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Activity coefficients of aqueous methanol solutions

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Abstract

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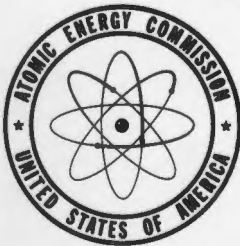
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ACTIVITY COEFFICIENTS OF AQUEOUS
METHANOL SOLUTIONS

By
William S. Brown
Don S. Martin

June 1951

Ames Laboratory



Technical Information Service, Oak Ridge, Tennessee

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TABLE OF CONTENTS

| | <u>Page</u> |
|-------------------------------------|-------------|
| I. ABSTRACT | 4 |
| II. INTRODUCTION | 4 |
| III. REVIEW OF LITERATURE | 5 |
| IV. THEORY | 7 |
| V. EXPERIMENTAL INVESTIGATION | 10 |
| A. General Method | 10 |
| B. Apparatus | 10 |
| C. Procedure | 12 |
| VI. RESULTS | 13 |
| VII. DISCUSSION | 26 |
| VIII. LITERATURE CITED | 28 |

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OF
AQUEOUS METHANOL SOLUTIONS*

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William S. Brown and Don S. Martin

I. ABSTRACT

The methods employed in determination of vapor pressures of liquids have been reviewed. The gas saturation method has been used to determine the partial and total vapor pressures of water-methanol solutions at 0°C. From the vapor pressure data thus obtained, activities and activity coefficients of water and methanol have been calculated and the results have been plotted against the mole fraction composition. The data obtained showed a positive deviation from Raoult's law for the solution. The activity coefficient curves have been analyzed and found to satisfy the requirements of the Duhem-Margules equation. These curves have also been fitted with an empirical equation which has made possible extrapolation of the curves to infinite dilution. A discrepancy between the data obtained and the data for higher temperatures has also been discussed.

II. INTRODUCTION

Studies of reactions in aqueous methanol solutions are greatly facilitated by a knowledge of the activities and activity coefficients of the components. Also, a knowledge of the activity coefficients of the water and of the methanol in aqueous methanol solutions provides a measure of the deviation of the solution from ideal behavior. Activity coefficient data were available for higher temperatures, as 25°C and 40°C, but had not been determined directly for temperatures as low as 0°C. The present work was undertaken to obtain such data for aqueous methanol solutions at 0°C.

* This report is based on an MS thesis by W. S. Brown prepared June 1951.

III. REVIEW OF LITERATURE

Activities can be obtained by determining the partial and total vapor pressures of binary liquid systems. This type of problem has been investigated by means of a number of different experimental procedures and by many different workers. The different procedures have been attended with widely varying degrees of success and often with considerable variation in results for similar types of measurements.

The earliest method employed with much success was that of distilling off a small amount of the solution being studied under a known total pressure and analyzing the collected sample. The amount of solution used was large enough so that the change in composition on distillation was presumably negligible. Such a method was employed by Zawidski (1) in 1900 who used a refractometer for analysis of the collected sample and by Brown (2) in 1879 who determined the composition of distillates by means of specific gravity determinations.

In 1909 Rosanoff, Lamb, and Breithut (3) devised a scheme for determination of vapor pressures of binary liquids which afforded assurance that the pressures and compositions measured were the true equilibrium values. The method consisted of passing a mixed vapor of constant composition through a liquid mixture of the same components. When equilibrium was reached the compositions of both vapor and liquid remained constant and no further change occurred in the temperature of the liquid. The total pressure was also observed. The constant-composition vapor was obtained by boiling a mixture of the two liquid components, the composition of which was maintained constant by the addition of the more volatile component at a steady rate. The method was applied to the determination of vapor pressures of binary mixtures by Rosanoff and Easley (4).

In 1912 Wrewsky (5) employed an apparatus similar to that used by Zawidski (1) with a modification to allow rapid stirring of the solution. Partial and total vapor pressures of methanol-water solutions were measured at temperatures of 39.90° C and 59.44° C.

In 1914 Rosanoff, Bacon, and White (6) devised a simpler, more rapid scheme for measurement of partial vapor pressures of mixtures. According to this method a sample of the liquid of known composition was distilled without refluxing and successive portions of distillate were collected, weighed and

analyzed. The composition of the distillates was then plotted against their weight and the plot was extrapolated to zero weight. The resulting extrapolation gave the composition of the first indefinitely small amount of distillate, this being the desired quantity.

In 1918 Sameshima (7) studied the system, acetone-ethyl ether, by boiling off samples of the liquid. In this work the boiling vessel was immersed in a thermostat and the total pressure of the system regulated to that value necessary to cause the liquid mixture to boil.

Another method used extensively in vapor pressure determinations consists of bubbling an inert gas slowly through the system to be studied and condensing and analyzing a portion of the mixed vapor carried over with the inert gas. In 1924 Dobson and Masson (8) employed such a method to determine the activity of water in hydrochloric acid solutions. A current of dry hydrogen gas was passed through the solution and then through absorbers for water and hydrogen chloride. In 1925 Dobson (9) employed the same method for the determination of partial vapor pressures of aqueous ethanol solutions at 25° C. A measured volume of dry nitrogen gas was bubbled through water-ethanol solutions of various concentrations of ethanol. The vapors were condensed in a dry ice bath and the composition of the vapor determined by means of a pycnometer. To obtain the weight of vapor for a given volume of nitrogen the vapors were condensed and weighed in a trap of concentrated sulfuric acid. The total pressure in the saturator was measured by means of a manometer and the volume of nitrogen was determined by collection in an aspirator.

In 1927 Calingaert and Hitchcock (10) employed another experimental arrangement for the determination of liquid and vapor compositions of binary liquid mixtures of hydrocarbons. The system consisted of a nitrometer tube and a gas buret, the volumes of which could be adjusted by means of leveling bulbs. A known volume of one of the components in liquid form was introduced into the nitrometer tube. The other component was allowed to vaporize into the gas buret where its pressure and volume were measured. The two were then connected and the system allowed to come to equilibrium, after which volume and pressure measurements were again taken.

In 1929 Ferguson and Funnell (11) measured the vapor pressures of aqueous methanol solutions at 39.9° C. A weighed sample of known composition was distilled into the apparatus. The vapor was then circulated over the liquid until equilibrium

was attained. The pressure of the system at equilibrium was measured by means of a manometer and a known volume of the vapor was condensed and weighed. The required vapor pressures were calculated in a variety of ways all of which gave consistent results. A plot of the vapor pressures versus the mole fraction composition of the liquid showed a positive deviation from Raoult's law.

