methylene (low interaction energy) rather than carboxyl or hydroxyl groups (higher interaction energy).

The specific free energy effects for water suggest that the carboxyl groups in the dimerized fatty acid "log piles" are less available than the hydroxyl groups in the more open alcohol structure. In the lowest homologoues the hydrocarbon chain is insufficient in length to lead to strong "log piling" through van der Waals forces, and the difference between acid and alcohol is therefore less pronounced.

B. Concentration Dependence of Activity Coefficients

No useable theory of concentration dependence of activity coefficients in binary solution exists for the general case of associating molecules of different sizes.

An understanding of some of the factors involved however, can be gained from an approximate treatment of binary solutions of non-associating molecules of the same size (so-called regular solutions). The following treatment parallels that of Guggenheim (6).

Consider a solution of A and B molecules; let Z be the coordination number of A molecules and B molecules (assumed identical), let ε_{AA}, ε_{AB}, and ε_{BB} be the standard molecular free energies of AA, AB, and BB contacts, and assume that AA, AB, and BB contacts are formed absolutely at random. Let N_A and N_B be the number of A and B molecules and X_A the mole fraction of A molecules. Then the number of contacts of each type will be:

$$\begin{aligned} AA &: \quad 1/2\ ZN_AX_A \\ AB &: \quad ZN_AX_B = ZN_BX_A \\ BB &: \quad 1/2\ ZN_BX_B \quad . \end{aligned}$$

The excess free energy of mixing, i.e., the free energy in excess of the ideal free energy of mixing, is therefore,

$$\Delta F_e = Z\left\{1/2 N_AX_A\ \varepsilon_{AA} + N_AX_B\ \varepsilon_{AB} + 1/2\ N_BX_B\ \varepsilon_{BB}\right\} - Z\left\{1/2\ N_A\ \varepsilon_{AA} + 1/2\ N_B\ \varepsilon_{BB}\right\} \quad .$$

Setting $N = N_A + N_B$, $N_A = X_AN$, $N_B = X_BN$, and $X_B = 1 - X_A$;

$$\begin{aligned} \Delta F_e &= 1/2N\ ZX_A(1-X_A)\ (2\ \varepsilon_{AB} - \varepsilon_{AA} - \varepsilon_{BB}) \\ &= NZX_A(1-X_A)\ w, \qquad (17) \end{aligned}$$

in which $$w = \mathcal{E}_{AB} - \frac{\mathcal{E}_{AA} + \mathcal{E}_{BB}}{2} ,$$

or

$$\Delta F_e = Zw \left[\frac{N_A N_B}{(N_A+N_B)} \right] .$$

Then

$$\overset{\approx}{F}_{Ae} - \overline{F}_A^{\circ} = \left(\frac{\partial \Delta F_e}{\partial N_A} \right)_{N_B} = Zw \left\{ \frac{N_B}{(N_A+N_B)} - \frac{N_A N_B}{(N_A+N_B)^2} \right\}$$

$$= ZwN_B \left\{ \frac{N_A+N_B-N_A}{(N_A+N_B)^2} \right\}$$

$$= Zw\ (1-X_A)^2 ,$$

where $\overset{\approx}{F}_{Ae}$ is the partial molecular excess free energy of A at mole fraction X_A and $\overline{F}_A^{\circ}$ is the chemical potential of pure liquid A. Hence,

$$RT \ln \gamma_A = N_0\ Zw(1-X_A)^2$$
$$= (1-X_A)^2 W$$

in which $W = N_0 Zw$ and N_0 is Avogadro's number. By similar reasoning or by application of the Duhem - Margules equation, it is easily shown that

$$RT \ln \gamma_B = X_A^2\ W ,$$

the values of W being identical. The condition for ideality of such regular solutions is evidently

$$W = 0,$$

$$\text{i.e.,} \quad \mathcal{E}_{AB} = \frac{\mathcal{E}_{AA} + \mathcal{E}_{BB}}{2} \; ,$$

for which it is sufficient that $\mathcal{E}_{AA} = \mathcal{E}_{BB} = \mathcal{E}_{AB}$, but not necessary as is sometimes assumed.

