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An apparatus for the determination of vapor-liquid enthalpy and phase equilibrium data

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**An Apparatus for the Determination
of Vapor-Liquid
Enthalpy and Phase Equilibrium Data**

By

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This research report is accepted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

April 8, 1960

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AN APPARATUS FOR THE DETERMINATION
OF VAPOR - LIQUID
ENTHALPY AND PHASE EQUILIBRIUM DATA

by
Colonel Hugh Bloom, Jr.

A Dissertation
Presented to the Graduate Faculty
of Lehigh University
in Candidacy for the Degree of
Master of Science

Lehigh University

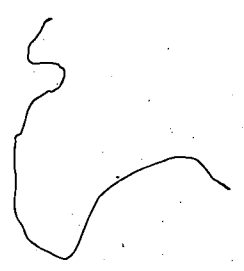
1960

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SUMMARY

An equilibrium still which may be used to determine vapor-liquid equilibrium, the equilibrium pressure and temperature, the isobaric heat of vaporization at the vapor composition of the system has been successfully tested. Vapor-liquid equilibrium data for the ethanol-water system compared with those of other investigators on a temperature-composition diagram showed a maximum deviation of $\pm 0.2^\circ\text{C}$ in the liquid phase and $\pm 0.6^\circ\text{C}$ in the vapor phase. Activity coefficients calculated from experimental data showed a maximum deviation of 2% from the values of other investigators. Thermodynamic consistency of the data was checked, and the data were found to fit the van Laar equation and to satisfy the Redlich-Kister criteria for consistency within 4%. Latent heat data were found to agree within 2% with that of other investigators.

The still as designed by Koechert is described in brief, and improvements to the apparatus are discussed. Thermodynamic considerations involved in vapor-liquid equilibrium and latent heat measurements are outlined.

INTRODUCTION

The determination of the vapor-liquid phase equilibrium and the enthalpy of a mixture is important for both industrial design calculations and theoretical comprehension of the thermodynamics of solutions and phase equilibrium. Determination of thermodynamic properties is also of utility to many industrial processes in determining minimum work or heat associated with a given change in the system.

Phase equilibrium data in conjunction with associated enthalpy values can be used to construct an entire enthalpy-concentration diagram for graphical solutions of binary distillation problems or may be used in tabular form for analytical solutions. The thermodynamic data required to establish graphical or analytical relationships is scattered throughout the literature, frequently inadequate, and most often non-existent. Therefore, diagrams for only a few binary systems have been constructed. Furthermore, if more than one interrelated thermodynamic property can be measured simultaneously on the same apparatus, a good check on internal consistency of data exists. Such an apparatus is described herein.

To completely define the enthalpy-composition network of a system, the following data are necessary:

- a. For the liquid phase-- isobaric specific heats of the pure components, heats of solution of the components at a reference temperature and pressure, and isobaric specific heats of the mixture from some reference temperature and pressure to the bubble point of the system.
- b. For the vapor phase-- isobaric latent heats of vaporization of the mixture at the reference pressure and vapor-liquid equilibrium data.

The present apparatus is designed to measure all the data required to complete the vapor phase structure; however, since a reference saturated liquid (bubble point) line must be established, the remainder of the necessary data must be either calculated or experimentally determined by another means. The latter alternative was considered beyond the scope of the initial investigation so that vapor-liquid equilibrium and enthalpy measurements were restricted to systems for which the bubble point line could be calculated.

The description and design criteria of the apparatus described in this report are reported by Koeckert (12) for the equilibrium still. This apparatus represents the complete revision of equipment which was constructed and operated to test the basic features of the design. The report describes thermodynamic considerations of the ap-

paratus and the results of a test run with the ethanol-water system. In general, attention is confined to non-electrolytic binary vapor-liquid systems at equilibrium. Non-idealities in the vapor phase were not considered.

DESCRIPTION OF APPARATUS

An equilibrium still designed for the simultaneous measurement of vapor-liquid equilibrium and heat of vaporization was constructed (12). The equilibrium still is a recirculating phase, flow-type calorimeter which provides the proper thermodynamic path for measurement of equilibrium values and isobaric latent heats of vaporization at the vapor composition. To eliminate contamination problems, the entire apparatus in contact with the system under study was fabricated of glass and Teflon.

As can be seen on Figure 1, liquid is vaporized in an external reboiler. Heat to the reboiler is supplied by two 4-foot 250 watt heating tapes wound around the glass tube of the boiler. The glass tube used was flattened on the bottom to provide for an increased area of heat transfer to the liquid. Vapor from the reboiler is directed up into a liquid reservoir in the equilibrium flask which consists of a single bubble cap to provide for effective vapor-liquid contact. The vapor temperature from the reboiler is measured by thermocouple TC-2 and the liquid temperature in the equilibrium pot by TC-5. A sample tube is provided to withdraw equilibrium liquid for analysis.

Vapor from the equilibrium flask passes through a counter-current vapor-liquid contacting section. This in-

sures that liquid from the condenser above is saturated at the bubble point. Temperature of the rising vapor is measured by TC-4, thermocouple TC-7 measures the temperature of the liquid in the condensate reservoir, and thermocouple TC-9 is taped to the side of the contactor wall and measures the temperature of the condensed vapor in equilibrium with the liquid in the equilibrium flask.

Heat is removed from the vapor with a standard West-type condenser inserted into the contactor. Enthalpy removed in the condenser is measured by metering the cooling water flow and noting the temperature rise of the water (thermocouple TC-1). This enthalpy represents the latent heat of the total mixture flowing at the vapor composition.

The condensate is collected and passed through a small Liebig cooler where the temperature is reduced from that of saturated liquid at the bubble point to approximately 25°C. At this point it might be possible to measure the sensible heat effect of the solution but no attempt has been made to do so. The liquid is then collected in a leveler which permits adjustment and observation of the liquid level in the condensate reservoir.

The liquid from the leveler represents the feed to the reboiler, i.e. recycle back to the equilibrium flask. The liquid feed rate is metered with a rotameter in the line and provision is made for obtaining liquid samples. To

To insure accurate determination of feed rate, the rotameter is jacketed with water at 25.0°C .

To minimize heat losses in the system and accompanying internal reflux, disruption of equilibrium, and errors in enthalpy measurements, it was found necessary to keep the heat losses below one percent. The use of simple insulating material would have produced too great a loss. Therefore, the principle of adiabatic walls was used to reduce losses. Two lengths of aluminum pipe were used -- one around the equilibrium flask and the other around the condenser. These sections of pipe were wound with heating tape and their temperatures controlled to that within the apparatus. Insulation was also placed between the pipes and the apparatus as well as on the outside of the pipes. The condenser section was insulated.

The cooling water system provides constant temperature coolant ($25.00 \pm 0.02^{\circ}\text{C}$) at a constant controlled rate to the calorimetric condenser and to the cooling water jacket of the feed rotameter. This water is also used to sub-cool the saturated liquid leaving the vapor-liquid condenser. Temperature control is provided by an on-off mercury regulator controlling a 50-watt heater. Water at constant head is provided by circulation of the cooling water between the upper and lower tanks.

Temperature measurement is provided by a Rubicon Type

B potentiometer and galvanometer used with copper-constantan thermocouples. The instrument is accurate to ± 0.5 microvolts or 0.02°C for enthalpy measurement or 1.1 microvolts or 0.05°C for equilibrium temperatures.

The pressure in the apparatus is maintained at 760 ± 0.1 mm.

DESIGN CRITEREA

Following is a brief description of the design criteria of the equilibrium still as presented by Koeckert (12).

1. Recirculating Path

Flow calorimeters which would provide for either a single-pass or a recirculating path for the vapor phase were considered. Designs of the single-pass type have been proposed by Dana (5) and modified by Tallmadge, Schroeder, Edminster, and Canjar (25). This latter type offers the advantage of accurate measurement of flow rate, but uncertainties in maintaining a constant liquid volume and uncertainties in correction for heat leaks precluded confidence in enthalpy measurements. A variation of this type has also been used by McCracken and Smith (13) and Callendar and Barnes (2), but neither type was adaptable to vapor-liquid equilibrium measurements.

The other alternative is a design in which the moving vapor phase is recirculated through the apparatus until equilibrium is attained. The two chief advantages of this type are that the moving vapor stream follows the exact thermodynamic path required for enthalpy measurements and that vapor-liquid equilibrium is assured. The chief disadvantage of this type of still lies in the difficulty of measurement of flow rates. Since it is inherently impractical to remove material from the system, a ball-type rota-

meter was chosen as the most accurate of in-line flow measuring devices.

2. Vaporizer Design

Two types of devices to generate vapor within the still were considered; in one case, condensate is vaporized in an external reboiler and, in the other case, the condensate is circulated directly to the equilibrium chamber prior to vaporization. Designs by Jones, Schoenborn, and Colburn (10) and Murti (15,16) incorporate vaporization of the recirculating phase prior to contact with the equilibrium liquid. The Othmer design (17,18,19) employing the direct return of recirculating liquid to the equilibrium flask appears to insure establishment of the equilibrium liquid composition. The results of Swientoslawski seem to indicate that the vapor formed by boiling within the equilibrium flask is superheated perhaps because it is in contact with the flask liquid for too short a time to establish equilibrium.

Since it is felt that truer equilibrium can be attained if the recirculating liquid is vaporized before contact with the equilibrium flask liquid, a tubular external reboiler has been employed.

3. Constant Liquid Level

To establish steady-state for enthalpy measurements, it is necessary to maintain fixed liquid levels in the system. One liquid level is fixed at the inlet of the

downsloping reboiler, and the quantity of liquid in the recirculating loop is fixed by the liquid level of the condensate collected from the condenser. The liquid quantity at the point of hold-up -- the equilibrium flask -- is then also fixed.