IV. THEORY

The activity, a_i , of a given component, "i," in a liquid solution is defined in terms of its partial molar free energy or chemical potential, μ_i , by the equation

$$\mu_i = \mu_i^0 + RT \ln a_i, \quad (1)$$

where μ_i^0 , a function of temperature only, is the partial molar free energy of a standard state for which a_i equals unity. The standard state chosen was that of the pure liquid component, "i," at one atmosphere pressure and a temperature of 0° C.

The fugacity, f_i , is defined by a similar equation,

$$\mu_i = \mu_i^* + RT \ln f_i, \quad (2)$$

in which μ_i^* is the chemical potential of constituent "i" when f_i is equal to unity. The standard state of unit fugacity is chosen so that as the pressure approaches zero and the behavior of the vapor approximates that of an ideal gas, the ratio f_i/p_i approaches unity. For a pure liquid at a given temperature and one atmosphere pressure the chemical potential is, then, given by

$$\mu_i^0 = \mu_i^* + RT \ln f_i^0, \quad (3)$$

where f_i^0 is the fugacity of the pure liquid.

By combining equations (1) and (3) and comparing the result with equation (2) an expression for the activity of the given constituent in terms of its fugacity may be obtained:

$$a_i = f_i/f_i^0. \quad (4)$$

If the vapor is assumed to behave ideally, partial pressures may be substituted for fugacities and the expression becomes

$$a_i = p_i/p_i^0, \quad (5)$$

where p_i is the partial pressure of constituent "i" and p_i^0 is the vapor pressure of pure liquid "i" at the given temperature and one atmosphere pressure.

For purposes of the present work the constituent "i" will be either methanol or water; p_i^0 will therefore be the vapor pressure of pure methanol or pure water at 0°C and one atmosphere pressure.

It is necessary, then, to find the values of the partial pressures of water and of methanol over the mixtures of varying mole percent of methanol at 0°C .

If it is assumed that the vapors in equilibrium with the liquid mixture form an ideal gas mixture, it follows that the partial pressure of one component in a given water-methanol mixture is equal to the product of the mole fraction of that component in the vapor and the total vapor pressure of the system; that is,

$$P_i = N_{ig} \cdot P_T. \quad (6)$$

N_{ig} may be found by an analysis of the vapor phase and P_T may be calculated by the use of the ideal gas law,

$$P_T = nRT/V. \quad (7)$$

In order to evaluate P_T in the above equation, n (the total moles of vapor) must be found from a knowledge of the vapor composition and the weight of a known volume of vapor.

The activity coefficient is defined as the ratio of the activity of a given component of a mixture to its mole fraction in the mixture. Therefore, if the activity of one component in a given solution is known, the activity coefficient of that component is given by the equation

$$\gamma_i = a_i/N_{il} \quad (8)$$

where γ_i is the activity coefficient of the component "i" and N_{il} is the mole fraction of component "i" in the liquid.

An ideal solution is defined as one which obeys an idealized form of Raoult's law over the entire range of compositions at all temperatures and pressures. Under these condi-

tions the fugacity of a given component, "i", of a solution of any composition will be equal to the product of its mole fraction in the solution and the fugacity of the pure component; that is,

$$f_i = N_{i1} f_i^0 . \quad (9)$$

If ideal behavior of the vapors is assumed, pressures may be substituted for fugacities and the above equation becomes

$$P_i = N_{i1} p_i^0 . \quad (10)$$

If equation (10) is divided by $N_{i1} p_i^0$, one obtains

$$P_i / N_{i1} p_i^0 = 1 . \quad (11)$$

Since $P_i / N_{i1} p_i^0$ is simply the expression for the activity coefficient of component "i," it follows that for an ideal solution the activity coefficients of its components must be equal to unity. The difference between the value of the activity coefficient and unity is, therefore, a measure of the deviation of the solution from ideal behavior.

Application of the Gibbs-Duhem equation to a system consisting of a binary liquid solution in equilibrium with its vapor at constant temperature and pressure yields the equation

$$N_1 d\mu_1 + N_2 d\mu_2 = 0, \quad (12)$$

where N_1 and N_2 are the mole fractions of the two components. If the temperature and pressure of the system are held constant, the change in chemical potential with change in composition is given by $d\mu_1 \left(\frac{\partial \mu_1}{\partial N_1} \right)_{P,T}$ and substitution of this equation

in equation (12) yields

$$N_1 \left(\frac{\partial \mu_1}{\partial N_1} \right)_{T,P} dN_1 + N_2 \left(\frac{\partial \mu_2}{\partial N_2} \right)_{T,P} dN_2 = 0. \quad (13)$$

The sum of the two mole fractions must be equal to unity; that is, $N_1 + N_2 = 1$. It follows that $dN_1 = -dN_2$, and equation (13) becomes

$$N_1 \left(\frac{\partial \mu_1}{\partial N_1} \right)_{T,P} = N_2 \left(\frac{\partial \mu_2}{\partial N_2} \right)_{T,P} . \quad (14)$$

By combining the equation for change of the fugacity of a given component at constant temperature and pressure in terms of its chemical potential, $d\mu_1 = RT \, d\ln f_1$, with equation (14) the following expression is obtained:

$$N_1 \left(\frac{\partial \ln f_1}{\partial N_1} \right)_{T,P} = N_2 \left(\frac{\partial \ln f_2}{\partial N_2} \right)_{T,P} \quad (15)$$

Similar expressions relating the change of activities and activity coefficients of the two components of a binary solution with change in composition may be derived by substituting the values for these quantities in terms of fugacity into equation (15). The resulting equations are as follows:

$$N_1 \left(\frac{\partial \ln a_1}{\partial N_1} \right)_{T,P} = N_2 \left(\frac{\partial \ln a_2}{\partial N_2} \right)_{T,P} \quad (16)$$

and

$$N_1 \left(\frac{\partial \ln \gamma_1}{\partial N_1} \right)_{T,P} = N_2 \left(\frac{\partial \ln \gamma_2}{\partial N_2} \right)_{T,P} \quad (17)$$

V. EXPERIMENTAL INVESTIGATION

A. General Method

As seen from the theoretical discussion, the quantities which must be experimentally determined are the composition of the vapor for a given liquid composition and the weight of the vapor occupying a given volume. The method employed in this case was similar to that of Dobson (9) as described on page 6, except that the volume of nitrogen was measured by means of a wet test gas meter and the weight of the combined vapors for a given volume was determined by absorption in two CaCl_2 traps rather than in a concentrated H_2SO_4 trap. Also, the analysis of the condensed vapor was accomplished by means of specific gravity measurements.