Refinements of the treatment outlined above have been carried out, and are summarized by Guggenheim (6). Basically, refined treatments of regular solutions involve approximations to account for the fact that neighbors of an A molecule are not selected completely at random but reflect preference for those contacts with strongest interaction energy. The refined theories approach that presented for small values of W, and since solutions investigated in this work are not regular, no useful purpose is served by further discussion of refined theories of regular solutions.

Superlattice treatments of solutions of molecules differing markedly in size, but in which the larger molecule can be considered composed of elements each of which is interchangeable in the superlattice with the smaller molecules, have been carried out by Guggenheim and others, and are reviewed by Guggenheim (6). The treatments used lead to marked deviations from ideality in entropy of mixing, reflecting mixing elements rather than molecules in combinatory formulae. Experimental data suitable for treatment according to these theories are limited, but results have not been encouraging. In particular, Hildebrand and Sweny (46) found that solutions of n- hexane and n- hexadecane were virtually ideal, the abnormal entropy predicted failing to appear. Hildebrand and Sweny suggested that the hydrocarbons tend to form linear chain arrangements, and Hildebrand (47) comments that for substances not too different in molar volume the entropy of mixing appears to be nearly ideal in general.

Further evidence as to the inapplicability of formulae developed by Guggenheim and others is furnished by the regularity of plots of $(\log \gamma_A)/(1-X_A)^2$. With the possible exception of the n- butyric acid - water system, these plots showed no singularities in the range $0 \leqslant X_A \leqslant 1$. The activity coefficient can be obtained from Formula 11.08.5 of Guggenheim (6) expanded to first order terms in the parameter W, and its logarithm can be shown to have a first order zero at $X_A = 0$. The quantity $(\log \gamma_A)/(1-X_A)^2$ should therefore have a first order pole at $X_A = 0$, contrary to the observed regularity of this plot.

The nature of the $\log \gamma_A/(1-X_A)^2$ plots suggests a treatment of concentration dependence of activity coefficient which appears qualitatively reasonable.

Data herein observed can be represented by,

$$\log \gamma_A = (1-X_A)^2 \; g(X_A)$$
$$\log \gamma_W = X_A^2 \; f(X_A) \quad ;$$

leading to an excess free energy of mixing of the form

$$\Delta F_e = RT \; X_A(1-X_A) \; [(1-X_A)g(X_A) + X_A \; f(X_A)] \; .$$

The corresponding expression for regular solutions from Equation 17 is,

$$\Delta F_e = N_0 Z \; X_A(1-X_A) \; w$$
$$= X_A(1-X_A) \; W$$

in which $W = N_0 Z w$.

If W_{eff} is defined by,

$$W_{eff} = RT \left\{ (1-X_A) \; g \; (X_A) + X_A \; f(X_A) \right\} \quad , \qquad (18)$$

then for actual solutions

$$\Delta F_e = X_A(1-X_A) \; W_{eff} \; ,$$

and the deviation of actual solutions from regularity can be discussed in terms of the variation of W_{eff}.

In general, $g(X_A)$ was of the form

$$g(X_A) = a + bX_A + cX_A^2 \quad ;$$

the Duhem - Margules equation then requiring that

$$f(X_A) = (a - b/2) + (b - 2/3c)X_A + cX_A^2 \quad .$$

Substitution in Equation 18 then leads to

$$\frac{W_{eff}}{RT} = a + bX_A/2 + cX_A^2/3 \quad .$$

The variation of W_{eff}/RT with concentration for the aqueous - alcohol and aqueous acid systems is presented graphically in Figure 14. The following observations are immediately apparent:

1. At low mole fractions of organic component, values of W_{eff} decrease with increasing mole fraction of organic component. The system methanol - water is a possible exception. The slope is more negative the higher the position in the homologous series.
2. Initial slopes in alcohol - water systems are nearly the same as those of fatty acid-water systems with a corresponding number of carbon atoms. Intercepts at $X_A = 0$ in alcohol - water systems are higher by nearly constant amounts than those of acid - water systems of corresponding numbers of carbon atoms.
3. W_{eff}/RT is a monotonically decreasing function of X_A over the entire concentration range in alcohol - water systems, but increases with X_A at higher values of X_A in the acid - water systems.

The following explanations for these observations are advanced:

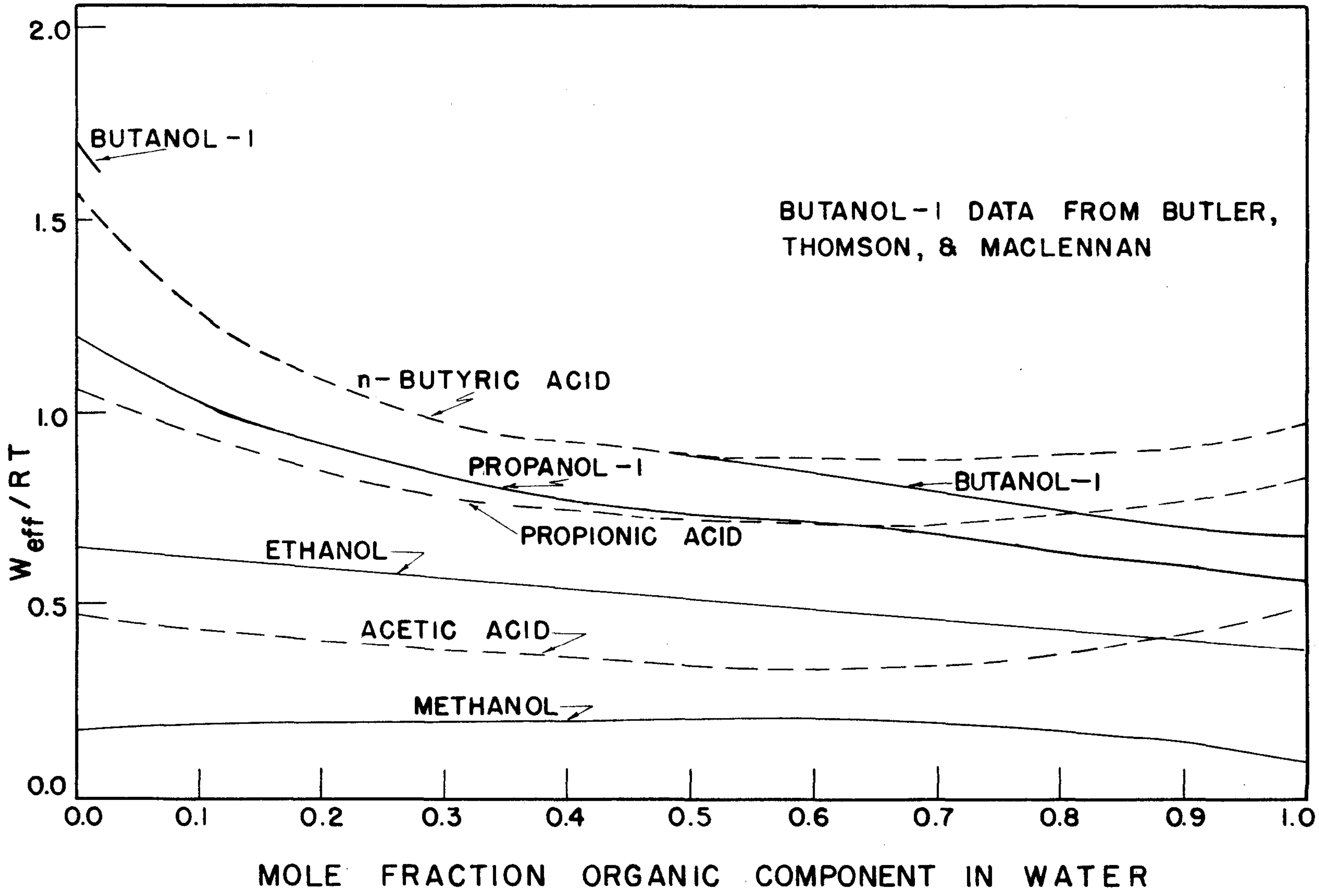

Figure 14. Variation of W_{eff}/RT with Concentration of Various Organic Components

1: Liquid water may be assumed to have a structure somewhat similar to that of ice, with each water molecule tetrahedrally coordinated to four nearest neighbors through hydrogen bonds. While of course the long range order is less than that of ice, assumption of a considerable degree of long range order in liquid water is reasonable.

A secondary effect of addition of comparatively large organic molecules is to break up the long range water structure, so that in addition to replacing water-water contacts with lower energy water-hydrocarbon contacts there is a small but uncompensated loss in energy through hydrogen bond ruptures in the destruction of long-range order. This effect should be greater, the greater the degree of long range order (i.e., the lower the mole fraction of organic component) and the longer the hydrocarbon chain.

2. The effect of destruction of long range order in acid-water systems should be nearly the same as in alcohol-water systems of the same number of carbon atoms, but at low values of X_A, W_{eff}/RT for the acid should lie below W_{eff}/RT for the corresponding alcohol because the bonding of water to a carboxyl group is stronger than that of water to a hydroxyl group. The difference should therefore be nearly constant, reflecting a

constant difference in the interaction energy between water and carboxyl groups on the one hand and between water and hydroxyl groups on the other hand. The initial slopes of alcohol - water and acid - water systems of the same number of carbon atoms should be nearly the same, reflecting similar secondary effects of the hydrocarbon chains in destroying long-range water structure.