4. Enthalpy Measurement

To isolate the latent heat and sensible heat effects, vapor must leave the condenser as saturated liquid so that the exact isobaric heat of condensation is removed in the condenser. It is likely that the vapor condensed in condenser such as is designed for the apparatus could be sub-cooled; however, by providing effective contact between the downflowing liquid and upflowing vapors, the vapor will be partially condensed and the liquid reheated to its bubble point. The net heat removed by the condenser is then the isobaric latent heat of vaporization.

5. Pressure Control

The various designs of recirculating stills which use a closed system and regulate the pressure by the adjustment of heating or cooling offer distinct disadvantages for enthalpy measurement. The simpler method of pressure control at one atmosphere involves use of a reflux condenser connected to a reservoir of confining gas. If the system is adjusted to a pressure of 760 mm Hg and sealed, condensation of the vapor automatically maintains the inter-

nal pressure at the control value.

6. Calorimeter

Involvement in the measurement of enthalpy is measurement of the temperature rise of the cooling water across the condenser. To damp fluctuations in this temperature difference caused by surging in the cooling water line, a holding tank (ca. 50cc) was placed in the water discharge line.

OPERATING PROCEDURE

At the start of the experimental run, the equilibrium flask, the vapor-liquid contactor, the leveler, and the recirculating lines are charged with the test mixture. After adjustment of the temperature and flow rate of the cooling water to the condenser and the liquid subcooler, heat is applied to the adiabatic walls and the reboiler. Flow is then slowly started until a steady-state boiling condition is reached and all liquid levels can be maintained at steady-state. The still is run in this manner until constant values of the liquid and vapor temperatures indicate that equilibrium is affected. The usual length of a run is about five hours.

After equilibrium is attained, the cooling water rate is measured. At the end of the run samples are taken of the liquid from the equilibrium flask and of the condensed vapor. Then the feed rotameter is calibrated with the condensed vapor feed.

THERMODYNAMIC CONSIDERATIONS

The following discussion is applied to a thermodynamic analysis of vapor-liquid equilibria in a closed system. Thermodynamic analysis starts from perfect solution and perfect gas behavior and, in the first approach, lumps together deviations into empirical and theoretical correction factors.

When two phases are present, each phase represents a complete system, and, for equilibrium to exist between the phases, if the restraints of constant temperature and pressure are applied to the system, the free energy change is zero if no means of performing work is present.

To define the thermodynamic properties of a solution of given mass, the one additional variable, in addition to temperature and pressure, introduced is chemical potential. Then for a small change in internal energy, the general relationship is given by

$$dF = -SdT + VdP + \sum (\mu_n)_{T,P,n_1,\dots} dn_n \quad (1)$$

- where F = free energy
- S = entropy
- T = absolute temperature
- P = pressure
- V = volume
- μ = chemical potential
- n = number of moles of 1, 2, 3,
- E = internal energy

and the chemical potentials are defined

$$(\mu_1)_{V,S} = \left(\frac{\partial F}{\partial n_1} \right)_{V,S,n_2,\dots} \quad (\mu_2)_{V,S} = \left(\frac{\partial F}{\partial n_2} \right)_{V,S,n_1,\dots}$$

The above equations apply to the whole phase or to the whole of any multiphase system. At equilibrium

$$dF = -SdT + VdP \quad (2)$$

From the definition of partial molal properties, the chemical potential of a component is equal to the partial molal free energy $\mu_i = \bar{F}_i$. Then on a molal basis for the entire system

$$VdP - SdT = \sum (X_i d\mu_i) \quad (3)$$

The fugacity of a component i is defined for a component of a solution as follows:

$$(d\bar{F}_i = d\mu_i = RT \ln f_i)_T \quad (4)$$

But since Equation (4) applies at constant temperature, it cannot be substituted into Equation (3) as long as it is the total derivative of μ_i as a result of changes in temperature as well as pressure and composition. Therefore, Equation (4) is integrated from the low pressure ideal gas reference state of the pure component to the actual state of the component in the solution.

$$\mu_i - F_i^* = RT \ln f_i - RT \ln f_i^* \quad (5)$$

where f_i^* = the fugacity at a low pressure such that $f_i^* = P^*$
 F_i^* = free energy at the above reference state

Differentiating Equation (5) with respect to temperature at constant pressure

$$d\mu_i = df_i^* + RT \ln f_i + R \ln f_i dT - R \ln f_i^* dT \quad (6)$$

Combining Equations (5) and (6)

$$\left(\frac{\partial F^*}{\partial T}\right)_P - \left(\frac{\partial M_i}{\partial T}\right)_P = \frac{F^*}{T} - \frac{M_i}{T} - RT \left(\frac{\partial \ln f_i}{\partial T}\right)_P \quad (7)$$

From the thermodynamic definition of free energy $F = H - TS$

and for component i $F_i^* = M_i^*$ and $F_i = H_i - TS_i$

$$-S_i^* + S_i = H_i^*/T - M_i^*/T - S_i^* + S_i - RT \left(\frac{\partial \ln f_i}{\partial T}\right)_P \quad (8)$$

where S^* = the entropy at the reference state

$$\left(\frac{\partial \ln f_i}{\partial T}\right)_P = \frac{H_i^* - H_i}{RT^2} \quad (9)$$

Writing Equation (9) for the same temperature and pressure and in the same phase as the solution in which i is a component, multiplication by x_i and summation over all components

$$\frac{\sum (x_i H_i^*) - \sum (x_i H_i)}{RT^2} dT = \sum (x_i d \ln f_i) \quad (10)$$

Derrivation of the Gibbs-Duhem Equation

The Gibbs-Duhem Equation is a relationship deduced from thermodynamics to correlate the effects of composition on all the components in the mixture. This relationship is expressed mathematically as an equation between the change in fugacity of each component with the composition and may be derived in the following manner:

The molal free energy of a solution at constant temperature and pressure is given by

$$F_{P,T} = (x_1 F_1 + x_2 F_2 + x_3 F_3 + \dots)_{P,T} \quad (11)$$

and since $\mu_i = F_i$

$$F_{P,T} = (x_1 \mu_1 + x_2 \mu_2 + x_3 \mu_3 + \dots)_{P,T} \quad (12)$$

For any change in state this equation may be differentiated generally.

$$(dF)_{P,T} = (x_1 d\mu_1 + \mu_1 dx_1 + x_2 d\mu_2 + \mu_2 dx_2 + \dots)_{P,T} \quad (13)$$

At constant temperature and pressure Equation (13)

reduces to

$$(dF)_{P,T} = (\mu_1 dx_1 + \mu_2 dx_2 + \dots)_{P,T} \quad (14)$$

Subtracting Equation (14) from (13)

$$(x_1 d\mu_1 + x_2 d\mu_2 + \dots)_{P,T} = 0 \quad (15)$$

and since $d\mu_i = RT \ln f_i$

$$\left[x_1 \left(\frac{d \ln f_1}{dx_1} \right) + x_2 \left(\frac{d \ln f_2}{dx_2} \right) + \dots = 0 \right]_{P,T} \quad (16)$$

Equation (16) is a general statement of the Gibbs-Duhem relationship and represents the restriction which thermodynamics places upon the variation of fugacity with composition for a two-phase system in equilibrium. When Equation (16) is applied to a binary system, it reduces to

$$\left[x_1 \left(\frac{d \ln f_1}{dx_1} \right) \right]_{P,T} = \left[x_2 \left(\frac{d \ln f_2}{dx_2} \right) \right]_{P,T} \quad (17)$$

Activity Coefficients

The departure of a solution from ideal behavior can be represented by an empirical correction factor known as the activity coefficient, γ . The numerical value of the

activity coefficient is dependent both on the standard state and on the units of expression for composition.

Commonly, the activity coefficient is defined as

$$\gamma_i = f_i / (f_i^\circ x_i) \quad (18)$$

where f_i° = fugacity of i at a standard state

The activity coefficient is found to vary in the following manner with pressure:

$$d\bar{F}_i = -\bar{S}_i dT + \bar{V}_i dP \quad (19)$$

where superscript - indicates a partial molal quantity.

At constant temperature

$$\left(\frac{d\bar{F}_i}{dP}\right)_T = \bar{V}_i \quad (20)$$

Since $d\bar{F}_i = RT \ln f_i$ and applying Equation (20) to both

$$f_i \text{ and } f_i^\circ$$

$$\frac{\partial \ln (f_i / f_i^\circ)}{\partial P} = \frac{\bar{V}_i - \bar{V}_i^\circ}{RT} \quad (21)$$

Similarly the activity coefficients are found to vary in the following manner with temperature at constant pressure and composition:

From Equations (10) and (18)

$$\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{P, X} = \left(\frac{H_i^\circ - \bar{H}_i}{RT^2}\right)_{P, X} \quad (22)$$

The term $H_i^\circ - \bar{H}_i$ is the integral heat of mixing of compound i from its standard state to the solution of given composition both in the same state of aggregation and pressure.

The Gibbs-Duhem Equation may also be expressed in terms of activity coefficients:

From Equation (17) substituting the definition of an activity coefficient in terms of fugacity

$$\left[x_1 \left(\frac{\partial \ln f_1}{\partial x_1} \right) \right]_{P,T} = \left[x_2 \left(\frac{\partial \ln f_2}{\partial x_2} \right) \right]_{P,T}$$

$$x_1 \left(\frac{\partial \ln f_1}{\partial x_1} \right) + x_1 \left(\frac{\partial \ln x_1}{\partial x_1} \right) = x_2 \left(\frac{\partial \ln f_2}{\partial x_2} \right) + x_2 \left(\frac{\partial \ln x_2}{\partial x_2} \right) = 0$$

$$\text{But } x_1 \left(\frac{\partial \ln x_1}{\partial x_1} \right) = \frac{x_1 \cdot 1}{x_1} = 1$$

$$\text{and similarly } x_2 \left(\frac{\partial \ln x_2}{\partial x_2} \right) = 1$$

$$\left[x_1 \left(\frac{\partial \ln f_1}{\partial x_1} \right) \right]_{P,T} = \left[x_2 \left(\frac{\partial \ln f_2}{\partial x_2} \right) \right]_{P,T} \quad (23)$$

Equation (23) is valid at constant temperature and constant pressure for non-electrolyte solutions.