B. Apparatus

Figure 1 shows a diagram of the apparatus used. The saturating vessel, A, was a round-bottom flask of approximately 200 ml. capacity. It was connected through a sidearm to a

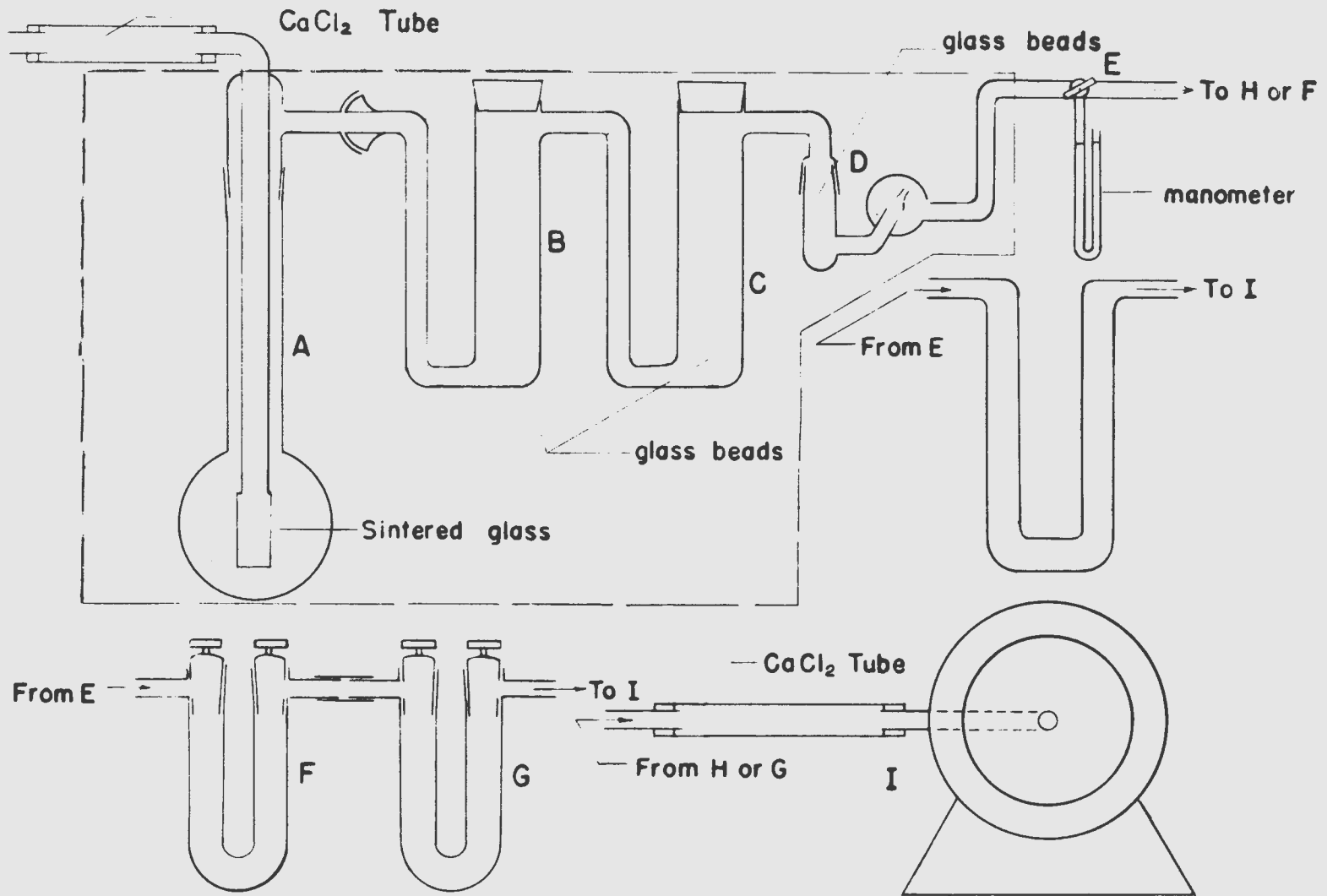


Fig. 1--Vapor pressure apparatus.

bubbling tower, B, consisting of a glass tube filled with glass beads which in turn led into a similar type of bubbling tower, C. These two towers served to ensure complete saturation of the nitrogen gas with vapor from the liquid. D was a trap which served to catch spray carried over from the saturators. A three way stopcock, E, was connected to a mercury manometer for measuring the total pressure of the system. F and G were glass stoppered U-tubes about six inches in height and filled with 20 mesh CaCl_2 . H was a U-tube about one foot high which was placed in a dry-ice trichlorethylene bath. The saturator, A, the bubbling towers, B and C, and the trap, D, were immersed in a thermostat as shown by the dashed lines in the diagram. The temperature in the thermostat was maintained at $0^\circ \text{C} \pm 0.05^\circ$ by means of an ice bath.

C. Procedure

The nitrogen gas from the tank was passed through a CaCl_2 drying tube and into the vessel A by way of a sintered glass bubbler which served to divide the gas stream into fine bubbles. It then passed through B and C in order to ensure complete saturation with the vapors of the solution. The saturated gas then passed through the trap, D, and either through F and G in turn or through H, according to whether the weight or the composition of the vapors was to be determined. The gas with the vapors removed then passed through a CaCl_2 tube and into the gas flow meter, I.

The saturating vessel, A, and bubbling towers, B and C, were filled with a methanol-water solution of known concentration. These solutions were made up by volume and the composition of the liquid in the second bubbler was checked by measuring its specific gravity before and after each run. It was found that in no case did a significant change in composition occur as a result of the run. The nitrogen gas was passed through the system at a rate of about 2 to 3 liters per hour until a total of from 20 to 40 liters had passed, depending on the volatility of the solution employed. Two separate runs were made with each solution. The first was to determine the total weight of vapors per volume of nitrogen collected. This was accomplished by passing the gas and vapors through two previously weighed CaCl_2 absorption tubes, F and G. The absorption tubes were again weighed at the conclusion of the run and the weight of vapor was obtained by difference. When weighing either of the absorption tubes, a third tube of the same type was used as a counterpoise.

The second run was made with U-tube H in the system in

place of F and G. The purpose of this run was to condense out a portion of the vapors for analysis. The condensed sample was then transferred at about 0° C (to prevent appreciable loss due to evaporation) to a pycnometer of about 2cc capacity. This pycnometer was used to determine the specific gravity of all solutions whose compositions were to be determined.