3. At high mole fractions of organic component, variation in W_{eff} will reflect the effect of water on long range structure, if any, in the organic component. Structures of liquid alcohols and fatty acids have already been discussed. In the alcohol systems, the structure is predominately determined by hydrogen bonding, each alcohol molecule being coordinated to two neighbors to form two dimensional nets. At least for lower homologues, it can be expected that cohesion between hydrocarbon chains will not be optimum, since packing of these chains must be secondary to hydrogen bonding requirements. The structure can be therefore considered somewhat open, and the water presumably could replace hydroxyl groups in the structure without extensive disarrangement of order or hydrocarbon chain cohesion. Failure of W_{eff} to increase with X_A at high X_A in alcohol water systems follows reasonably from the above discussion.

On the other hand, the tendency of fatty acids to dimerize and of the dimers to "log-pile", has already been mentioned. Cohesion of hydrocarbon chains is expected to be much stronger, therefore, in the acid - water systems. Increase in W_{eff}/RT at high X_A can therefore be explained either by assuming water to be effective in destroying long range ordering of hydrocarbon chains, or, more simply, by assuming that coordination of water to carboxyl groups and consequent dimer rupture leads also to a small number of uncompensated ruptures of hydrocarbon-hydrocarbon contacts.

It would be interesting to examine the qualitative explanation of variation of excess free energy of mixing herein presented, in the light of enthalpy, entropy, and molar volume data. Reasonably accurate enthalpy and partial molar volume data are available for the ethanol - water system. However, reasonably accurate enthalpy data and rather poor molar volume data are available for the acetic acid - water system. In both systems, mixing is accompanied by a dimunition of volume over the entire concentration range. Mixing of ethanol and water is exothermic over the entire concentration range; mixing of acetic acid and water is exothermic if the mole fraction of acetic acid is less than 0.111 and endothermic otherwise. In both systems, the excess entropy of mixing is negative over the entire concentration range.