General Forms of the Gibbs-Duhem Equation

Since Equation (23) applies only at conditions of simultaneous constant pressure and temperature and vaporization operations are carried out at either constant temperature and variable pressure or constant pressure and varying temperature, modifications to the Gibbs-Duhem Equation are of considerable practical importance. These modifications follow the procedure of Ibl and Dodge (8).

For a two component system Equation (3) reduces to

$$\frac{d \ln f_1}{d \ln x} = \frac{d \ln f_2}{d \ln (1-x)} + \frac{v_m}{RT} \frac{dP}{dx} \quad (24)$$

where v_m = molal volume of the liquid phase.

$$\text{From } f_1 = f_1^*/x \quad f_2 = f_2^*/(1-x)$$

and Equation (24)

$$\frac{d \ln f_1}{d \ln x} = \frac{d \ln f_2}{d \ln(1-x)} + [V_m - xV_1^* - (1-x)V_2^*] \frac{1}{RT} \frac{dP}{dx}$$

at T constant (25)

where V_1^* and V_2^* are the mean molal volumes of the pure liquids at the pressure and temperature of the mixture, and the term $V_m - xV_1^* - (1-x)V_2^*$ is, therefore, the molal volume change accompanying the mixing.

Similarly, by writing Equation (9) for a two component system

$$x \left(\frac{d \ln f_1}{dT} \right)_{P,x} + (1-x) \left(\frac{d \ln f_2}{dT} \right)_{P,(1-x)} = \frac{\Delta H}{RT^2} \quad (26)$$

where $\Delta H = xH_1^0 + (1-x)H_2^0 - x\bar{H}_1 - (1-x)\bar{H}_2$
 H^0 = molal enthalpies of the pure components in the ideal gas state.

ΔH = molal heat of vaporization.

Applying the Gibbs-Duhem Equation

$$\frac{d \ln f_1}{d \ln x} = \frac{d \ln f_2}{d \ln(1-x)} + \frac{\Delta H}{RT^2} \frac{dT}{dx} \quad (27)$$

where Equation (27) is an exact form of the Gibbs-Duhem Equation valid at constant total pressure and variable temperature.

Equation (27) can also be written in terms of activity coefficients

$$\left(\frac{d \ln f_1}{d \ln x} \right) = \frac{d \ln f_2}{d \ln(1-x)} - [x\bar{H}_1 + (1-x)\bar{H}_2 - xH_1^* - (1-x)H_2^*] \frac{1}{RT^2} \frac{dT}{dx}$$

at constant P (28)

where the term $x\bar{H}_1 + (1-x)\bar{H}_2 - xH_1^* - (1-x)H_2^*$ is the molal integral heat of mixing.

Equations (25) and (28) apply to either phase under consideration. The volumes and the enthalpies refer to the phase under consideration. However, for the vapor phase at low pressures the activity coefficients are near unity. In the liquid phase the unmodified Gibbs-Duhem Equation is usually applicable in the case of constant temperature, variable pressure.

Excess Thermodynamic Properties

To predict vapor-liquid equilibrium in non-ideal systems, the concept of excess thermodynamic properties becomes useful. It becomes possible to evaluate the deviation of the non-ideal solution in terms of the excess properties and activity coefficients.

When a mole of solution at standard state and unit fugacity is added to a solution at the same pressure and temperature

$$\mu_i - RT \ln f_i = \mu_i^\circ - RT \ln f_i^\circ \quad (29)$$

Redefining the activity coefficient

$$f_i = f_i^\circ \gamma_i$$

Defining μ^* as the chemical potential at a pressure sufficiently small that

$$\mu_i^* = \mu_i - \mu^* = RT \ln \gamma_i \quad (30)$$

where μ_i^E = excess chemical potential.

Then, the excess free energy F^E per mole of solution becomes

$$F^E = \sum x_i \mu_i^E = \sum x_i RT \ln \gamma_i \quad (31)$$

Redlich-Kister Equation

One common method of representing activity coefficients is that developed by Redlich and Kister (22). In this approach, excess free energy is related to composition at conditions of constant temperature and pressure by use of a series function with sufficient terms to accurately represent the experimental data.

The function Φ for a binary mixture is defined by

$$\Phi = x_1 \log \gamma_1 + x_2 \log \gamma_2 \quad (32)$$

The function Φ is zero for a perfect solution at any concentration and is also zero for any solution at the end points $x_1 = 1$ and $x_2 = 1$. Then the most suitable representation of Φ is

$$\Phi = x_1 x_2 [B + C(x_1 - x_2) + D(x_1 - x_2)^2 + \dots] \quad (33)$$

where the coefficients B, C, D are temperature dependent, and the term $x_1 x_2$ provides for the zero value of Φ at compositions corresponding to the separate pure components.

If the activity coefficients are given by the relations

$$\ln \gamma_1 = \Phi + x_2 d\Phi/dx_2 ; \quad \ln \gamma_2 = \Phi - x_1 d\Phi/dx_1$$

$$\text{then } \ln Y_1 = X_2^2 [B + C(3X_1 - X_2) + D(X_1 - X_2)(5X_1 - X_2) + E(X_1 - X_2)^2(7X_1 - X_2) + \dots] \quad (34)$$

$$\ln Y_2 = X_1^2 [B + C(X_1 - 3X_2) + D(X_1 - X_2)(X_1 - 5X_2) + E(X_1 - X_2)^2(X_1 - 7X_2) + \dots] \quad (35)$$

For most applications, the following quantity is used:

$$\ln(Y_1/X_2) = dQ/dX_1 = B(X_2 - X_1) + C(6X_1X_2 - 1) + D(X_1 - X_2)(8X_1X_2 - 1) + E(X_1 - X_2)^2(10X_1X_2 - 1) + \dots \quad (36)$$

Equation (36) is very useful for practical application since the relation between relative volatility α and vapor pressures P_1° and P_2° of the components is given by

$$\alpha = \frac{y_1 X_2 / X_1 y_2}{x_1 P_1^\circ / x_2 P_2^\circ}$$

if the vapor is a perfect gas mixture. Since measurements were all taken at one atmosphere, this assumption is well justified.

In general, Equation (36) is a convenient representation since only the first term is required for a nearly perfect solution, two terms for a less ideal solution, and only extremely imperfect solutions require as many as four terms. Thus, experimental data on activity coefficients for binary systems are correlated by a single expression which is applicable at the simultaneous criteria of constant temperature and constant pressure. A modification of the Redlich-Kister Equation by Chao and Hougen (3) has alleviated this difficulty and is discussed be-

low.

To clarify this explanation an exact expression for excess molal free energy from exact forms of the Gibbs-Duhem Equation will be derived. This derivation has been performed by Van Ness ().

From Equations (5) and (6)

$$R \ln f_i dT - R \ln p^* dT = \left(\frac{\mu_i - F_i^*}{T} \right) dT \quad (37)$$

Then, since $F = H - TS$ and $S_i^* + F_i^*/T = H_i^*/T$

$$d\mu_i = -S_i^* dT + \left(\frac{\mu_i - F_i^*}{T} \right) dT + RT \ln f_i$$

Multiply through by X_i and sum over all components

$$\sum X_i d\mu_i = \frac{-\sum (X_i H_i^*) dT}{T} + \frac{\sum (X_i \mu_i) dT}{T} + RT \sum (X_i d \ln f_i) \quad (38)$$

$$\text{But } \sum (X_i H_i^*) = H^* ; \sum (X_i \mu_i) = F$$

where H^* = molal ideal gas enthalpy of the solution
 F = actual molal free energy of the solution

Then,

$$\sum (X_i d\mu_i) = -(H^*/T) dT + (F/T) dT + RT \sum (X_i d \ln f_i) \quad (39)$$

$$V dP - S dT = \sum (X_i d\mu_i)$$

$$S + F/T = H^*/T$$

$$\frac{V}{RT} dP + \frac{(H^* - H)}{RT^2} dT = \sum (X_i d \ln f_i) \quad (40)$$

Writing Equation (40) for pure i at the same temperature and pressure in the same phase as the solution in which i is a component, multiplication by X_i and summation over all components

$$\frac{\sum (X_i V_i)}{RT} dP + \frac{\sum (X_i H_i^*) - \sum (X_i H_i)}{RT^2} dT = \sum (X_i d \ln f_i) \quad (41)$$

Let $V - \sum(x_i v_i) = \Delta V$ the volume change on mixing

$H - \sum(x_i H_i) = \Delta H$ the heat of mixing

$$\sum x_i d \ln(f_i / f_i^0) = \sum (x_i d \ln \gamma_i)$$

$$\text{then, } \frac{\Delta V}{RT} dP - \frac{\Delta H}{RT^2} dT = \sum (x_i d \ln \gamma_i) \quad (42)$$

In terms of the molal free energy, if

$$d(x_i \ln \gamma_i) = x_i \ln d\gamma_i + \ln \gamma_i dx_i$$

$$\sum (x_i d \ln \gamma_i) = d \sum (x_i \ln \gamma_i) - \sum (\ln \gamma_i dx_i)$$

$$\Delta F^E / RT = \sum (x_i \ln \gamma_i)$$

then from Equation (42)

$$d(\Delta F^E / RT) = \Delta V / RT dP - \Delta H / RT^2 dT + \sum (\ln \gamma_i dx_i) \quad (43)$$

and integrating Equation (43)

$$\left(\frac{\Delta F^E}{RT}\right)_2 - \left(\frac{\Delta F^E}{RT}\right)_1 = \int_1^2 \frac{\Delta V}{RT} dP - \int_1^2 \frac{\Delta H}{RT^2} dT + \sum \int_1^2 \ln \gamma_i dx_i \quad (44)$$

If the data are taken for a phase at constant composition, the last term of Equation (44) is zero and

$$\Delta H = T \Delta V \left(\frac{dP}{dT} \right)_X - T^2 \left(\frac{d(\Delta F^E / T)}{dT} \right)_X$$

Equation (45) applies at the simultaneous restrictions of constant temperature and constant pressure.

