

EVALUATION OF TOTAL PRESSURE METHOD
FOR DETERMINING VAPOR-LIQUID EQUILIBRIA

by

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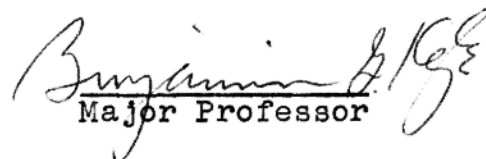

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PURPOSE

The purpose of this work was to investigate the feasibility of calculating binary vapor-liquid equilibria from measurements of total pressures and liquid compositions, without analyzing the compositions of the vapor and the liquid phases.

NOMENCLATURE

A	Constant in Wohl's activity coefficient equations
a	Empirical constant in Wohl's activity coefficient equation
B	Constant in Wohl's equation and Redlich-Kister's equation
C	Constant in Redlich-Kister's activity coefficient equations
D	Constant in Redlich-Kister's activity coefficient equations
F	Flow rate of circulating stream in equilibrium still
f	fraction of F vaporized
H	Number of moles in vapor space of equilibrium still
n	Number of moles
P	Total pressure of a mixture
P*	Total pressure of an equimolar binary mixture
P ^o	Vapor pressure of pure component
Q	Number of moles charged into the equilibrium still
q	Effective volume
T	Temperature
V	Molar volume
W	Ratio of q_2/q_1

x	Equilibrium liquid composition
y	Equilibrium vapor composition
Z	Charged liquid composition
\bar{v}	Effective volume fraction
γ	Activity coefficient
ΔF_m^e	Excess free energy of mixing

subscripts

1	Component one
2	Component two
c	Calculated value
i	Component i
k	Total number of sets of data
m	Measured value
o	First approximation value

INTRODUCTION AND THEORETICAL BACKGROUND

Introduction

In designing distillation or other separation equipment, vapor-liquid equilibrium data are necessary for the estimation of heat requirements, separation efficiencies, and number of equilibrium stages needed to accomplish a desired separation. The determination of vapor-liquid equilibria often starts from binary systems, because it is noted that ternary or quaternary vapor-liquid equilibria can be predicted from binary equilibrium data (1) by only introducing a ternary constant (2), or quaternary constants (3), but binary data can not be predicted so easily from the pure components. Hence a great deal of experimental work has been done on determining binary vapor-liquid equilibria which not only solves the binary problem, but also forms the basis for further investigations into multicomponent systems.

Although many binary data are available in the literature, very often it is found that the equilibrium data one desires are not listed in the literature. Hence an accurate and fast method of determining vapor-liquid equilibria is necessary. A method of determining binary vapor-liquid equilibria from total pressure versus liquid composition data is discussed in this work.

To date, most binary data have been obtained from direct analysis of vapor and liquid compositions which are in equi-

librium at a certain temperature or pressure. This direct method has two principal disadvantages: first, the error involved in composition analysis is often large; and second, the experimental work is usually lengthy. The first disadvantage becomes more marked when the relative volatility of a given system is high, because the higher the relative volatility, the more difficult it is to obtain a vapor sample which is in true equilibrium with the liquid phase (4).

For these reasons an indirect method of determining phase equilibria without composition analysis is desirable. Several people have proposed an indirect method for calculating binary vapor-liquid equilibria from measurements of total pressures and liquid compositions at constant temperature, and this is often called the total pressure method. A general discussion of the relative advantages of direct and indirect methods is given by Scatchard (5).

The history of the total pressure method has been traced by Othmer (6) from its beginning in 1885. In this year the Gibbs-Duhem equation was derived. In the same year, Margules (7) integrated parts of the equation as an infinite series. And in 1900, Zawidzki (8) found a method of determining the coefficients of the Margules equation from the slopes at the ends of the total pressure and liquid composition diagram (i. e., P vs x at constant T)*.

* See page 1 for nomenclature.

Dolezalek (9) and van Laar (10, 11) modified the Margules' expressions by assuming molecular association and the applicability of the van der Waals' equation to the liquid phase, while Bose (12), Marshall (13), and Krichewskii (14) offered methods of solving the Gibbs-Duhem equation directly without Margules' formula. These methods, however, are very laborious and have had little practical application.

In 1914, Rosanoff et. al. (15) proposed a semiempirical formula for calculating equilibrium relations, which Levy (16) showed to be inaccurate.

In 1924, Lewis and Murphree (17) derived a thermodynamic equation for constant temperature systems and developed a trial and error method for stepwise integration of the Gibbs-Duhem equation.

In 1941 Levy (16) improved Zawidzki's method in determining the slopes of the total pressure curve.

In 1942 Carlson and Colburn (18) correlated and predicted vapor-liquid equilibrium values for binaries using a modified form of the van Laar equation.

In 1948 Redlich and Kister (19) proposed several equations which were successfully used in correlating vapor-liquid equilibrium for both binary and multicomponent systems. The next year (20), they calculated vapor compositions from total pressure versus liquid composition data for systems with small deviations from ideal solution behavior by a trial and error method using a simple one-constant activity coefficient

equation.

In 1953, Barker (4) described a least squares method for calculating constants in activity coefficient equations from total pressure-liquid composition data, using the non-ideal vapor phase correction proposed by Scatchard and Raymond (21).

In 1957, Kenny (22) measured the total pressure-liquid composition data by a static equilibrium method and calculated vapor compositions by the method proposed by Barker for the systems: benzene--iso-octane, benzene--furfural, and iso-octane--furfural. In the same year, Prengle and Palm (23) obtained the total pressure-liquid composition data from a dynamic equilibrium apparatus and calculated vapor compositions by a trial and error method for the system iso-octane--toluene.

In 1961, James Ho (24) developed IBM 650 computer programs for determining the constants in the Redlich-Kister activity coefficient equations and for calculating vapor compositions, using the least squares method proposed by Barker and also using a method of stepwise integration of the Gibbs-Duhem equation.

In general, all these methods involve either evaluation of constants in an activity coefficient equation, or evaluation of vapor compositions directly by a stepwise integration procedure. However, all are based on the Gibbs-Duhem equation.