The existence of negative excess entropies of mixing with positive excess free energies of mixing is puzzling, and leads one to seek an explanation of the former in an effect which would have little influence on the latter. It can be predicted, confidently, that a quantitative explanation when found will not be simple, but it seems reasonable to correlate the negative excess entropy with the volume contraction.

The mixing of two components to form a solution can be imagined as a two-step process: first, the mixing of the components of solution without any shrinkage of total volume, and second, a volume contraction. Let it be assumed that the free energy of the system at the end of step 1 is substantially the equilibrium free energy and that the entropy change in step 1 is the ideal entropy of mixing. It is entirely possible that step 2 could occur with negligible free energy change but with marked enthalpy and entropy changes.

The possibility of this occurence is perhaps most simply illustrated by the van der Waals liquid. For step 2

$$\begin{aligned} \Delta F &= \Delta U + \Delta(PV) - T\Delta S \\ &= \Delta U - T\Delta S \end{aligned}$$

neglecting the $\Delta(PV)$ term in the condensed system. Where

V_i and V_f are initial and final volumes in the concentration process,

$$\Delta F = \frac{a(V_f - V_i)}{V_f V_i} - RT \ln \frac{V_f - b}{V_i - b} .$$

The first term on the right is ΔU, the second $(-T\Delta S)$; evidently ΔU and $T\Delta S$ are both negative if $V_f < V_i$; if they were nearly equal the free energy change could be negligible even if both entropy and enthalpy changes were appreciable.

In general, the equilibrium configuration of a system corresponds to a minimum free energy, and not necessarily to a minimum enthalpy or a maximum entropy. This point is illustrated in Figure 15.

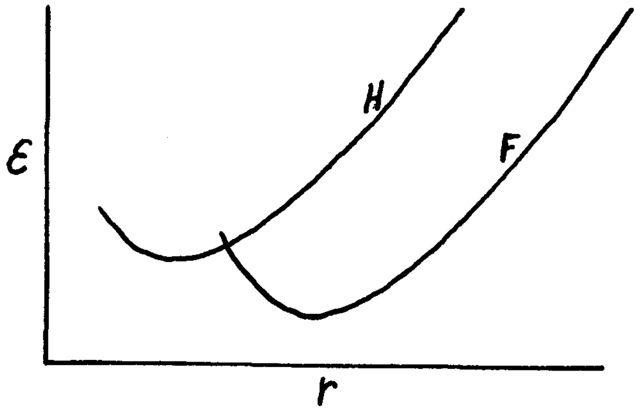

Figure 15. Free Energy and Enthalpy Potential Curves.

With regard to the systems of interest, volume contraction will certainly be accompanied by negative enthalpy and entropy changes of the order of magnitude observed; these changes will not, however, be well represented in general by van der Waals or similar equations of state.

C. Evaluation of Measurement Procedure Developed

1. Discussion of errors

The author believes the method described herein could be made quite free of errors without too much additional work or care. One of the greatest sources of error was the impurity of the materials used for preparing samples and standard solutions. Minor impurities were not troublesome if the solution had a high vapor pressure so that the impurity would contribute only to a small portion to the total vapor pressure. If the impurity should have a refractive index much different from that of either of the solution components, interferometric analyses could be incorrect by a significant amount. In aqueous solutions, the organic component is most likely to carry the impurity with it. All organic components must be purified, stored and handled with the greatest care.