Chao and Hougen (3) have applied a similar analysis to the Redlich Kister Equation. Redlich and Kister relate excess free energy to composition by a series function

$$Q = F^E / RT = x_1 x_2 [B + C(x_1 - x_2) + D(x_1 - x_2)^2 + \dots]$$

at constant temperature or pressure. By using slightly different constants in the above equation as temperature or pressure are not independent variables, the following

can be written for an isobaric process:

$$FE = RT X_1 X_2 [B' + C'(X_1 - X_2) + D'(X_1 - X_2)^2 + \dots] \quad (46)$$

The exact differential equation is written

$$\left[d \ln \gamma_1 = \left(\frac{\partial \ln \gamma_1}{\partial T} \right)_{P, X_i} dT + \left(\frac{\partial \ln \gamma_1}{\partial \ln X_1} \right)_{P, T} d \ln X_1 \right]_P$$

and similarly for component 2. The variation of activity coefficients with temperature at constant pressure and composition has been given by Equation (22)

$$\left(\frac{\partial \ln \gamma_i}{\partial T} \right)_{P, X_i} = (H_i^\circ - \bar{H}_i) / RT^2$$

Combining Equations (22), (46), and the Gibbs-Duhem Relationship (Equation 23):

$$\left[\frac{d \ln \gamma_1}{d \ln X_1} = \frac{d \ln \gamma_2}{d \ln X_2} + Z \right]_P$$

where $Z = -(\Delta H / RT^2) (dT/dX_1)_P$

$$\Delta H = H - X_1 H_1^\circ - X_2 H_2^\circ$$

and H , H_1° , and H_2° = molal enthalpies of the mixture and the pure components respectively.

ΔH = integral heat of solution in dissolving liquids in their standard state to form a liquid solution of given composition at constant pressure and corresponding temperature.

From Equation (47)

$$[X_1 d \ln \gamma_1 + X_2 d \ln \gamma_2 + Z dX_1]_P \quad (48)$$

$$\begin{aligned} \left[\frac{dFE/RT}{dX_1} = \ln \gamma_1 - \ln \gamma_2 + \frac{d \ln \gamma_1}{d \ln X_2} - \frac{d \ln \gamma_2}{d \ln X_2} \right. \\ \left. = \ln \gamma_1 - \ln \gamma_2 + Z \right]_P \quad (49) \end{aligned}$$

Equation (49) may be compared with Equation (43) as

applied to an isobaric process. As described by Chao and Hougen (3) the values of Z are difficult to determine. These values involve measurement of variations of temperature with composition at constant pressure and measurement of heats of solutions which involve hypothetical standard states (the more volatile component at the bubble point). To avoid these measurements the effect of Z is included in the empirical equation for the ratio of the activity coefficients.

$$\ln \gamma_1/x_1 = b(x_2-x_1) + c(bx_1x_2-1) + d(x_2-x_1)(1-\theta x_1x_2) + \dots \quad (50)$$

Combining with the Redlich-Kister Equation

$$\ln \gamma_1 = x_1 x_2 [B + c(x_1-x_2) + D(x_1-x_2)^2 + \dots] - x_2 [b(x_2-x_1) + c(bx_1x_2-1) + d(x_1-x_2)(\theta x_1x_2-1) + \dots] \quad (51)$$

and similarly for $\ln \gamma_2$.

Other Equations for Excess Free Energy

An equation for excess free energy was developed by Wohl (28) in terms of composition, effective molal volume, and volumetric fraction of the separate components.

$$\frac{FE}{RT(\sum z_i x_i)} = \sum_{ih} z_i z_h a_{ih} + \sum_{ihj} z_i z_h z_j a_{ihj} + \sum_{ihjk} z_i z_h z_j z_k a_{ihjkl} + \dots \quad (52)$$

where for component i

- x_i = mole fraction of i
- z_i = effective molal volume
- \bar{v}_i = effective volume fraction

Subscripts i, h, j, and l correspond to the separate components of the mixture.

a_{ih}, a_{inj} = empirical constants

$$z_i = \frac{x_i}{x_i + \sum_{j \neq i} \frac{q_j x_j}{z_i}}$$

where j = any component other than i.

The term $\sum z_i z_h a_{jh}$ represents the contribution due to the molecular interaction between unlike components in groups of two. The term $\sum z_i z_h z_j a_{ihj}$ is analogous for groups of three. As in the case of the Redlich-Kister Equation as many empirical constants as are required to represent the experimental data accurately may be used.

For a binary system, a three suffix equation of the form of Equation (51) may be written

$$\frac{FE}{RT(\delta_1 x_1 + \delta_2 x_2)} = z_1 z_2 2a_{12} + z_1^2 z_2 3a_{112} + z_1 z_2^2 3a_{112} \quad (53)$$

and since $z_1 + z_2 = 1$

$$\begin{aligned} FE/RT = (x_1 + \delta_2/\delta_1 x_2) z_1 z_2 [z_1 \delta_1 (2a_{12} + 3a_{112}) \\ + z_2 \delta_1 (2a_{12} + 3a_{112})] \end{aligned} \quad (54)$$

By letting $A = \delta_1 (2a_{12} + 3a_{112})$

$$B = \delta_2 (2a_{12} + 3a_{112})$$

Equation (54) becomes

$$FE/RT = (x_1 + \delta_2/\delta_1 x_2) z_1 z_2 (z_1 \delta_1 B + z_2 A) \quad (55)$$

By expressing x in terms of z

$$\ln \delta_1 = z_1^2 [A + 2(B\delta_1/\delta_2 - A)z_1] \quad (56)$$

$$\ln \delta_2 = z_2^2 [B + 2(A\delta_2/\delta_1 - B)z_2] \quad (57)$$

When γ_i/g_i reduces to one, then Equations (56) and (57) become the Margules Equations:

$$\ln \gamma_1 = X_2^2 [A + 2(B-A)X_1]$$

$$\ln \gamma_2 = X_1^2 [B + 2(A-B)X_2]$$

When $\gamma_i/g_i = A/B$, Equations (56) and (57) reduce to the two-suffix form of the equations as developed by Van Laar (26).

$$\ln \gamma_1 = \frac{AX_2^2}{(A/B X_1 + X_2)^2}$$

$$\ln \gamma_2 = \frac{BX_1^2}{(X_1 + B/A X_2)^2}$$

Gaseous Mixtures

The foregoing considerations of thermodynamic equilibrium as applied to activity coefficients were derived to account for non-ideality in the liquid phase. For a description of behavior of gaseous mixtures it is desirable to substitute a quantity analogous to the activity coefficient called the fugacity coefficient. The fugacity coefficient, ϕ_i , of the component i is defined by

$$f_i = y_i \phi_i P$$

The fugacity coefficient is calculated from P-V-T data or any equation of state by means of

$$\ln \phi_i = \int_0^P (\bar{z}_i - 1) dP/P$$

where $\bar{z}_i = P\bar{v}_i/RT$ and is called by partial molal compressibility factor. \bar{v}_i is the partial molal volume of component i .

Pressure dependence of the thermodynamic properties in the gas phase presents no problems as long as the pressure remains low. Since the scope of this project involves only atmospheric pressure measurements, ideality of the gas phase may be assumed to be valid, and the behavior of gaseous mixtures will not be considered further.

Testing Experimental Data

One of the simplest tests of the validity of thermodynamic data is obtained by the integration of the Redlich-Kister Equation (Equation 36).

$$\ln(\gamma_1/\gamma_2) = dQ/dx_1 \quad (58)$$

Since the excess free energy of the solution, Q , is zero for both $x_1 = 0$, $x_1 = 1$, then

$$\int_0^1 \ln(\gamma_1/\gamma_2) dx = 0 \quad (59)$$

If $\ln(\gamma_1/\gamma_2)$ is plotted against x_1 , the area above the abscissa axis must equal that below. This condition applies strictly for an isobaric process only at constant temperature. Generally, it can be applied to data in a moderately small boiling interval.

Noting the results of Equation (47), it is possible that at non-isothermal conditions the negative and positive areas may not be equal. This difference may then be due to the "Z" effect and not to inconsistent measurements.

GENERAL COMMENTS ON THE CONSTRUCTION OF THE ENTHALPY-
CONCENTRATION DIAGRAM

Construction of the enthalpy-concentration diagram may be divided into two parts. First, construction of the liquid portion of the diagram which requires knowledge of

- (1) Isobaric specific heats of the pure liquid components.
- (2) Heat of solution data of the components at a reference temperature and pressure.
- (3) Isobaric specific heats of the mixture from the reference temperature and pressure to the bubble point of the mixture.

Second, construction of the vapor portion of the diagram which requires a knowledge of

- (1) Isobaric latent heat of vaporization of the mixture at the reference pressure.
- (2) Liquid-vapor equilibrium data.