Theoretical Background

It is shown in most thermodynamic textbooks that under the

assumption of an ideal vapor phase, the equilibrium partial pressure of component one (P_1) in the vapor phase can be related to the liquid composition (x_1) by

$$P_1 = x_1 \gamma_1 P_1^{\circ} \quad (1)$$

where γ_1 is the activity coefficient of component one, and P_1° is the vapor pressure of pure component one at the system temperature.

Similarly, equation (1) can be written for component two as:

$$P_2 = x_2 \gamma_2 P_2^{\circ} \quad (2)$$

For a binary system, the total pressure (P) is the sum of the two partial pressures P_1 and P_2 , hence from equations (1) and (2),

$$P = x_1 \gamma_1 P_1^{\circ} + x_2 \gamma_2 P_2^{\circ} \quad (3)$$

Also it is found in thermodynamics that the excess Gibbs free energy of mixing (ΔF_m^e) of a binary liquid mixture can be related to its activity coefficients by

$$\left(\frac{\partial \Delta F_m^e}{\partial n_1} \right)_{T, n_2} = RT \ln \gamma_1 \quad (4)$$

and

$$\left(\frac{\partial \Delta F_m^e}{\partial n_2} \right)_{T, n_1} = RT \ln \gamma_2 \quad (5)$$

where n_1 and n_2 are number of moles of component one and

component two in liquid phase.

Wohl has investigated the excess free energy of mixing (ΔF_m^e) from a statistical viewpoint and has proposed an expression for it in terms of liquid composition (x). His third order binary expression is

$$\frac{\Delta F_m^e}{2.303 RT(q_1 n_1 + q_2 n_2)} = 2j_1 j_2 a_{12} + 3j_1^2 j_2 a_{112} + 3j_1 j_2^2 a_{122} \quad (6)$$

where q_1 , q_2 are constants which Wohl called the effective volumes of component one and component two; and j_1 , j_2 are the effective volume fractions of component one and component two, and are defined as

$$j_1 = \frac{n_1}{n_1 + n_2(q_2/q_1)} = \frac{x_1}{x_1 + x_2(q_2/q_1)} \quad (7)$$

$$j_2 = \frac{n_2(q_2/q_1)}{n_1 + n_2(q_2/q_1)} = \frac{x_2(q_2/q_1)}{x_1 + x_2(q_2/q_1)} \quad (8)$$

and a_{12} , a_{112} , a_{122} are empirical constants which measure the interactions between different groups of molecules.

By partially differentiating equation (6) with respect to n_1 and n_2 , substituting into equations (4) and (5) and after suitably collecting the constants involved, it can be shown that (1)

$$\ln \gamma_1 = j_2^2 \left[A + 2j_1 \left(B \frac{q_1}{q_2} - A \right) \right] \quad (9)$$

$$\ln \gamma_2 = \gamma_1^2 \left[B + 2\gamma_2 \left(A \frac{q_2}{q_1} - B \right) \right] \quad (10)$$

where A and B are constants.

These are Wohl's two constant activity coefficient expressions for a binary system. They actually represent three types of equations, because the parameter q_2/q_1 can be assigned different values. When $q_2/q_1 = 1$, it reduces to the Margules equation, when $q_2/q_1 = v_2/v_1$, it reduces to the Scatchard-Hammer equation, and when $q_2/q_1 = B/A$, it reduces to the van Laar equation.

Equations (3), (7), (8), (9) and (10) are sufficient for determining the constants A and B. Because \bar{f}_1 , \bar{f}_2 , γ_1 and γ_2 can be eliminated by subsequently substituting equations (8), (9) into equations (10), (11) and then equations (10), (11) into equation (3). The resulting equation is

$$P = x_1 P_1^{\circ} \text{EXP} \left\{ \left[\frac{x_2 (q_2/q_1)}{x_1 + x_2 (q_2/q_1)} \right]^2 \left[A + \frac{2x_1}{x_1 + x_2 (q_2/q_1)} \left(\frac{B}{(q_2/q_1)} - A \right) \right] \right\} + x_2 P_2^{\circ} \text{EXP} \left\{ \left[\frac{x_1}{x_1 + x_2 (q_2/q_1)} \right]^2 \left[B + \frac{2x_2 (q_2/q_1)}{x_1 + x_2 (q_2/q_1)} \left(A \left(\frac{q_2}{q_1} \right) - B \right) \right] \right\} \quad (11)$$

After fixing the value of q_2/q_1 (i. e., 1 or B/A or v_2/v_1), equation (11) shows that two total pressure (P)-

liquid composition (x) data points are theoretically sufficient for the determination of A and B , provided that the vapor pressures P_1^0 and P_2^0 are known. From a practical standpoint, due to the errors involved in the total pressure-liquid composition data, it is preferable to determine A and B from more than two P - x data points. The best way of determining A and B is by the least square method with a large number of P - x data points.

Discussion of the Total Pressure Method

Three assumptions were made in deriving equations (3), (7), (8), (9) and (10). They are: 1). the assumption of an ideal vapor phase; 2). the assumption of the validity of the Gibbs-Duhem equation under varying pressure; and 3). the assumption of the fitness of the Wohl and the Redlich-Kister equations. Each one will be separately discussed below.

1). The assumption of an ideal vapor phase: This assumption greatly simplified the problem, and is generally recognized as being a valid assumption at low pressures. Scatchard and Raymond (21) have proposed an approximate equation for treating the non-ideal vapor phase, but it is quite tedious to apply.

2). The validity of the Gibbs-Duhem equation under varying pressure: Strictly speaking, the Gibbs-Duhem equation is valid only under constant temperature and constant pressure. But due to the fact that a binary system has only two degrees of freedom, it is impossible to vary its composition under constant

temperature and constant pressure. The effect of a change in pressure on the Gibbs-Duhem equation has been shown to be quite small (1). Hence the Gibbs-Duhem equation can be used under conditions of varying pressure with negligible error.

3). The fitness of the Wohl and the Redlich-Kister equations: The Wohl's two constant equations or the Redlich-Kister's three constant equations are widely used for relating activity coefficients to liquid compositions. The choice of an activity coefficient equation for a given binary system is important, for the accuracy of the total pressure method does depend on how close the chosen activity coefficient equations can fit the behavior of the given binary system. Since the errors caused by the former two assumptions are all negligible, this is the only assumption which might cause a serious error in the total pressure method.