To measure small pressures accurately by a mercury manometer is a very difficult task. Manometry is actually a very complex field, amounting to much more than just reading the top of a meniscus. Cawood and Patterson (48) have a very excellent discussion of the capillary depressions of mercury in cylindrical tubes and some of the errors of glass manometers. They measured the difference of the mercury level in cylindrical tubes of wide and narrow diameters, since the capillary depression in a wide tube (about 38 mm. diameter) is negligible compared with that in a narrow. They present tables of the capillary depression as a function of meniscus height for a number of different tubes from about 10.5 to 18.5 mm. inside diameter. The capillary correction for a tube of 10.52 mm. and a meniscus height of 1.41 mm. amounts to 0.415 mm; by no means a negligible correction. The correction range from the above value down to 0.015 mm. for a meniscus height of 0.45 mm. in a 18.43 mm. tube. At the same time they studies the refraction error due to irregularities in the manometer tube and concluded that for ordinary tubes of 15 mm. or so diameter, the errors due to refraction in the glass may be as great as the capillary depressions themselves. Thin-walled glass tubes of about test tube thickness (0.3 mm. wall) were found necessary in order to cut the refraction error to less than 0.01 mm.

A theoretical claculation of the capillary depression is difficult because two of the quantities necessary in the calculation, namely the surface tension of mercury and the angle of contact of mercury with the glass tube, are not easily determined. The surface tension of mercury is changed extensively by small traces of impurities, this having a greater effect on the capillary depression in small tubes.

Analytic errors are thought to be quite small except in some cases where the solution concentration was at an insensitive part of the interferometric calibration curve. This made it necessary to dilute out of this region, usually with water, to get to a concentration where the refractive index was sensitive to concentration changes. Any error made in the analysis of the diluted sample was multiplied by the dilution factor in the final corrected concentration. The accuracy of the interferometric method varied from system to system and varied within the individual systems. The aqueous methanol system was the most difficult from an analytical standpoint since the refractive index changes slowly with concentration changes. All the interferometric calibration curves were sensitive at the ends of the concentration ranges. In the case of ethanol there was good analytical sensitivity except in the region from 0.4 to 0.75 mole fraction ethanol. The analytic error in this system should not have exceeded 0.0008 mole fraction except when dilutions were necessary, where the error would be slightly greater. The n- butyric acid - water system had good analytical sensitivity except in the range from 0.7 to 0.85 mole fraction acid. Errors of about 0.0005 would be maximum in this system except in the small range mentioned. In general, the acid sensitivity was better than the corresponding alcohol except in narrow regions. The alcohol sensitivity was adequate, the maximum expected error ranging from about 0.0015 in methanol to about 0.0006 in the case of propanol-1.

Evaporation losses while solutions were stored should not have been serious. The volume of the sample flasks was small so not much vapor was distilled from the solution to alter the composition appreciably. Transfer operations by hypodermic syringe cut down any evaporation errors to a minimum.

Residual air in the apparatus and in the solution to be determined was a minor factor which would increase the total pressure to a small extent. This error was unimportant if several vaporizations were needed to collect a vapor sample. It was found that the total pressure of the first and second collected vaporizations differed by not more than 0.15 mm. Hg., indicating an almost complete removal of air after the initial air removal vaporization. If three vaporizations were needed, the total pressure was taken as the average of the last two pressure readings.

A small error was introduced by assuming the alcohol and water vapors to behave as ideal vapors. By using the van der Waals equation and constants for the vapors to calculate the fugacities, it was found that the fugacities and the ideal pressures differed by less than 0.1 per cent under the least favorable circumstances.

The problem of solution concentration changes in the generating flask of the apparatus during a determination, leaves one to choose between two evils. If the amount of solution is too small, the concentration changes too much. If the amount of solution is too great, the amount of purified liquids needed is great and stirring becomes a problem. In most cases, the concentration of the liquid at the close of a determination differed from that at the beginning by about 0.004 mole fraction and very rarely was this difference greater than 0.010 mole fraction.

2. Limits of applicability and extension of method

The apparatus as constructed in this research would be applicable to any system in which the total vapor pressure varies from near 0 mm. to about 300 mm. Hg. About the only limiting factor in this region would be if either one or both of the components would react with mercury or with the stopcock grease used. In this research, Apiezon-N was used as the stopcock lubricant. It was the best vacuum-tight grease tried and fortunately it was insoluble in the organic components used in this research. A high vacuum silicone stopcock grease was tried in the apparatus but it was not vacuum-tight and channeled badly.