If the enthalpies of the pure components are equal to zero at a standard state $t = 32^\circ\text{F}$ and $P = 1$ atmosphere,

$$H_L = X(H_1) + (1-X)H_2 + \Delta H_M + \int_{t_R}^T (C_P)_{1,2} dT$$

where $H_1 = \int_{t_0}^{t_R} \left(\frac{\partial H}{\partial P}\right)_{t_0} dP + \int_{t_0}^{t_R} C_{P_1} dP$

$\Delta H_M =$ heat of mixing

- C_{p1} = molal specific heat of component 1
 C_{p12} = molal specific heat of the mixture
 t_0 = standard state temperature of the liquid
 P_0 = saturation pressure of the compound corresponding to t_0
 t_R = reference temperature at which the heat of mixing is known

Similarly

$$H_L = \int_{P_0}^{P^M} \left(\frac{\partial H}{\partial P} \right)_{t_0} dP + \int_{t_0}^{t_R} C_{p2} dT$$

For liquids, however, the pressure integral is negligible and Equation (58) reduces to

$$H_L = X_1 \int_{t_0}^{t_R} C_{p1} dT + X_2 \int_{t_0}^{t_R} C_{p2} dT + \Delta H_M + \int_{t_R}^t (C_p)_{1,2} dT$$

The enthalpy of the vapor at the dew point is then equal to

$$H = H_L + \lambda_{1,2}$$

where $\lambda_{1,2}$ = molal latent heat of vaporization at the temperature and pressure of the liquid at its bubble point.

The scope of the present investigation includes the measurement of vapor-liquid equilibrium data and of the molal latent heat data required to construct the diagram. Assuming that, in general, specific heat data is available for most pure compounds, then data remaining to be measured include the heat of mixing at a reference temperature and the specific heat of the solution. A number of methods are available for the measurement of these data, and to complete the thermodynamic system the scope of future investigations will be expanded to include them.

An interesting relationship exists between the heat of mixing of a solution and vapor pressure data and the excess free energy of solutions. By means of Equation (45) the heat of mixing can be calculated from experimental values taken at constant temperature and at varying pressure along the saturation curve. From these values the activity coefficients and excess free energy values may be calculated.

$$\Delta H_M = -T^2 \left(\frac{\partial \Delta F^E / T}{\partial T} \right)_{\text{sat}, X} + T \Delta V \left(\frac{\partial P}{\partial T} \right)_{\text{sat}, X} \quad (45)$$

As the present investigation is restricted to constant pressure, the variation of temperature with pressure cannot be calculated, and of course the above expression cannot be evaluated.

EXPERIMENTAL RESULTS

To check the design of the equilibrium still, the binary system, ethanol-water, was used. It was felt that, if vapor-liquid equilibrium results compared favorably to those of other investigators and the results were thermodynamically consistent, the validity of the vapor-liquid equilibrium measurements would be substantiated. Latent heats were to be compared with those of Bosnjakovic (1) and those of Smith, Kuong, Brown, and White (24).

Analyses were made by a modified method of Karl Fischer (14) for water. Ethanol was determined by difference except in the range of low alcohol concentrations (less than 20%w) where refractive indexes were used.

Absolute ethyl alcohol of USP grade supplied by United States Industries was used without further purification.

VAPOR-LIQUID EQUILIBRIUM DATA

The vapor-liquid equilibrium data obtained in this study are presented in Table 1. Activity coefficients were calculated from the definitions (Equation 18). In computing the values the vapor pressures were interpolated from data in the International Critical Tables (9) and

the vapor pressures of water from the data of Kennan and Keyes (11).

The data are also plotted on a temperature-composition diagram (see Figure 2) and compared with what is considered reliable data of other investigators (20, 4, 10). In the liquid region, the best line through the data points of this work does not deviate from the values of the other investigators by more than $\pm 0.2^\circ\text{C}$. In the vapor region, the best line through the data of this work does not deviate from the data of other investigators by more than $\pm 0.6^\circ\text{C}$. This is considered an adequate representation of the data since the deviations among the comparative data are as much as 0.3°C in the liquid phase and 0.8°C in the vapor phase.

Calculated values of the activity coefficients of ethanol and water were also plotted (see Figure 3) and compared to the values obtained by Otsuki and Williams (20) and Jones, Schoenborn, and Colburn (10). The values of activity coefficients do not deviate by more than 2% from those of the other investigators.

The applicability of the Van Laar Equation was determined by calculating the values of A and B from the values of the activity coefficients from a smoothed curve at the liquid mole fractions of 0.2, 0.4, 0.6, and 0.8. The values of the activity coefficients determined from these con-

stants are compared in Table 3 with the experimental values obtained from the smoothed curve. The close agreement obtained from this comparison indicates that the data fit the prediction of the Van Laar Equation. Therefore, it appears that a two constant equation is a suitable representation of the ethanol-water vapor-liquid equilibrium system.

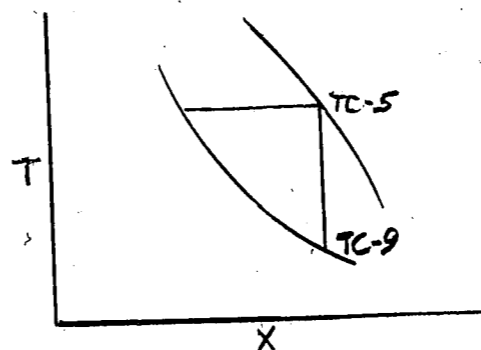
As seen in Equation (59) a method of testing for the consistency of the experimental vapor-liquid equilibrium data is the use of Scatchard's free energy of mixing as shown by Redlich and Kister (21).

$$Q = \int_{x=0}^{x=1} \ln \gamma_1/\gamma_2 dx = 0$$

The condition of constant temperature and constant pressure must be simultaneously imposed on the above equation. Since the temperature range involved in the ethanol-water system is small, the assumption that the effect of this temperature change is negligible will be made. The values for the ratio of the activity coefficients vs. the mole fraction ethanol in the liquid are plotted on Figure 4. The integrated areas of the positive and negative segments of the plot agree within 4%, indicating thermodynamic consistency of the experimental data.

A further check on the internal consistency of the experimental data is provided by measurement of the temperature of the condensed vapor in equilibrium with the

saturated liquid in the equilibrium pot. This relationship is illustrated on the following temperature composition diagram. Thermocouples used for each measurement are also indicated.



The temperatures measured by thermocouple TC-9 should fall on the saturated liquid line at the composition of the vapor leaving the equilibrium pot. In this investigation, the saturated liquid and vapor lines were first established, and then the temperatures measured by thermocouple TC-9 were plotted. As can be seen on Figure 5 the agreement is reasonably good (less than $\pm 0.2^\circ\text{C}$ average deviation) thus further substantiating the consistency of the equilibrium data.

Latent Heat of Vaporization Data

Due to operating and experimental difficulties encountered with the first nine runs, the experimental latent heat values deviated by as much as 6-7% from the reference values and show no systematic error. It was

found that these large errors were caused by inaccuracies in calibrating the rotameter and by a surging encountered in the cooling water system. After these difficulties were corrected, experimental values of latent heat for the remaining runs were in all cases within 2% of the reference values of Bosnjakovic.

Latent heats were calculated by a heat balance as determined by the following equation:

$$m_w C_p \Delta T = \lambda m_s + Q$$

where m_w = mass of water flowing per minute
 C_p = specific heat of water
 ΔT = difference in water inlet and outlet temperatures
 m_s = mass of system flowing per minute
 λ = isobaric latent heat
 Q = heat leak correction. There is an opportunity for heat transfer between the adiabatic wall (the upper aluminum cylinder) and the condenser jacket water. Heat transfer was dependent only on the temperature of the aluminum wall and was found to be 13, 18, and 23 cal/min at 80, 90, and 100°C respectively. These values, which represent approximately 5% of the total heat load, were included in the latent heat evaluations.

The reference enthalpy data for the pure components were taken from the International Critical Tables (9). The reference enthalpy data for the mixtures was determined by Bosnjakovic (1) and by Smith, Kuong, Brown, and White (24). The results of these two investigations are compared with the results of this work on Figure 6 and in Table 6. It was found that experimental results compare to within 2% of the values of Bosnjakovic and to within 4% of

those of Smith et al.

The saturated liquid line on the enthalpy-composition diagram was calculated for this work by the same method as used by Smith et al. Data for the heats of mixing of ethanol-water and the specific heats of the pure components are available in the International Critical Tables (9). Heats of solution data are tabulated in Table 5. The enthalpy-concentration diagram for the ethanol-water system is presented on Figure 6.

OPERATIONAL CONSIDERATIONS

The following is a list of current significant considerations in the operation of the equilibrium still.

1. The liquid leaving the condenser may be considered saturated (i.e. at its bubble point) since its temperature as measured by thermocouple TC-9 corresponds to that of the bubble point temperature.
2. Surging of the vapor through the equilibrium flask was reported by Koeckert (12). This has been eliminated by reducing the liquid holdup on the equilibrium tray from about 400 ml to about 200 ml.
3. It is felt that errors in measurement of the system flow rate have been reduced to below 1% since the reproducibility of duplicate measurements was in all cases within 0.5%.
4. Surging in the condenser cooling water flow rate as determined by the absence of cyclic fluctuations in the inlet and outlet temperature difference and by constant cooling water flow rates measured in duplicate was considered eliminated.
5. From calibrations of the thermocouple TC-1 by Koeckert (12), it is felt that errors in the reproducibility and stability of enthalpy measurements would not exceed 0.3% of the measured potential. From calibrations of the re-

maintaining thermocouples, it is felt that errors in temperature measurement would not exceed 0.05°C .

6. An unexpected heat leak was encountered when it was found that the vapor rising from the equilibrium flask could transfer heat to the condensed liquid in the condensate collector. The temperature of this liquid was, at equilibrium, as much as 9°C less than the temperature of the vapor from the equilibrium flask. The difference in temperatures between this superheated liquid and saturated liquid as measured respectively by thermocouples TC-7 and TC-9 indicated the extent of heat transferred. This temperature difference amounted to as much as 3°C .