Some people have proposed another method (24) which directly integrates the Gibbs-Duhem equation without using the activity coefficient equations, and hence avoids the error due to the fitting of the activity coefficient equations. This method starts from the Gibbs-Duhem equation of the following form

$$x_1 \left(\frac{\partial \ln P_1}{\partial x_1} \right) + x_2 \left(\frac{\partial \ln P_2}{\partial x_1} \right) = 0 \quad (12)$$

and because

$$P_1 = P y_1$$

$$P_2 = P y_2$$

hence
$$dP_1 = P dy_1 + y_1 dP$$

$$dP_2 = P dy_2 + y_2 dP$$

substituting the above equations into equation (12) and rearranging it gives

$$\frac{dP}{P} = \frac{y_1 - x_1}{y_1(1-y_1)} dy_1$$

This can be written in the difference form

$$\frac{\Delta P}{P} = \frac{y_1 - x_1}{y_1(1-y_1)} \Delta y_1 \quad (13)$$

Equation (13) can be solved by a stepwise integration method, provided P-x data are available for each small interval of x. Let the increments be defined as $\Delta x_1^i = x_1^{i+1} - x_1^i$, $\Delta y_1^i = y_1^{i+1} - y_1^i$ and $\Delta P^i = P^{i+1} - P^i$, where x_1^i , y_1^i and P^i is one set of equilibrium (x₁-y₁) - P values and x_1^{i+1} , y_1^{i+1} , P^{i+1} is the next set of equilibrium values, also let the mean values be defined as

$$\bar{x}_1^i = \frac{x_1^{i+1} + x_1^i}{2}, \quad \bar{y}_1^i = \frac{y_1^{i+1} + y_1^i}{2}, \quad \text{and} \quad \bar{P}^i = \frac{P^{i+1} + P^i}{2}.$$

If starting from $x_1^1 = 0$, $y_1^1 = 0$, the procedure would be

- 1). Choose a desirable value of Δx_1^1 , so that $x_1^1 = 0$;

$$x_1^2 = x_1^1 \quad \text{and} \quad \bar{x}_1^1 = \frac{x_1^1}{2}$$

2). Find the corresponding equilibrium values P^1 and P^2 from the experimental P-x curve and calculate $\Delta P^1 = P^2 - P^1$; $\bar{P}^1 = \frac{P^2 + P^1}{2}$.

3). Substitute $\Delta P = P^1$, $P = \bar{P}^1$, $y_1 = 0$ and $x_1 = \bar{x}_1^1$ into equation (17) to calculate Δy_1 , and then replace y_1 by $\frac{\Delta y_1}{2}$ to recalculate Δy_1 , this second Δy_1 will be the vapor composition of the second point. (i.e., $y_1^2 = \Delta y_1$)

4). Using x_1^2 and y_1^2 as initial values return to step 1 to calculate x_1^3 and y_1^3 , etc.

This stepwise integration method can also be started from $x_1^1 = 1$, $y_1^1 = 1$; or started from azeotropic point if it can be easily picked up from the P-x curve.

The vital disadvantage of this method is that it is tedious and time consuming, yet it has the advantage of avoiding curve fitting procedures. Hence in the case of a binary system whose behavior can not be fitted by an activity coefficient equation, this method might be desirable.

CALCULATION PROCEDURE

The calculation procedure seeks to determine vapor mole fractions (y's) from several sets of isothermal liquid mole fraction (x)-total pressure (P) equilibrium data by first determining the constants in an equation relating activity coefficients to composition and then using these constants to calculate the vapor mole fractions (y's).

For the i th set of P-x data, equations (3), (7), (8), (9) and (10) can be written as

$$P_{xi} = x_{1i} \gamma_{1i} P_1^0 + x_{2i} \gamma_{2i} P_2^0 \quad (3a)$$

$$\beta_{1i} = \frac{x_{1i}}{x_{1i} + x_{2i} (q_2/q_1)} \quad (7a)$$

$$\beta_{2i} = \frac{x_{2i} (q_2/q_1)}{x_{1i} + x_{2i} (q_2/q_1)} \quad (8a)$$

$$\ln \gamma_{1i} = \beta_{2i}^2 \left[A + 2\beta_{1i} (B/W - A) \right] \quad (9a)$$

$$\ln \gamma_{2i} = \beta_{1i}^2 \left[B + 2\beta_{2i} (AW - B) \right] \quad (10a)$$

where P_{ci} is the calculated pressure of the i th set of data and W is the ratio of q_2/q_1 .

By the least square method, the residue equation is

$$\Delta P_i = P_{mi} - P_{ci} \quad (14)$$

where P_{mi} is the measured pressure.

And by differentiating the square sum of the residue (ΔP_i) with respect to A and B, two normal equations are obtained.

$$\frac{\partial}{\partial A} \left[\sum_{i=1}^k (\Delta P_i)^2 \right] = 0 \quad (15)$$

and

$$\frac{\partial}{\partial B} \left[\sum_{i=1}^k (\Delta P_i)^2 \right] = 0 \quad (16)$$

where k is the total number of sets of data.

Investigation of equations (3a), (7a), (8a), (9a) and (10a) shows that there are seven unknowns (i.e., γ_{1i} , γ_{2i} , β_{1i} , β_{2i} , P_{ci} , A and B). However all the unknowns can be expressed in terms of A and B. Hence let F(A,B) and G(A,B) be defined as

$$F(A,B) = -\frac{1}{2} \frac{\partial}{\partial A} \left[\sum_{i=1}^k (\Delta P_i)^2 \right] = 0$$

and

$$G(A,B) = -\frac{1}{2} \frac{\partial}{\partial B} \left[\sum_{i=1}^k (\Delta P_i)^2 \right] = 0$$

Substituting equations (3a) and (14) into the above equations and differentiating them gives

$$F(A,B) = \sum_{i=1}^k (P_{mi} - P_{ci}) \left(x_{1i} P_1^0 \frac{\partial \gamma_{1i}}{\partial A} + x_{2i} P_2^0 \frac{\partial \gamma_{2i}}{\partial A} \right) = 0 \quad (17)$$

$$G(A,B) = \sum_{i=1}^k (P_{mi} - P_{ci}) (x_{1i} P_1^0 \frac{\partial Y_{1i}}{\partial B} + x_{2i} P_2^0 \frac{\partial Y_{2i}}{\partial B}) = 0 \quad (18)$$

Equations (17) and (18) are non-linear simultaneous equations of A and B and can not be solved directly, but the Newton-Raphson method can be applied. With this method A and B are obtained by a series of iterations.