Initial runs were made on pure water and on pure methanol and duplicate runs were made in every case. The water used was doubly distilled and the methanol was purified by distilling from anhydrous CaSO_4 .

It was found that two absorption tubes (F and G) were sufficient for the removal of aqueous and methanol vapors. A third tube of similar type showed no appreciable gain in weight when placed in the system for the duration of a run.

VI. RESULTS

Since the volume of gas as measured by the wet test meter was the volume of nitrogen after the vapors of water and methanol had been removed, a correction must be applied in calculating P_T to account for the greater volume occupied by the nitrogen gas when saturated with water and methanol vapors. In addition, the measurements of the volume of gas were made at room temperature. It was necessary, therefore, to also correct the measured volume to 0° C.

The application of both of these corrections to the perfect gas law equation yields the following expression for the total pressure at 0° C:

$$P_T = nRT_0 / V'(1+nRT_0 / PV') \quad (18)$$

Where T_0 is the temperature (room temperature) at which the volume was measured and P is the barometric pressure. R has the value 0.08205 liter atmospheres and V' is the measured volume at temperature T_0 . The value of "n" may be readily found when the total weight and composition of the vapor are known. The partial pressures, p_w and p_a , and activities, a_w and a_a , of water and methanol respectively may then be found from equations (6) and (5). Equation (8) gives the activity coefficient of either component, γ_w or γ_a .

The experimental data are given in Table I and the results of the calculations are given in Table II.

TABLE I
Experimental Data

| N_{a1} | Wt. % MeOH in vapor | Wt. of vapors in grams | V' liters | T_o | P atm. |
|----------|------------------------------|---------------------------------|--------------|-------|-----------|
| 0.00 | 0.00 | 0.4068 | 51.15 | 297.0 | 0.972 |
| 0.05 | 55.36 | 0.3397 | 34.76 | 297.2 | 0.957 |
| 0.13 | 74.12 | 0.4126 | 26.40 | 296.7 | 0.953 |
| 0.18 | 79.49 | 0.3971 | 21.00 | 296.5 | 0.969 |
| 0.31 | 86.63 | 0.4981 | 19.25 | 296.5 | 0.938 |
| 0.48 | 91.45 | 0.6001 | 17.70 | 295.5 | 0.961 |
| 0.57 | 93.14 | 0.4560 | 12.30 | 296.7 | 0.952 |
| 0.64 | 94.36 | 0.8973 | 22.50 | 295.8 | 0.979 |
| 0.73 | 95.68 | 1.1719 | 27.07 | 295.2 | 0.970 |
| 0.85 | 97.52 | 0.9788 | 20.60 | 297.3 | 0.980 |
| 1.00 | 100.00 | 1.3741 | 25.70 | 297.0 | 0.981 |

TABLE II

Values Calculated from Experimental Data

| N_{a_1} | N_{a_g} | n | $P_{T_{mm}}$ | $P_{a_{mm}}$ | a_a | γ_a | $P_{w_{mm}}$ | a_w | γ_w |
|-----------|-----------|--------|--------------|--------------|-------|------------|--------------|-------|------------|
| 0.00 | 0.000 | 0.0127 | 4.57 | | | | | | |
| 0.05 | 0.411 | 0.0143 | 7.55 | 3.10 | 0.104 | 2.08 | 4.45 | 0.972 | 1.02 |
| 0.13 | 0.617 | 0.0155 | 10.71 | 6.61 | 0.222 | 1.71 | 4.10 | 0.896 | 1.03 |
| 0.18 | 0.685 | 0.0144 | 12.47 | 8.52 | 0.286 | 1.59 | 3.95 | 0.862 | 1.05 |
| 0.31 | 0.785 | 0.0172 | 16.17 | 12.65 | 0.425 | 1.37 | 3.52 | 0.770 | 1.12 |
| 0.48 | 0.858 | 0.0200 | 20.27 | 17.39 | 0.585 | 1.22 | 2.88 | 0.629 | 1.21 |
| 0.57 | 0.885 | 0.0150 | 21.91 | 19.39 | 0.653 | 1.14 | 2.52 | 0.550 | 1.28 |
| 0.64 | 0.904 | 0.0293 | 23.29 | 21.05 | 0.710 | 1.11 | 2.24 | 0.489 | 1.36 |
| 0.73 | 0.927 | 0.0379 | 25.00 | 23.18 | 0.785 | 1.07 | 1.82 | 0.397 | 1.47 |
| 0.85 | 0.957 | 0.0312 | 27.08 | 25.92 | 0.872 | 1.03 | 1.16 | 0.254 | 1.69 |
| 1.00 | 1.000 | 0.0429 | 29.69 | | | | | | |

The relation between liquid and vapor compositions is shown by a plot of the mole fraction of methanol in the liquid versus the mole fraction of methanol in the vapor in Figure 2.

Figure 3 shows the plot of the total and the partial vapor pressures versus the mole fraction composition of the liquid. It is seen that the total vapor pressure and the partial pressures of both water and methanol are greater than they would be if the solution behaved ideally.

Figures 4 and 5 show a logarithmic plot of the activity coefficients versus the mole fraction of water in the solution. As seen from these figures and Table II the values of the activity coefficients of both water and methanol are greater than unity for all concentrations. This indicates that for all values of composition of the solution both the water and the methanol exhibit positive deviations from Raoult's law.

The relation expressed by equation (17) served as a test of the data obtained. For the system methanol-water, equation (17) becomes

$$N_w \left(\frac{\partial \ln \gamma_w}{\partial N_w} \right)_{T,P} = N_a \left(\frac{\partial \ln \gamma_a}{\partial N_a} \right)_{T,P} \quad (19)$$

The terms $\left(\frac{\partial \ln \gamma_w}{\partial N_w} \right)_{T,P}$ and $\left(\frac{\partial \ln \gamma_a}{\partial N_a} \right)_{T,P}$ were evaluated by

measuring the slopes of the two curves in Figure 4 for a particular value of the mole fraction of water, N_w , and the corresponding mole fraction of methanol, N_a , in the same solution. The data were thus shown to agree satisfactorily with equation (19) within the limits of experimental accuracy as indicated by the measured values given in Table III.