Since this heat transfer represented a net heat loss to the system, a like amount of heat must be supplied as superheat to the vapor leaving the reboiler. The superheat supplied and the heat loss are compared in Table . From this table it can be seen that the maximum heat loss is less than 0.7% of the total. To eliminate this loss, it is recommended that the condensed liquid reservoir be removed from contact with the rising vapor and be placed outside the upper adiabatic wall.

8. To insure that a large pressure drop through the apparatus did not cause errors in vapor-liquid equilibrium measurements, Kosckert (12) calculated the pressure drop of the flowing vapor. It was found to be negligible (1.5×10^{-3} mm Hg).

CONCLUSIONS AND LIMITATIONS

The reflux design for latent heat measurements has proven to be a promising device with but two limitations:

1. Heat transfer between vapor from the equilibrium flask and the condensed vapor in the condensate chamber has caused a heat loss in the system. It is proposed to alleviate this situation by relocating the condensate chamber away from intimate contact with the upflowing vapor.
2. Heat transfer from the adiabatic wall to the cooling water used for enthalpy measurements has necessitated the use of a factor to correct for this error in enthalpy measurements.

There are certain limitations imposed by the present design on the utility of the apparatus:

1. Data are restricted to one atmosphere pressure.
2. Systems are restricted to intermediate boiling substances which can be condensed with 25° C cooling water and which are completely miscible in each other.
3. In addition to the enthalpy and vapor-liquid measurements from the proposed apparatus, heats of solutions and specific heat data are necessary to complete an enthalpy-concentration diagram.

In spite of the above considerations, it is felt that data from the ethanol-water system have proven the applicability of this new design to the simultaneous measurement

of latent heat and vapor-liquid equilibrium. It is hoped to incorporate a method of measurement of heats of mixing and isobaric specific heats of mixtures into the scope of the project so that the complete thermodynamic network necessary for the construction of enthalpy-composition diagrams can be determined. It may also be possible to apply the apparatus to systems of three components.

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TABLE 1

VAPOR-LIQUID EQUILIBRIUM DATA EtOH-H₂O

<u>Run No.</u>	<u>Liq.</u> <u>%m</u>	<u>Vap.</u> <u>%m</u>	<u>Liq.</u> <u>Temp</u> <u>°C</u>	<u>Vap.</u> ¹ <u>Temp</u> <u>°C</u>	<u>Condensate</u> ² <u>Temp</u> <u>°C</u>
1	12.5	48.8	85.2	81.2	81.5
2	10.6	45.8	86.1	80.7	81.7
4	5.0	35.3	90.0	81.2	81.3
6	80.5	81.4	78.3	78.3	78.2
7	68.9	74.1	78.6	78.4	78.4
8	60.2	69.5	79.2	78.6	78.8
9	64.3	71.3	79.1	78.6	78.8
10	55.6	67.5	79.5	78.8	79.0
11	40.3	62.5	80.2	78.8	79.1
12	40.3	61.9	80.6	79.2	79.3
13	32.1	57.2	81.6	79.7	80.0
14	31.5	57.1	81.8	79.7	80.0
15	13.5	48.4	84.7	80.0	80.9
16	8.5	41.1	87.2	80.4	81.7
17	3.3	27.2	91.9	82.0	84.7
18	2.1	19.9	94.3	82.1	85.6
20	98.7	98.5	78.2	78.2	78.2
21	92.6	91.7	78.3	78.2	78.3

(1). As measured by thermocouple TC-9.

(2). As measured by thermocouple TC-7.

TABLE 2

EXPERIMENTAL ACTIVITY COEFFICIENTS EtOH-H₂O

Run No.	Liq. Temp. °C	Mole fr.		P° EtOH	P° H ₂ O	γ_{EtOH}	γ_{EtOH}
		x _{EtOH}	y _{EtOH}				
1	85.2	0.125	0.488	995	418	2.98	1.05
2	86.1	0.106	0.458	1020	455	3.22	1.01
4	90.0	0.050	0.353	1180	525	4.55	0.999
6	78.3	0.805	0.814	760	332	1.01	2.18
7	78.6	0.689	0.741	770	336	1.07	1.88
8	79.2	0.602	0.695	785	345	1.11	1.69
9	79.1	0.643	0.713	782	343	1.08	1.78
10	79.5	0.556	0.675	795	348	1.16	1.60
11	80.2	0.403	0.625	825	360	1.43	1.33
12	80.6	0.403	0.619	835	365	1.40	1.33
13	81.6	0.321	0.572	865	378	1.56	1.27
14	81.8	0.315	0.571	870	381	1.58	1.26
15	84.7	0.135	0.484	970	430	2.81	1.055
16	87.3	0.085	0.411	1070	475	3.41	1.030
17	91.9	0.033	0.272	1260	565	4.97	1.012
18	94.3	0.021	0.199	1430	625	5.03	1.000
20	78.2	0.987	0.985	755	331	1.01	2.64
21	78.3	0.926	0.917	760	332	0.990	2.53

TABLE 3

COMPARISON OF ACTIVITY COEFFICIENTS CALCULATED FROM
VAN LAAR CONSTANTS AND EXPERIMENTALLY DETERMINED VALUES

Van Laar Equations:

$$\ln \gamma_1 = \frac{A}{\left[1 + \frac{Ax}{B(1-x)}\right]^2}$$

$$\ln \gamma_2 = \frac{B}{\left[1 + \frac{B(1-x)}{Ax}\right]^2}$$

where from a average of experimental data A was found to equal 0.775 and B 0.378.

Mole fr. EtOH	From Van Laar Constants		Experimental Values	
	γ_1	γ_2	γ_1	γ_2
0.10	3.10	1.03	3.19	1.03
0.20	2.17	1.11	2.17	1.10
0.30	1.66	1.22	1.69	1.22
0.40	1.38	1.34	1.41	1.31
0.50	1.21	1.48	1.25	1.46
0.60	1.11	1.63	1.13	1.64
0.70	1.05	1.81	1.05	1.93
0.80	1.02	2.00	1.02	2.23

TABLE 4

COMPARISON OF HEAT TRANSFERRED AT THE CONDENSED LIQUID

RESERVOIR AND SUPERHEAT FROM REBOILER

<u>Run No.</u>	<u>Superheat From Reboiler (1).</u>	<u>Heat Transferred at Condensed Liq. Reservoir (1).</u>	<u>Net Heat Loss % of Total</u>
1	1.6	2.8	0.4
2	0.2	1.0	0.3
4	0.1	0.1	0.0
6	0.0	0.0	0.0
7	0.0	0.1	0.0
8	0.0	0.2	0.1
9	0.0	0.1	0.0
10	0.0	0.0	0.0
11	0.0	0.2	0.1
12	0.0	0.1	0.0
13	0.0	0.3	0.1
14	0.0	0.3	0.1
15	0.0	0.6	0.2
16	0.9	3.3	0.7
17	0.9	2.7	0.5
18	0.7	2.7	0.6
20	0.0	0.0	0.0
21	0.0	0.0	0.0

(1). Cal/gm-min.

TABLE 5
HEATS OF SOLUTION FOR ETHANOL-WATER⁽¹⁾

Mole % H ₂ O	t = 0°C		t = 17.33°C		t = 42.05°C	
	Q	Q'	Q	Q'	Q	Q'
5	.088	.0044	.042	.0021	.0029	.00015
10	.176	.0176	.092	.0092	.0063	.00063
15	.289	.0433	.167	.0250	.013	.00195
20	.410	.0820	.251	.0502	.023	.00460
25	.498	.124	.335	.084	.042	.0105
30	.590	.207	.423	.150	.075	.0263
35	.691	.242	.519	.182	.109	.0381
40	.824	.330	.636	.254	.167	.0667
45	1.004	.452	.757	.340	.243	.105
50	1.251	.626	.946	.473	.343	.172
55	1.523	.838	1.201	.660	.465	.256
60	1.900	1.14	1.507	.904	.649	.389
65	2.385	1.55	1.925	1.25	.870	.559
70	3.038	2.13	2.478	1.73	1.209	.845
75	3.972	2.98	3.218	2.34	1.691	1.27
80	5.428	4.34	4.269	3.42	2.356	1.88
85	7.407	6.30	5.821	4.94	3.281	2.79
90	9.856	8.88	7.801	7.03	4.528	4.07
95	12.54	11.92	9.818	9.32	6.36	5.93

Mole % H ₂ O	t, °C	Q'
64.0	77.0	-0.078
84.3	79.2	+0.159

Q = kilojoules heat evolved per mole of water
 Q' = kilojoules heat evolved per mole of mixture

1. International Critical Tables, Vol. V, 137, 138, 148, 154, 159, McGraw-Hill Book Co., N.Y. (1928).

TABLE 6

COMPARISON OF LATENT HEAT DATA EtOH-H₂O

<u>Run No.</u>	Vap. Comp. Mole fr. <u>EtOH</u>	Latent Heats, Btu/lb		
		<u>This Work</u>	<u>Ref. (1)</u>	<u>Ref. (24)</u>
10	0.675	462	460	473
11	0.625	482	484	495
12	0.619	472	486	497
13	0.572	508	503	516
14	0.571	493	503	516
15	0.484	550	548	563
16	0.411	585	580	603
17	0.272	694	690	695
18	0.199	774	756	753
20	0.985	367	370	375
21	0.917	379	382	378
22	0.000	962	972	972