The values of A and B obtained on the $i + 1$ th iteration differ from the values obtained on the i th iteration by the correction terms ΔA and ΔB

$$A_{i+1} = A_i + \Delta A \quad (19a)$$

$$B_{i+1} = B_i + \Delta B \quad (19b)$$

The expressions for evaluating ΔA and ΔB are

$$A = \frac{\begin{vmatrix} F(A,B) & \frac{\partial F}{\partial B} \\ G(A,B) & \frac{\partial G}{\partial B} \end{vmatrix}}{\begin{vmatrix} \frac{\partial F}{\partial A} & \frac{\partial F}{\partial B} \\ \frac{\partial G}{\partial A} & \frac{\partial G}{\partial B} \end{vmatrix}}_{A_i, B_i} \quad (20a)$$

$$B = \frac{\begin{vmatrix} \frac{\partial F}{\partial A} & F(A,B) \\ \frac{\partial G}{\partial A} & G(A,B) \end{vmatrix}}{\begin{vmatrix} \frac{\partial F}{\partial A} & \frac{\partial F}{\partial B} \\ \frac{\partial G}{\partial A} & \frac{\partial G}{\partial B} \end{vmatrix}} \quad A_i, B_i \quad (20b)$$

Since all terms in the determinants are essentially functions of A and B only, ΔA and ΔB can be evaluated if initial values A and B are known. The iteration steps are shown below:

- 1). Assume an initial set of A and B.
- 2). Evaluate ΔA and ΔB from equations (20a) and (20b).
- 3). Calculate a new set of A and B from equations (19a) and (19b).
- 4). Repeat the iteration process until ΔA and ΔB are both smaller than the accuracy required.

Once A and B are determined, δ'_{1i} and δ'_{2i} can be calculated easily from equations (9a) and (10a), and the corresponding vapor compositions can be evaluated from

$$y_{1i} = \frac{x_{1i} \gamma_{1i} P_1^0}{P_{ci}} \quad \text{and} \quad y_{2i} = \frac{x_{2i} \gamma_{2i} P_2^0}{P_{ci}}$$

Two IBM 1620 Fortran computer programs were written for this calculation, one based on Wohl's two constant activity coefficient equations and the other based on Redlich and Kister's three constant activity coefficient equations. The former program actually contains three subprograms (i.e., Margules, van Laar and Scatchard-Hammer equations) which are selected by controlling the computer sense switches. The flow diagram, which shows the scheme of the calculation, as well as the two computer programs developed in this work are given in appendix I.

Nine binary systems taken from the literature were used to check this method and the developed computer programs. The data reported for these systems included liquid and vapor compositions and total pressure at a constant temperature. The liquid composition (x) - total pressure (P) data from these systems were used as input data for the computer programs and the calculated values of vapor compositions (y 's) were compared with the experimental values. It was found that the results calculated by using Redlich and Kister's three constant equations fitted the experimental data better than those calculated by using Wohl's two constant equations. A comparison of the results calculated from the Redlich and Kister equations with the experimental values is shown in table 1.

Column 4 in table 1 gives the average of the least squares of the deviations between the measured total pressures (P_m 's) and the calculated total pressures (P_c 's). This term is merely

the sum of the squares divided by the number of data points and provides a judgement about the fitness of the activity coefficient equations to the actual P-x data of a binary system. The smaller the "average least square" means the better the chosen activity coefficient equations fit the behavior of the actual system. Also because the P-x data are obtained from experiments and are not smoothed, the experimental errors involved in the P-x data are again involved in the "average least square". Hence a large value in this column implies either poor fitting of the activity coefficient equations or poor accuracy of the experimental P-x data or both.

Column 5 gives the average of the absolute deviations between P_m and P_c . Its value is always less than the square root of the "average least square". It provides a similar judgement as that of the "average least square", but allows an easier intuitive judgement than the squared values.

Column 6 shows the average absolute percentage error of the calculated vapor compositions (y_c 's) with respect to the measured vapor compositions (y_m 's). Since the latter were obtained from experiments and are not smoothed, the errors listed in column 6 include both the experimental errors of y_m 's and the errors involved in y_c 's. Hence the values listed in column 6 do not represent the true errors of the calculated vapor compositions (y_c 's).

It was also shown in table 1 that the system with the smallest value in the "average least square" column does not

Table 1. Comparison of Calculated and Experimental Results.

System*	T°C	Constants in the Redlich and Kister equation			Av. least square $(\Delta P)^2$ mm Hg.	Av. pres. dev. $ \Delta P $ mm Hg.	Average $\frac{ \Delta y }{y_m} \times 100$ %	No. of data points
		B	C	D				
Acetonitrile-benzene(25)	45	1.00914	-0.00154	0.09835	0.06995	0.2347	0.5717	12
Acetonitrile-nitromethane (25)	60	-0.02408	0.00066	-0.00317	0.01832	0.1052	0.7554	10
Carbon tetrachloride-acetonitrile (26)	45	1.81092	0.22117	0.23241	2.92642	1.2155	1.6254	13
	25	-0.98456	-0.25440	0.13141	0.90429	0.7141	4.7400	6
	35	-0.89264	-0.21680	0.10045	0.13839	0.3278	2.3422	6
Chloroform-acetone (27)	50	-0.76987	-0.16136	0.82202	0.29019	0.4703	5.2153	6
Ethanol-benzene (28)	45	1.70596	-0.37693	0.27011	3.72442	1.6053	1.9066	12
	25	2.26533	-0.17049	0.52271	1.71720	1.1215	1.8890	10
Ethanol--iso-octane (29)	50	2.17783	-0.19328	0.60097	56.53140	5.7715	3.7711	13
Ethanol-methylcyclohexane (30)	35	2.18707	-0.24731	0.54303	5.35498	1.8718	1.7722	8
	55	2.11496	-0.19955	0.52042	30.53400	4.7875	1.8911	8
Nitromethane-benzene(31)	45	1.14799	0.02592	0.06195	0.02171	0.1116	1.4765	13
Nitromethane-carbon tetrachloride(31)	45	2.03162	-0.18175	0.24473	1.50496	1.0062	1.9155	12

* Pressure-composition data are taken from the literature cited after each system.

necessarily correspond to the system with the smallest value of the average percentage errors listed in column 6. However, for a given system the "average least square" values can be used in comparing the fit of different activity coefficient equations.