An analytical expression for γ_1 or γ_2 which satisfies the Gibbs-Duhem requirements as stated in equation (17) has been used by van Laar (12) and may be written in the following form:

$$\log \gamma_1 = \frac{A}{\left(1 + \frac{AN_1}{BN_2} \right)^2} \quad (20)$$

and

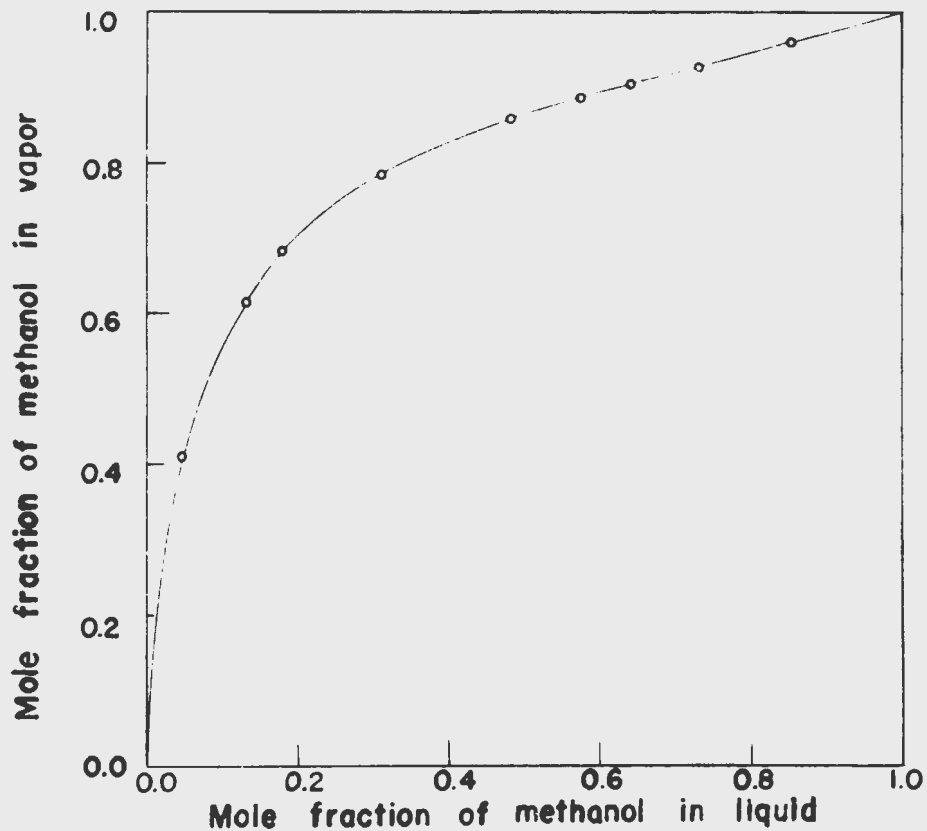


Fig. 2--Liquid and vapor compositions.

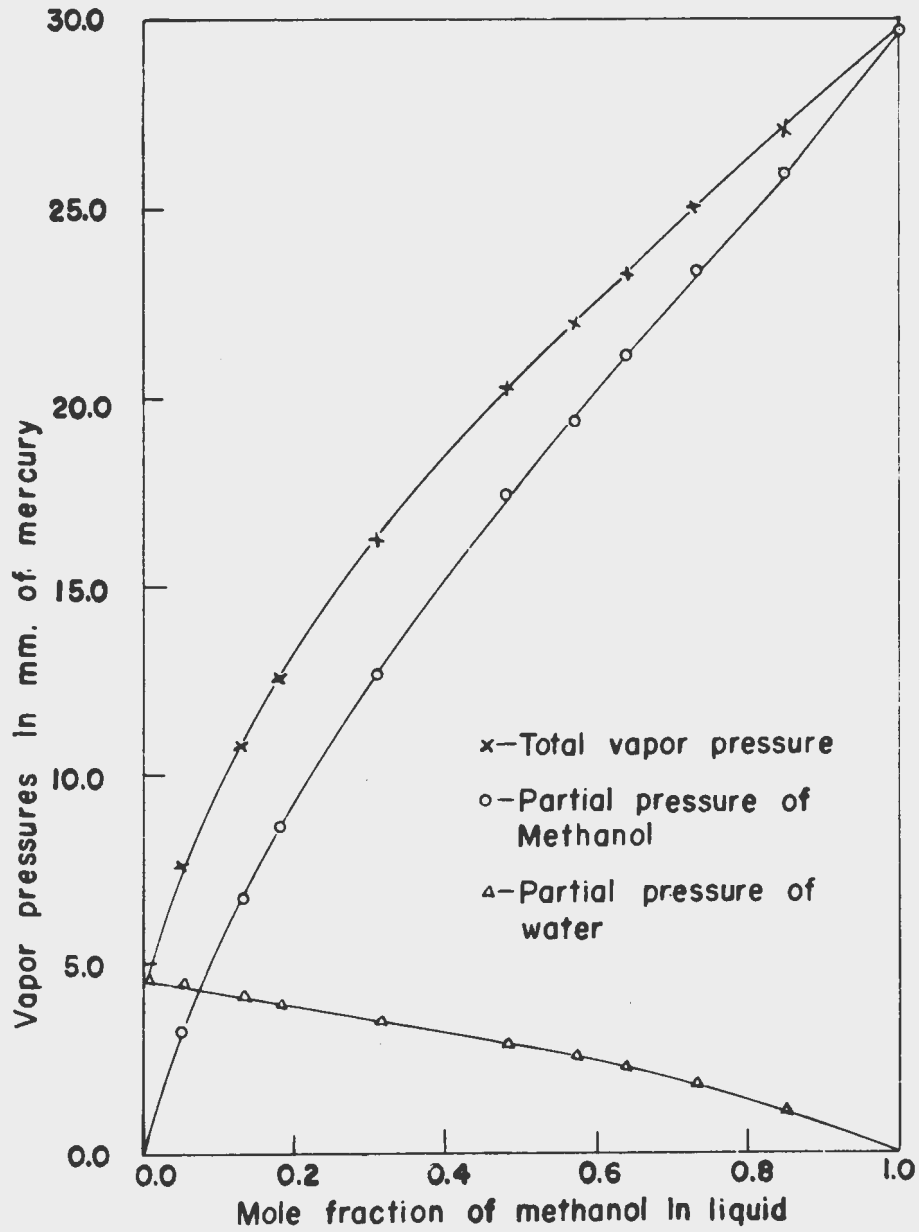


Fig. 3--Vapor pressures of methanol solutions.