FIGURE 1
 SCHEMATIC DIAGRAM
 OF THE APPARATUS

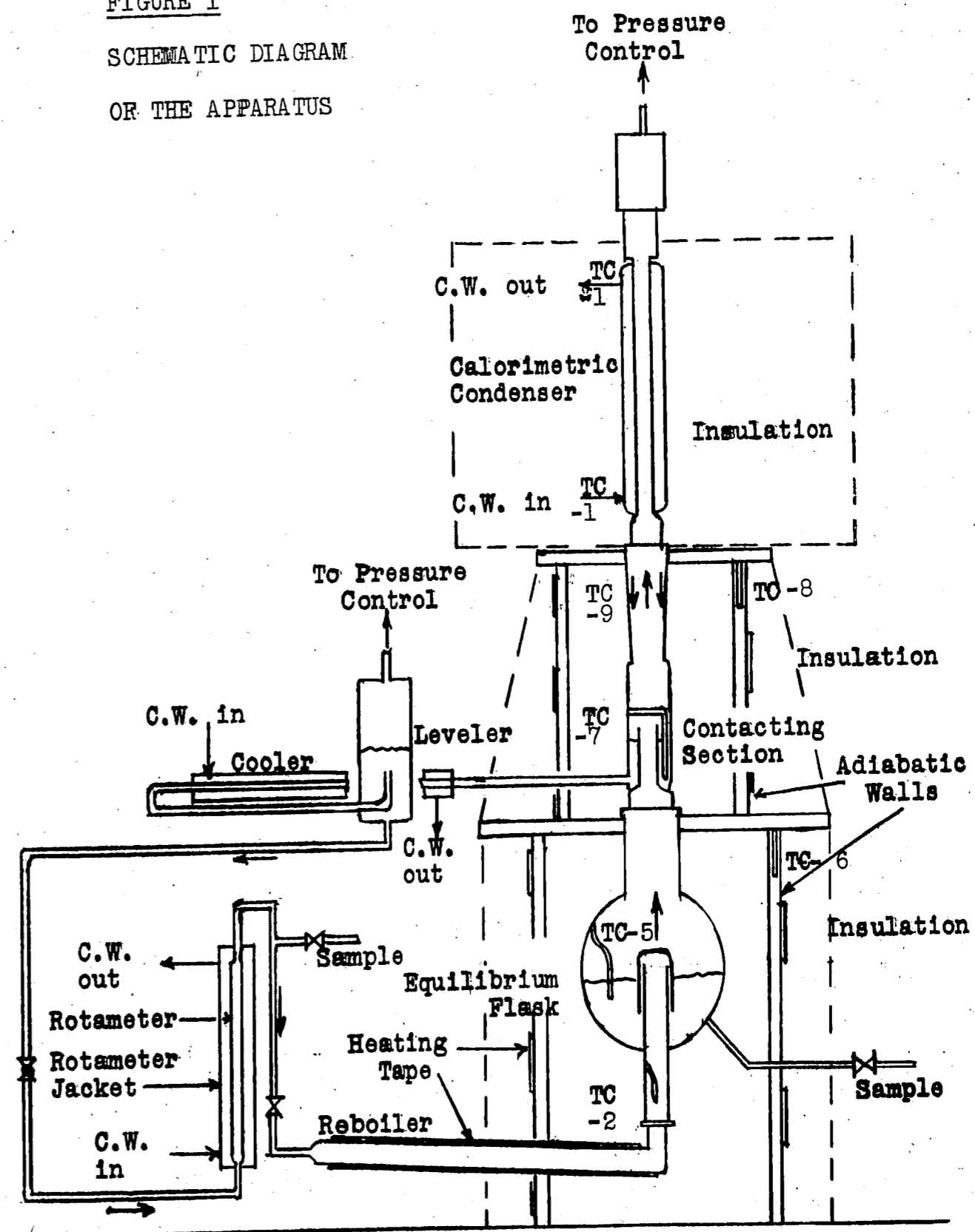


FIGURE 2

TEMPERATURE-COMPOSITION DIAGRAM FOR
ETHANOL-WATER

- This Work
- Otsuki and Williams
- Cornell and Montonna
- Jones, Schoenborn, and Colburn