The required computing time per point of data was found to be greatly affected by the choice of the initial values of A_0 and B_0 . Barker (4) showed that a good first approximation of A_0 and B_0 can be calculated by assuming the solution behaves as a regular solution. Thus, in case of Wohl's equation the first approximation will be

$$A_0 = B_0 = 4 \ln \left(\frac{2P^*}{P_1^0 + P_2^0} \right)$$

or, in case of the Redlich and Kister equation, the first approximation will be

$$B_0 = 4 \ln \left(\frac{4P^*}{P_1^0 + P_2^0} \right); \quad C_0 = D_0 = 0$$

where P^* is the total pressure of equimolar mixture, which can be approximately estimated from the total pressure (P)-liquid composition (x) curve. Using this kind of first approximation, the required computing time per point of data was found to be about 1.5 minutes, and was dependent on the characteristics of each system.

EXPERIMENTS

In order to use the total pressure method to calculate vapor-liquid equilibria, we must be able to obtain the equilibrium total pressure-liquid composition data at a constant temperature from experiments. The liquid composition should not be obtained from composition analysis, since the principal advantage of the total pressure method is to avoid the composition analysis work. To achieve the full advantage of this method, the best way of obtaining total pressure-liquid composition data would be as follows:

- 1). Make up liquid mixtures of known compositions by weighing suitable amounts of pure components.

- 2). Design an apparatus to bring the mixture into an equilibrium state without changing the liquid composition or by producing only a slight composition change. The equilibrium liquid composition could then be obtained directly from the previously weighed liquid composition or by making a slight correction to the predetermined liquid composition.

- 3). Measure the total pressure of the system at this equilibrium state.

The author has worked with two especially designed equilibrium stills, attempting to obtain the equilibrium total pressure-liquid composition data according to the above procedure, and has found that:

- 1). Vapor pressures of pure components can be determined accurately with both these stills.

2). Due to fractional vaporization, the equilibrium liquid composition inside the still is different from that of the liquid charged into the still, and this difference is found not to be negligible. Therefore, the previously weighed liquid composition can not be regarded as the equilibrium liquid composition inside the still.

Since the charged liquid composition can not be used as the equilibrium liquid composition, the relation between these two liquid compositions must be found so that the equilibrium liquid composition can be calculated from the charged liquid composition. An approximate linear equation was derived for relating these liquid compositions, and this was found to be successful for the ideal system n-hexane--iso-octane. The experiments done on this work will be briefly described below.

Test of Stills with Pure Components

Two stills, still A and still B, are shown in figure 1 and figure 2. The temperature was measured by a thermocouple and the pressure by a manometer with a range of 0 to 800 mm Hg. The still was connected to a pressure-vacuum system so as to maintain a constant pressure. Pressures below atmospheric were obtained with a vacuum pump and pressures above atmospheric were obtained by using dried compressed air. Because of the difficulty in adjusting the system exactly to the desired temperature, three nearby temperatures and pressures were measured instead of measuring the desired point; these three measured pressures

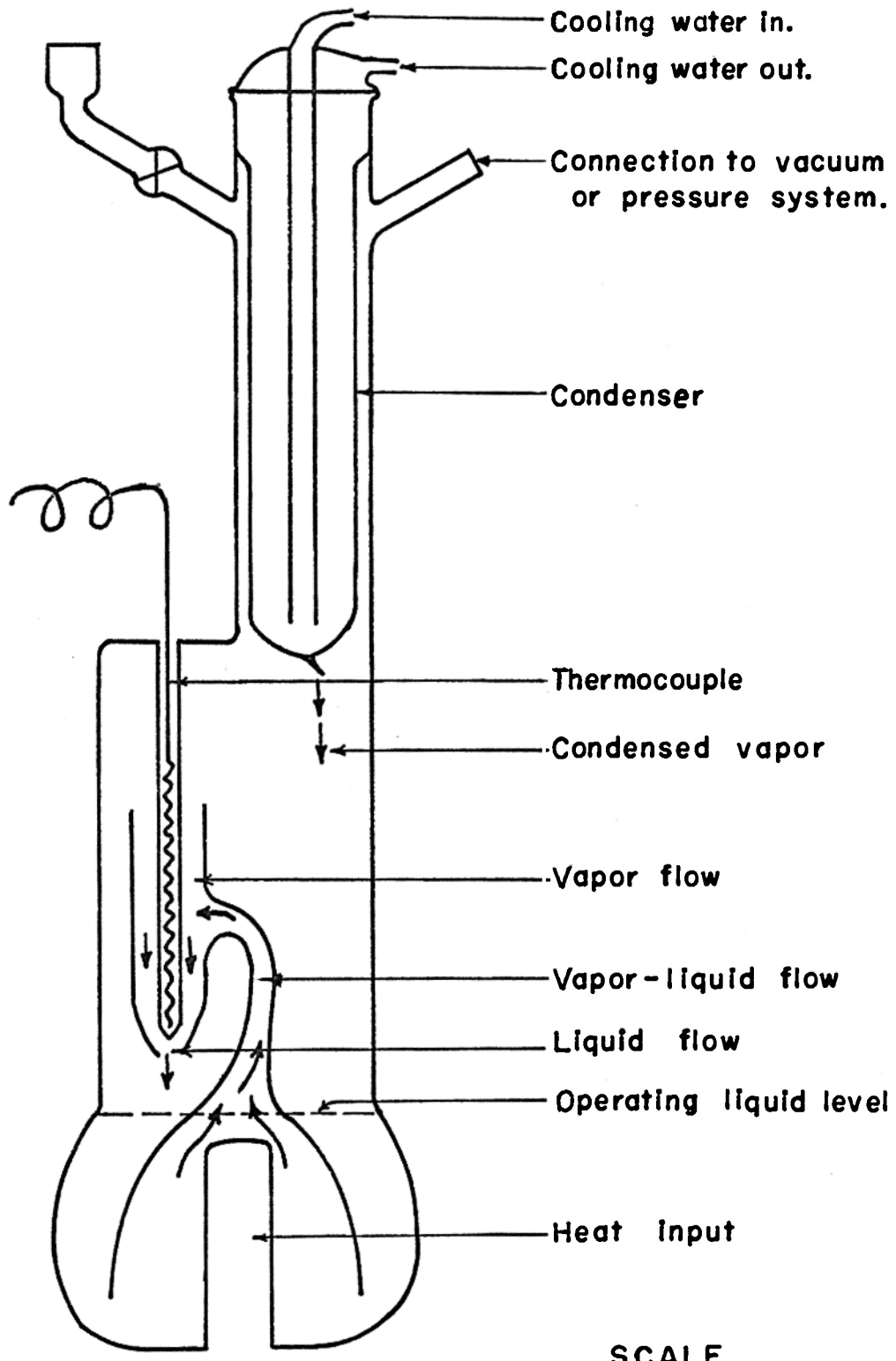
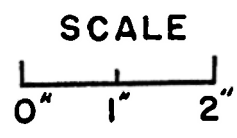