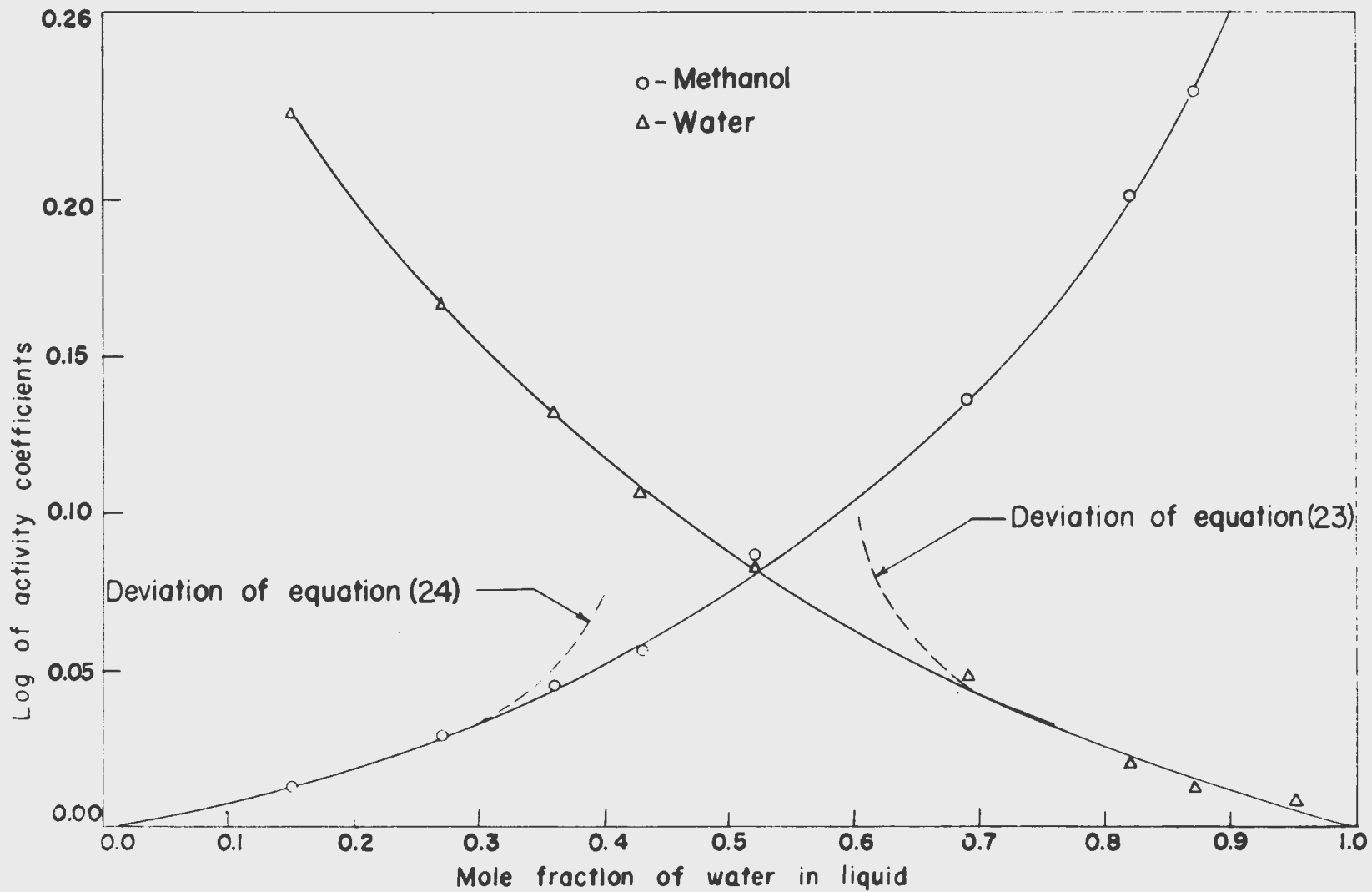


Fig. 4--Activity coefficients of water and methanol.