To determine the future applicability of the method to other systems, a quantity of n- heptane was put into the generating flask and allowed to vaporize into the reservoir flask. The system was then left this way for a period of one day. During this time the heptane had dissolved the Apiezon-N stopcock grease from one of the stopcocks and the system leaked badly. This demonstrated that the apparatus as constructed could not be used for systems which contained paraffin hydrocarbons as one component. Since Apiezon-N dissolves readily in acetone, benzene, carbon tetrachloride, and related compounds, it is improbable that systems of these components could be investigated under the present procedure.

A sample of a perfluoro-stopcock grease has been obtained from Minnesota Mining and Manufacturing Co. which may make it possible to investigate the Apiezon-N grease dissolving components with the present apparatus. Most likely the perfluoro grease will be insoluble in most organic solvents, but it remains to be seen if the grease will be vacuum-tight.

If all ordinary type greases fail, it may be possible to eliminate as many standard taper joints as possible, cement the others in with a vacuum-tight cement, and use graphite lubricated-mercury sealed stopcocks instead of the conventional type.

One of the crucial features of the apparatus which should be changed is the manometer. The manometer used was found to give low readings by 0.25 mm. when compared to a manometer which had equal capillary effects in both arms. To eliminate all capillary effects, a manometer with bore size of at least 15 mm. should be used. In addition, the bore should be perfectly uniform, perhaps precision bore. To prevent refraction errors when sighting through the manometer tube with the cathetometer telescope, thin-walled tubing should be used. As the manometer stands in contact with vapors in the apparatus, the mercury becomes saturated with these vapors. It would be best to design the manometer so it could be degassed by boiling the mercury at reduced pressure at regular intervals.

In conclusion, the author believes the basic procedure is sound, but small changes will have to be made to adapt the apparatus to the system of interest. Further refinements in manometry as suggested would improve accuracy.

3. Contributions of method to thermodynamic investigation

The general methods of investigation used by previous workers in the field of solution thermodynamics have been outlined in the first section of this dissertation along with some of the limitations inherent in each method. The method as herein described depends on the direct measurement of the total pressure and vapor composition at the temperature of interest and does not necessitate the introduction of a third component as in the gas-saturation method.

The chief advantage of the method as described is in the rapidity with which a determination can be made. For the systems determined, not more than three vaporizations, and in general only two, were needed to collect a sufficient sample for analysis. The time required for two collected vaporizations was about 1 1/2 hours, including the preparation of the solution to be determined and the degassing vaporization. The method is about six times as rapid as the gas-saturation method and is of comparable accuracy.

VII. SUMMARY

1. A new method for measuring activity coefficients of both components in binary solutions of volatile components has been developed which appears to have important advantages in speed and accuracy over existing methods applicable to similar systems. The method involves transfer of equilibrium vapors from a generator flask containing binary solution through an intermittent bleeder valve to an evacuated reservoir flask, measurement of total pressure in the reservoir flask, and trapping and analyzing reservoir flask vapors.
2. The method developed has been used to measure activities over the entire concentration range of both components in methanol - water, ethanol - water, and propanol-1 - water systems at 25°C. for which reasonably good literature data exist. Results are in excellent agreement with, and in general appear to be superior to best existing literature values for these systems, and show excellent Duhem - Margules consistency.
3. Activities of both components of acetic acid - water, propionic acid - water, and n- butyric acid - water systems have been measured over the entire concentration range at 25°C., and constitute original data for these systems.

4. Results for both alcohol - water and acid - water systems have been interpreted comparatively and in progression in homologous series; first in terms of specific free energy effects calculated from activity coefficients at infinite dilution, and second, in terms of secondary structure effects affecting variation in activity coefficient with concentration.

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