FIG. 1. STILL A



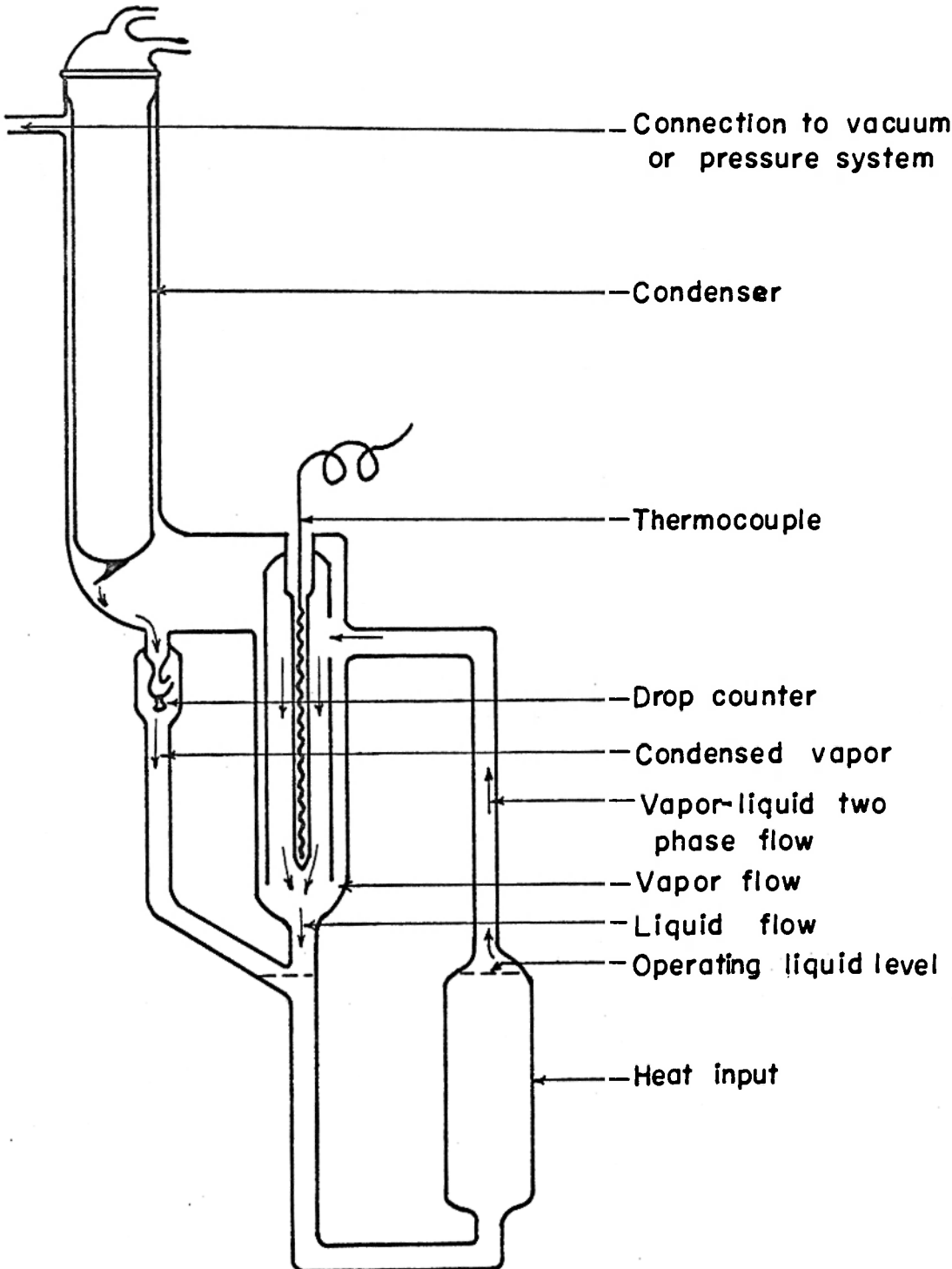


FIG. 2. STILL B

SCALE
0" 1" 2"

(P) and temperatures (T) were plotted on a Log P vs $1/T$ diagram and the pressure at the desired temperature was then read off of the resulting straight line.

Pure n-hexane and pure iso-octane (2,2,4-trimethylpentane) were used to test the stills. It was found that the vapor pressure data obtained from both the stills agreed well with the published literature values. The results of both stills were plotted on Log P vs $1/T$ diagrams which are given in appendix II. It was also found that the stills could be operated with a wide variation in heat input and still maintain the correct boiling temperature.