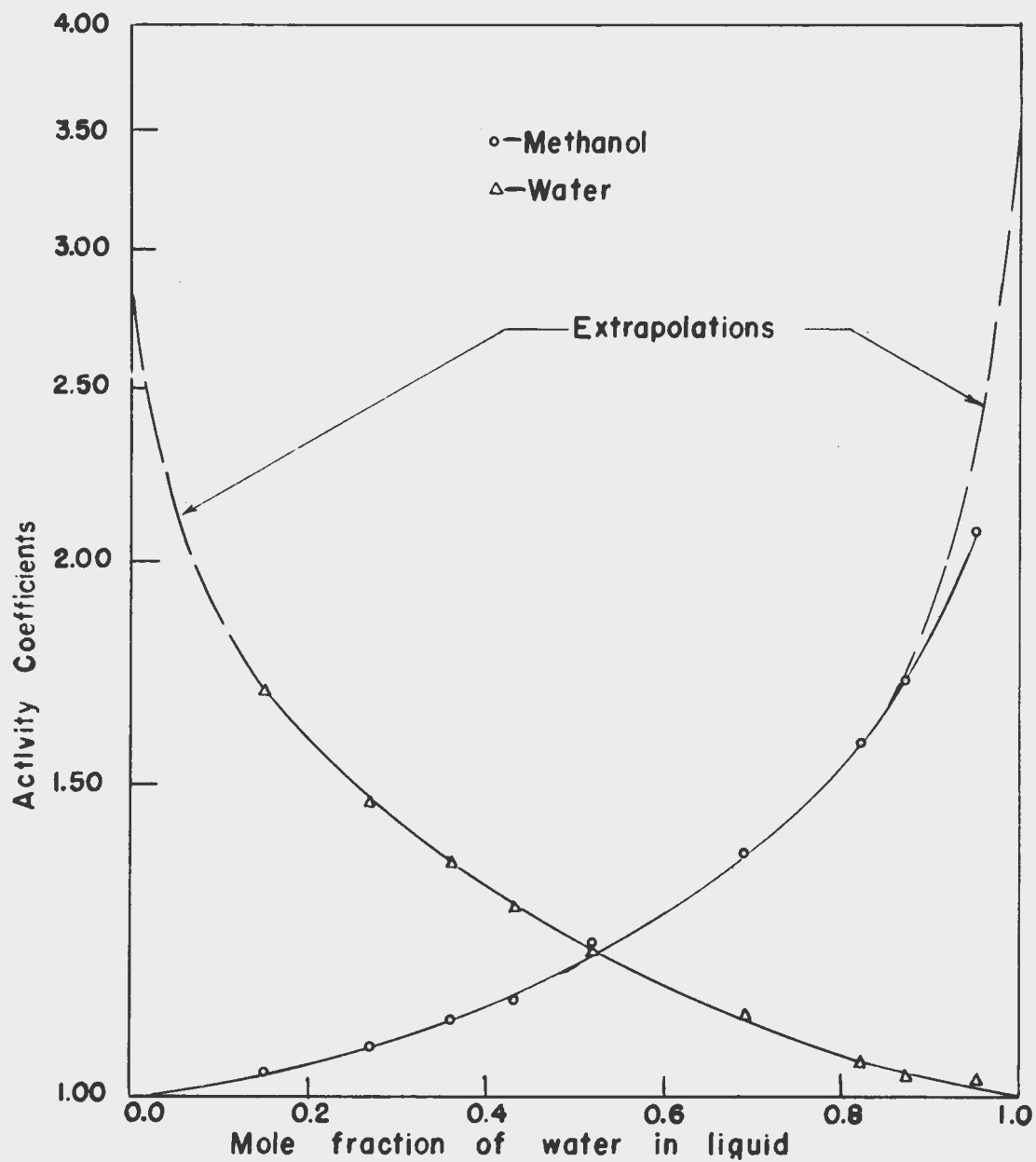


Fig. 5--Activity coefficients of water and methanol.

TABLE III

Slopes of Activity Coefficient Curves

| N_a | N_w | $\left(\frac{\partial \log \gamma_a}{\partial N_a}\right)$ | $N_a \left(\frac{\partial \log \gamma_a}{\partial N_a}\right)$ | $\left(\frac{\partial \log \gamma_w}{\partial N_w}\right)$ | $N_w \left(\frac{\partial \log \gamma_w}{\partial N_w}\right)$ |
|-------|-------|--|--|--|--|
| 0.8 | 0.2 | 0.320 | 2.56 | 1.28 | 2.56 |
| 0.6 | 0.4 | 0.548 | 3.29 | 0.852 | 3.41 |
| 0.4 | 0.6 | 0.804 | 3.22 | 0.559 | 3.35 |
| 0.2 | 0.8 | 1.48 | 2.96 | 0.379 | 3.03 |

$$\log \gamma_2 = \frac{B}{\left(1 + \frac{BN_2}{AN_1}\right)^2} \quad (21)$$

where A and B are constants. Rearrangement of equations (20) and (21) gives the following explicit expressions for the constants A and B:

$$A = \log \gamma_1 \left(1 + \frac{N_2 \log \gamma_2}{N_1 \log \gamma_1}\right)^2 \quad (22)$$

and

$$B = \log \gamma_2 \left(1 + \frac{N_1 \log \gamma_1}{N_2 \log \gamma_2}\right)^2 \quad (23)$$

It is seen from equation (20) that the value of $\log \gamma_1$ is equal to A when N_1 is zero. Likewise, from equation (21) $\log \gamma_2$ is seen to be equal to B when N_2 is equal to zero. For the system methanol-water, component "1" is water and component "2" is methanol.

Values of A and B were calculated from equations (22) and (23) by using values of γ_w and γ_a corresponding to different compositions of the solution. The calculated values of A and B were considerably different for the various compositions of the solution, thus indicating that equations (20) and (21) do not satisfactorily represent the experimental activity coefficient curves.

Margules (1895) suggested expressing $\log \gamma_1$ and $\log \gamma_2$ as a power series function of N_2 and N_1 respectively according to the following equations:

$$\log \gamma_1 = 1/2 \alpha_1 N_2^2 + 1/3 \beta_1 N_2^3 + 1/4 \delta_1 N_2^4 + \dots \quad (24)$$

and

$$\log \gamma_2 = 1/2 \alpha_2 N_1^2 + 1/3 \beta_2 N_1^3 + 1/4 \delta_2 N_1^4 + \dots \quad (25)$$

Using values of N_2 and N_1 equal to 0.1, 0.2, and 0.3 and the corresponding values of $\log \gamma_1$ and $\log \gamma_2$ obtained from the smoothed curves of figure 4, the constants $\alpha_1, \alpha_2, \beta_1$, etc. were evaluated to yield the following expressions:

$$\log \gamma_1 = 2.13 N_2^2 - 11.2 N_2^3 + 18.83 N_2^4 + \dots \quad (26)$$

and

$$\log \gamma_2 = 1.34 N_1^2 - 6.50 N_1^3 + 10.83 N_1^4 + \dots \quad (27)$$

Values of $\log \gamma_1$ ($\log \gamma_w$) and $\log \gamma_2$ ($\log \gamma_a$) were calculated from these expressions and are given in Table IV. These values are plotted as the dashed curves in figure 4 and seem to represent the data satisfactorily in the region 0.0 to 0.3, but deviate seriously at large values of the mole fraction.

Rearrangement of equation (17) gives

$$\frac{N_1}{N_2} \left(\frac{\partial \ln \gamma_1}{\partial N_1} \right)_{T,P} = \left(\frac{\partial \ln \gamma_2}{\partial N_2} \right)_{T,P} \quad (28)$$

TABLE IV

Activity Coefficients from Equations (26 and (27)

| N_a | $\log \gamma_w$ | N_w | $\log \gamma_a$ |
|-------|-----------------|-------|-----------------|
| 0.05 | 0.00405 | 0.05 | 0.0026 |
| 0.08 | 0.0087 | 0.10 | 0.0080 |
| 0.10 | 0.0120 | 0.15 | 0.0137 |
| 0.15 | 0.0198 | 0.20 | 0.0190 |
| 0.16 | 0.0210 | 0.25 | 0.0243 |
| 0.20 | 0.0260 | 0.30 | 0.0330 |
| 0.25 | 0.0322 | 0.40 | 0.0760 |
| 0.30 | 0.0420 | | |
| 0.40 | 0.1060 | | |

and, since $dN_1 = -dN_2$, equation (28) may be written as

$$\frac{N_1}{N_2} d \ln \gamma_1 = -d \ln \gamma_2 \quad (29)$$

Conversion of logarithms and substitution of the expression for $\log \gamma_1$ [equation (24)] into the above equation yields:

$$N_1 (\alpha_1 + \beta_1 N_2 + \delta_1 N_2^2) dN_2 = -d \log \gamma_2 \quad (30)$$

Substitution of $(1-N_2)$ for N_1 and integration of the resulting equation gives an analytical expression for $\log \gamma_2$ in the region in which equation (26) is valid. This expression is as follows:

$$\begin{aligned} & \left[\alpha_1 (N_2 - N_2^2/2) + \beta_1 (N_2^2/2 - N_2^3/3) + \right. \\ & \left. \delta_1 (N_2^3/3 - N_2^4/4) \right] - \left[\alpha_1 (N_2^* - N_2^{*2}/2) + \right. \\ & \left. \beta_1 (N_2^{*2}/2 - N_2^{*3}/3) + \delta_1 (N_2^{*3}/3 - N_2^{*4}/4) \right] = \\ & \log \gamma_2^* - \log \gamma_2, \end{aligned} \quad (31)$$

where N_2^* is a reference composition corresponding to a known value of $\log \gamma_2$ ($\log \gamma_2^*$) and N_2 represents a composition corresponding to $\log \gamma_2$ whose value is to be determined. Such an expression is useful for extrapolation purposes.