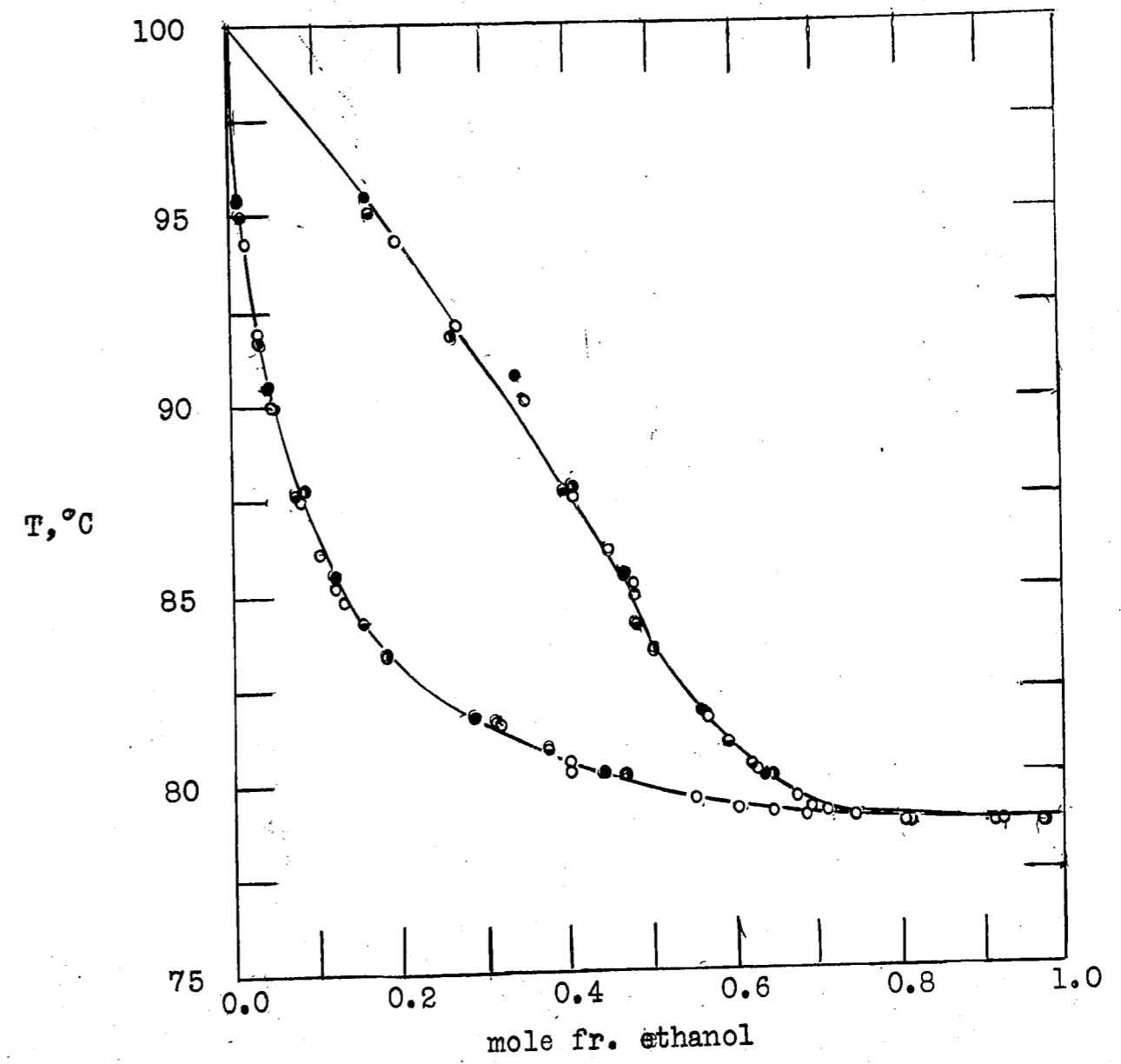


FIGURE 3
ACTIVITY COEFFICIENTS FOR THE
ETHANOL-WATER SYSTEM

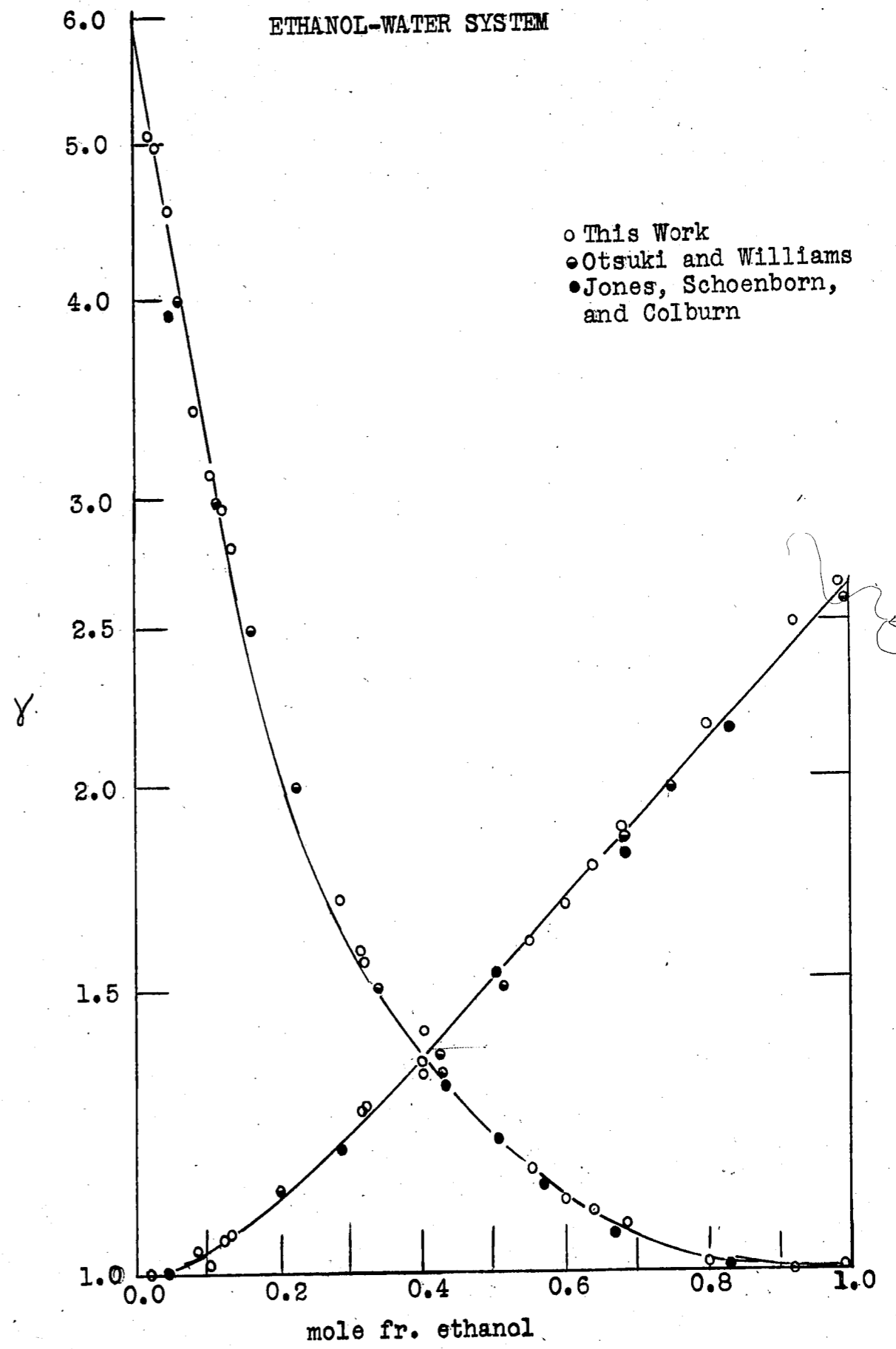


FIGURE 4

REDLICH-KISTER DIAGRAM FOR
ETHANOL-WATER

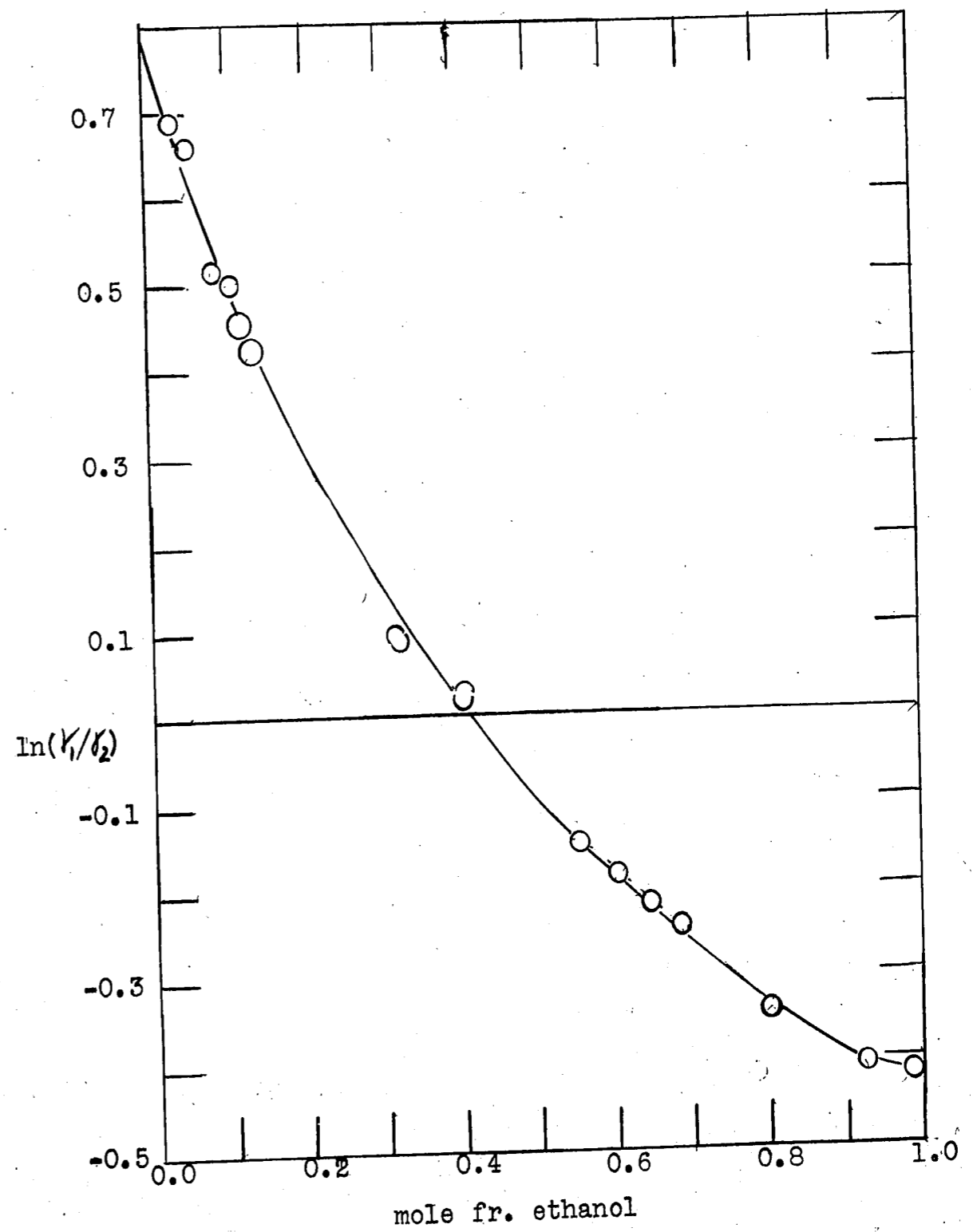


FIGURE 5

TEMPERATURE OF SATURATED LIQUID IN EQUILIBRIUM WITH
THE CONDENSED VAPOR

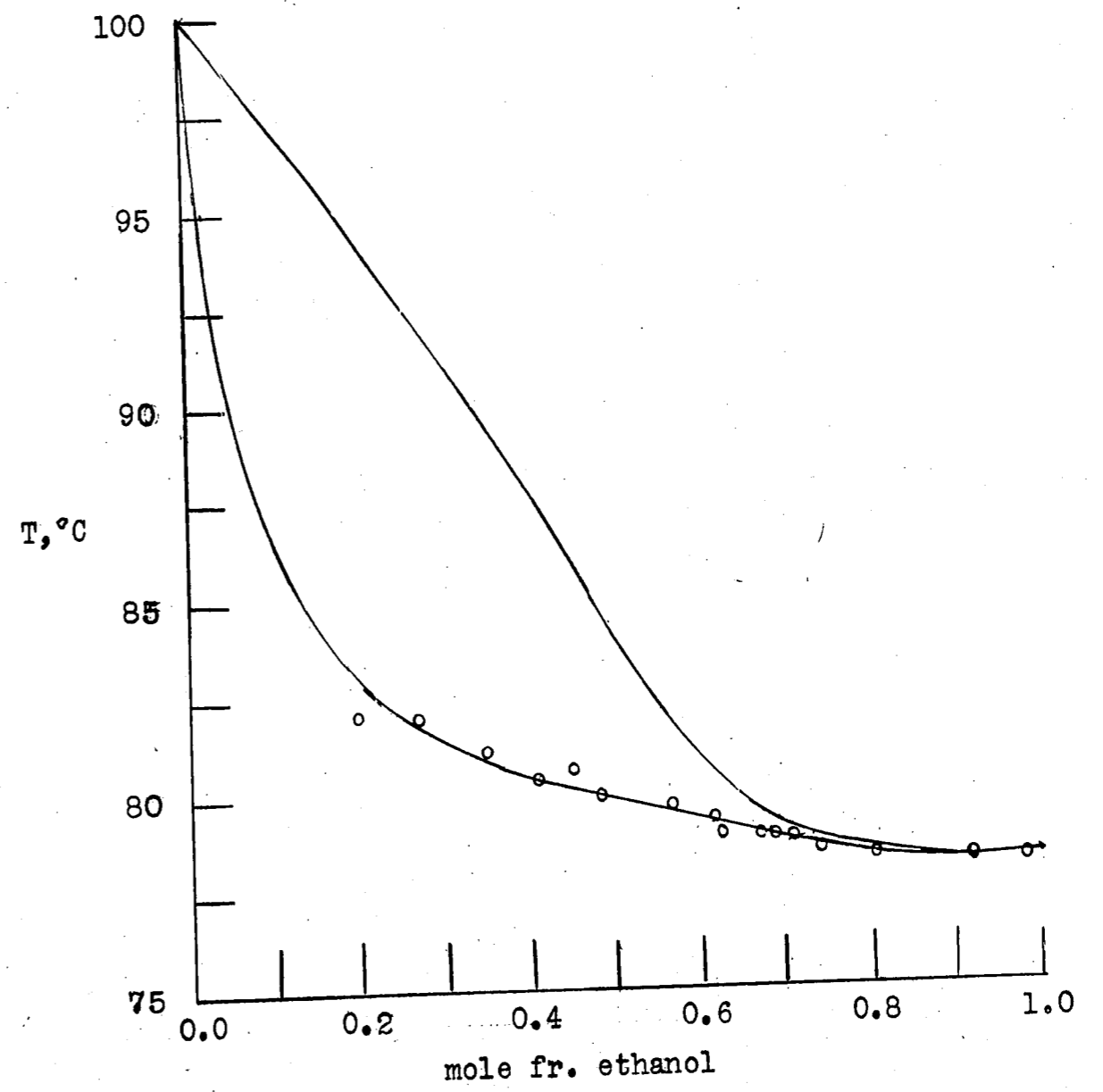


FIGURE 6

ENTHALPY-CONCENTRATION DIAGRAM FOR
ETHANOL-WATER