Test of Stills with an Ideal Solution

The purpose of this test is to see whether the equilibrium liquid composition inside the still can be approximately regarded as equal to the composition of the liquid charged into the still. This was done by charging an ideal mixture of known composition into the still and by measuring the equilibrium temperature and pressure. The measured temperature and pressure were then used to calculate the equilibrium liquid composition by means of Raoult's law. This calculated equilibrium liquid composition can then be compared with the composition of the liquid charged into the still.

n-Hexane--iso-octane mixtures were used for testing, because this system is known to follow Raoult's law. Three carefully weighed mixtures (about 0.25; 0.50 and 0.75 mole

fraction of n-hexane) were charged into the stills to measure the equilibrium temperatures and pressures. The equilibrium liquid compositions were calculated from

$$x_1 = \frac{P - P_1^0}{P_1^0 - P_2^0}$$

this equation comes from a combination of Raoult's law and Dalton's law with the assumption of an ideal vapor phase, i.e.,

$$P = x_1 P_1^0 + (1 - x_1) P_2^0$$

To avoid the possibility of material flowing out of the still when reducing the system pressure, each run of the experiment was started from the lower pressure, hence the system pressure was only increased and never reduced during operation.

The results obtained from still A and still B are shown in tables 2 and 3. The listed temperatures and pressures were not the actually measured points, but were read off of linear Log P vs 1/T plots for each composition. The measured temperatures and pressures are listed in appendix II.

Tables 2 and 3 show that the difference between the equilibrium liquid composition and the charged liquid composition is considerable. To determine why this discrepancy exists the following analysis of the stills' performance was made.

Table 2. Still A Performance Test

System: n-hexane-iso-octane at 67°C

Equilibrium total pressure, mm Hg.	Mole fraction of n-hexane			Deviation x/Z
	Charged liquid(Z)	Equilibrium liquid(x)	Equilibrium vapor(y)	
277.3	0.000	0.000	0.000	
358.9	0.199	0.184	0.369	0.925
501.8	0.526	0.505	0.727	0.960
619.0	0.778	0.769	0.897	0.989
721.5	1.000	1.000	1.000	1.000

Table 3. Still B Performance Test

System: n-hexane-iso-octane at 70°C

Equilibrium total pressure, mm Hg.	Mole fraction of n-hexane			Deviation x/Z
	Charged liquid(Z)	Equilibrium liquid(x)	Equilibrium vapor(y)	
308.0	0.000	0.000	0.000	
417.5	0.253	0.228	0.430	0.903
525.0	0.466	0.451	0.669	0.969
641.1	0.705	0.693	0.852	0.984
788.9	1.000	1.000	1.000	1.000

Analysis of Still Performance

Considering the flow of fluid inside the stills (see figures 1 and 2), suppose Q moles of liquid mixture with Z mole fraction of n-hexane is charged into the still. Then, at steady state, let there be H moles in vapor phase apart from the circulating stream. There is a stream of liquid and vapor (F moles/hr.) circulating inside the still. If f is the fraction of the stream (F) vaporized, and because of steady state, there must be also fF moles/hr. of vapor condensed. By a material balance based on the whole still, (n-hexane charged to the still) = (n-hexane in liquid phase) + (n-hexane in vapor phase)

or
$$QZ = (Q-H)Z_0 + Hy$$

where Z is the mole fraction of the charged liquid, y is the mole fraction in the vapor phase, and Z_0 is the overall composition of the stream F .

A material balance based on the circulating stream gives

$$FZ_0 = (1-f)Fx + fFy$$

where x is the liquid mole fraction in the circulating stream F . It is assumed that x and y are equilibrium values.

Elimination of Z_0 from the above material balance equations gives

$$x = \frac{Q}{(Q-H)(1-f)} Z - \left[\frac{Q}{(Q-H)(1-f)} - 1 \right] y \quad (21)$$

In this equation, the number of moles of non circulating vapor (H) would be function of temperature and pressure and the fraction of the circulating stream vaporized (f) would be function of heat input, latent heat and other physical properties of the mixture. But for simplicity, H and f will be temporarily regarded as characteristics of the still and be considered constant. Hence equation (21) can be simplified as

$$x = KZ - (K-1)y$$

or

$$\frac{x}{y} = K \frac{Z}{y} + (1-K) \quad (22)$$

where K is regarded as a constant.

$$K = \frac{Q}{(Q-H)(1-f)} = \frac{1}{\left(1 - \frac{H}{Q}\right)(1-f)} \quad (23)$$

To test equation (22), x-y-Z data taken from tables 2 and 3 were plotted as x/y versus Z/y on figure 3. It was found that the results of both the stills appeared nearly as one straight line as is required by equation 22. The value of K as found from the slope of the straight line was about 1.09 for both stills.

Discussion of Experimental Results

Although equation (22) was found to be successful in correlating the experimental x-y-Z data for the system n-hexane--iso-octane, the equilibrium liquid composition (x) still can not be calculated from the known charged liquid composition (Z) since equation (26) involves the equilibrium vapor composition (y) which is unknown. Moreover, the value of k would be expected to vary for different binary systems, because the fraction of the circulating stream vaporized (f) would be a fairly complicated function of many physical properties of the binary systems (such as heat of vaporization, molecular weight and densities, viscosities of the liquid and the vapor phases etc.), and hence would probably change from system to system as these physical properties are changed. Therefore, instead of attempting to correlate x with Z by equation (22), it would be more desirable to design an apparatus to reduce the value of k to 1, so that from equation (22) the equilibrium liquid composition (Z) would be equal to the charged liquid composition (x) and no correction would be needed.