Using the previously determined values of constants α_1 , β_1 and δ_1 [from equation (26)] and taking $N_2^* = 0.2$, values of $\log \gamma_2$ were calculated from equation (31). These calculated values of $\log \gamma_2$ ($\log \gamma_a$) are given in Table V.

TABLE V

Extrapolation Values from Equation (31)

| N_w | $\log \gamma_w$ | γ_w | N_a | $\log \gamma_a$ | γ_a |
|-------|-----------------|------------|-------|-----------------|------------|
| 0.00 | 0.4453 | 2.79 | 0.00 | 0.5476 | 3.53 |
| 0.04 | 0.3546 | 2.26 | 0.04 | 0.4051 | 2.54 |
| 0.08 | 0.2914 | 1.95 | 0.10 | 0.2766 | 1.89 |
| 0.15 | 0.2250 | 1.68 | 0.15 | 0.2204 | 1.66 |

A plot of these values is shown as a broken line in Figure 5.

An expression for $\log \gamma_1$ in terms of N_1 analogous to equation (31) was used to calculate values of $\log \gamma_w$. Constants α_2 , β_2 , and δ_2 were obtained from equation (27) and the calculated values of $\log \gamma_w$ are also shown plotted as a broken line in figure 5.

The variation of the activity coefficient of a component of a liquid solution is given by the equation;

$$\left(\frac{\partial \ln \gamma_i}{\partial T} \right)_{P,N} = \frac{H_1^{\circ} - \bar{H}_i}{RT^2}, \quad (32)$$

where H_1° is the heat content of component "1" in its standard state and \bar{H}_1 is the partial molar heat content of component "1" in the solution. This equation indicates that if γ_1 increases with increase in temperature the value of H_1° must be greater than that of \bar{H}_1 and the corresponding contribution to the heat of mixing must, therefore, be negative.

The data obtained in the present work at 0°C was compared with that of Ferguson and Funnell (10) at 39.9°C , and it was found that the values of γ_w and γ_a at 0°C were somewhat larger than those at 39.9°C . This would seem to indicate that \bar{H}_1 in the above equation is greater than H_1° and the heat of mixing should, therefore, be positive. This, however, is not the case as heat is actually liberated on mixing the two liquids. It thus appears that a discrepancy exists between the two sets of data. However, the difference between the values of γ_w and γ_a at the two temperatures is rather small and, further, about the same difference was found between the data of Ferguson and Funnell (10) and that of Wrewsky (11) at the same temperature, that is 39.9°C .

The most probable source of experimental error which might account for this discrepancy is the determination of the composition of the vapor. Various methods have been employed for these measurements, among them being specific gravity determinations and measurements of refractive index using a refractometer or interferometer. The method of measuring specific gravities is potentially quite accurate but is complicated by the necessity of condensing out the vapors and transferring them to a pycnometer. It was found that such a transfer could be made without appreciable loss due to evaporation if carried out rather rapidly and at low temperature. By exercising proper precautions, the measurements may be carried out by this method to within an accuracy of about 0.2%. It would, nevertheless, be advantageous to determine the composition without having to effect a transfer of the solution. It would be most convenient to determine the composition of the vapor directly, possibly employing a gas interferometer in this connection.

Initial measurements were made on pure water, and its vapor pressure was found to be equal to 4.57 ± 0.01 mm. The accepted value for the vapor pressure of water at 0°C is 4.579 mm. Thus, the error involved in weighing the absorbed vapors was no greater than that encountered in determining the vapor composition. The vapor pressure of the 100% methanol was also determined and was found to have a value of 29.69 ± 0.04 mm. The literature value for the vapor pressure of methanol at 0°C is 29.67 mm. This measurement

served as a check on the purity of the methanol employed in the work.

The deviation of water and methanol vapors from ideal gas behavior was calculated by employing the van der Waal equation of state for which constants a and b were calculated from critical data. These calculations showed a deviation of only about 0.01% for water vapor and 0.1% for methanol. Thus, the assumption of ideal behavior of the vapors is accurate within the limits of experimental error.

VII. DISCUSSION

The quantity, $T\left(\frac{\partial P}{\partial T}\right)_V$, as applied to a liquid solution is known as the internal pressure. It is an important factor in determining the deviation of the solution from Raoult's law. The significance of the quantity is seen from the thermodynamic equation of state,

$$P + \left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V, \quad (33)$$

where $T\left(\frac{\partial P}{\partial T}\right)_V$ represents the force which is necessary to balance the combined effects of external pressure, P , and the "thermal pressure," $\left(\frac{\partial E}{\partial V}\right)_T$. It can be shown that if a solution is to behave ideally at any temperature and pressure the value of $\left(\frac{\partial P}{\partial T}\right)_V$ for the solution must be constant. If

this quantity is constant, it follows that its value for all components of the solution must be the same. Then for a given value of P and T the equations of state for the separate components of the solution are identical. The difference in the value of $\left(\frac{\partial P}{\partial T}\right)_V$ for the different components is, then, an im-

portant factor in determining the deviation from Raoult's law.

The values of the relative internal pressures of different substances based on solubility data have been given by Mortimer. The values for water and methanol are 4.60 and 3.35 respectively as compared to 0.84 for CCl_4 and 1.00 for naphthalene.

Since the values of the internal pressures of water and methanol are different, it is to be expected that aqueous methanol solutions would show deviations from Raoult's law.

The difference in internal pressures between the two components is probably due largely to the greater effect of hydrogen bonding in the water. This results in a greater attractive force between water molecules in solution than between methanol molecules or between molecules of water and molecules of methanol. The water molecules, therefore, tend to "squeeze out" the methanol molecules with the result that the partial pressures of the components in solution are greater than the vapor pressures of the pure liquid components and the solution shows a positive deviation from ideal behavior.

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