Some explanation should be made here for the obvious difference between the changes of liquid compositions (Z-x) observed in this work and that observed by Prengle and Palm (23). They used an ebulliometer similar to still B used in this work but did not mention any correction made to the charged liquid composition due to the effect of vaporizing a fraction of the

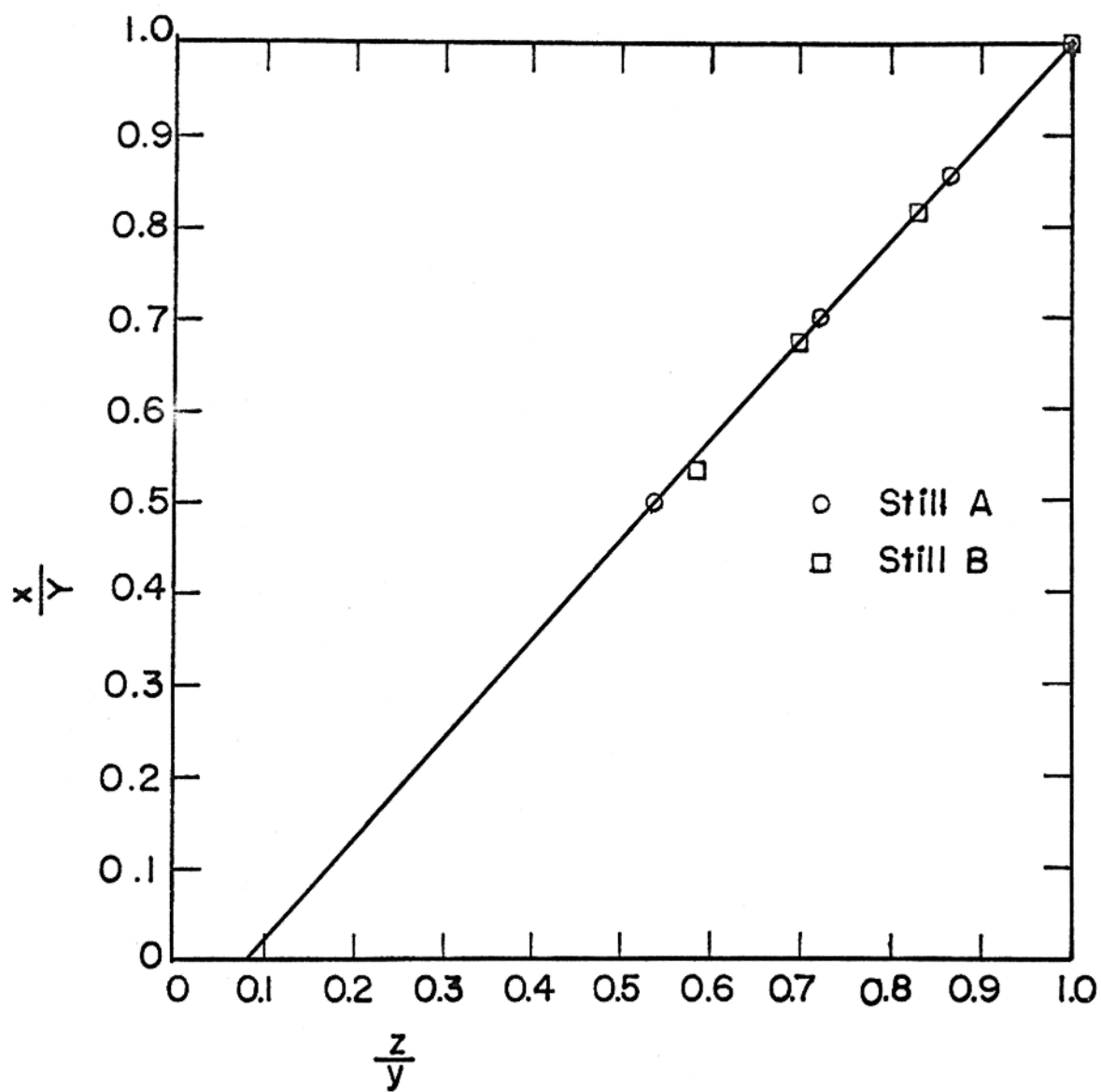


FIG.3. Correlation of Experimental x-y-z data.

recirculating stream. Yet in the present work it was found that for the system n-hexane--iso-octane the changes of the liquid compositions (Z-x) were considerable (see tables 2 and 3).

In this work it was possible to calculate reliably the equilibrium liquid and vapor compositions from the equilibrium temperature and pressure and the knowledge that the system behaved ideally. But Prengle and Palm studied a non ideal system and hence could not make this check of the equilibrium liquid composition. However, their results calculated from the total pressure method did agree reasonably well with published data on the same system.

Since it was observed by Prengle and Palm that for systems of high relative volatility the measured temperature was sensitive to the boiling rate, the discrepancy between this work and their work is probably due to the fact that the relative volatility of the system studied in this work was between 2.5 and 2.6 while the relative volatility of their system was between 1.1 and 1.8.

In the above experiments done on the system n-hexane--iso-octane with the stills A and B, the values of H/Q were found to be between 0.003 and 0.007 (the values of Q were calculated from the amount of material charged into the still and the values of H were found by measuring the vapor space volumes of both stills and then using the ideal gas law). The values of f were approximately 0.078 for both the stills (this was found by substituting the average value of $H/Q = 0.005$ and the value

of $k = 1.09$ as found from fig.3 into equation 22). These values of H/Q and f show that the effect of f is much larger than that of H/Q . Hence in designing a proper still, the effect of f will be the first one which should be eliminated or be reduced to a great extent. From this viewpoint, it was concluded that a static equilibrium apparatus which would bring the vapor and the liquid into equilibrium without circulating a stream of liquid and vapor would be more desirable.

Equation (22) is still valid for a static equilibrium apparatus except that $f = 0$ in this case. The value of x could then be made to approach the value of Z by having a small ratio of vapor to liquid moles (H/Q). Also any small correction necessary in obtaining x from Z could be reliably calculated from the geometry of the apparatus.

CONCLUSION

Two conclusions are obtained from this work:

1). Binary vapor-liquid equilibria can be calculated in a few minutes from the experimental total pressure-liquid composition data with the aid of a high speed electronic computer.

2). For obtaining the total pressure-liquid composition data from experiments, a static equilibrium apparatus with a large liquid volume and a small vapor volume is desirable. This is because it eliminates the effect of a circulating vaporized stream (f) and reduces the effect of vapor-to-liquid mole ratio (H/Q) to a fairly small extent, so that the equilibrium liquid composition (x) can be regarded as the charged liquid composition (Z) which can be determined easily and accurately by weighing the pure components.

ACKNOWLEDGMENT

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A P P E N D I X

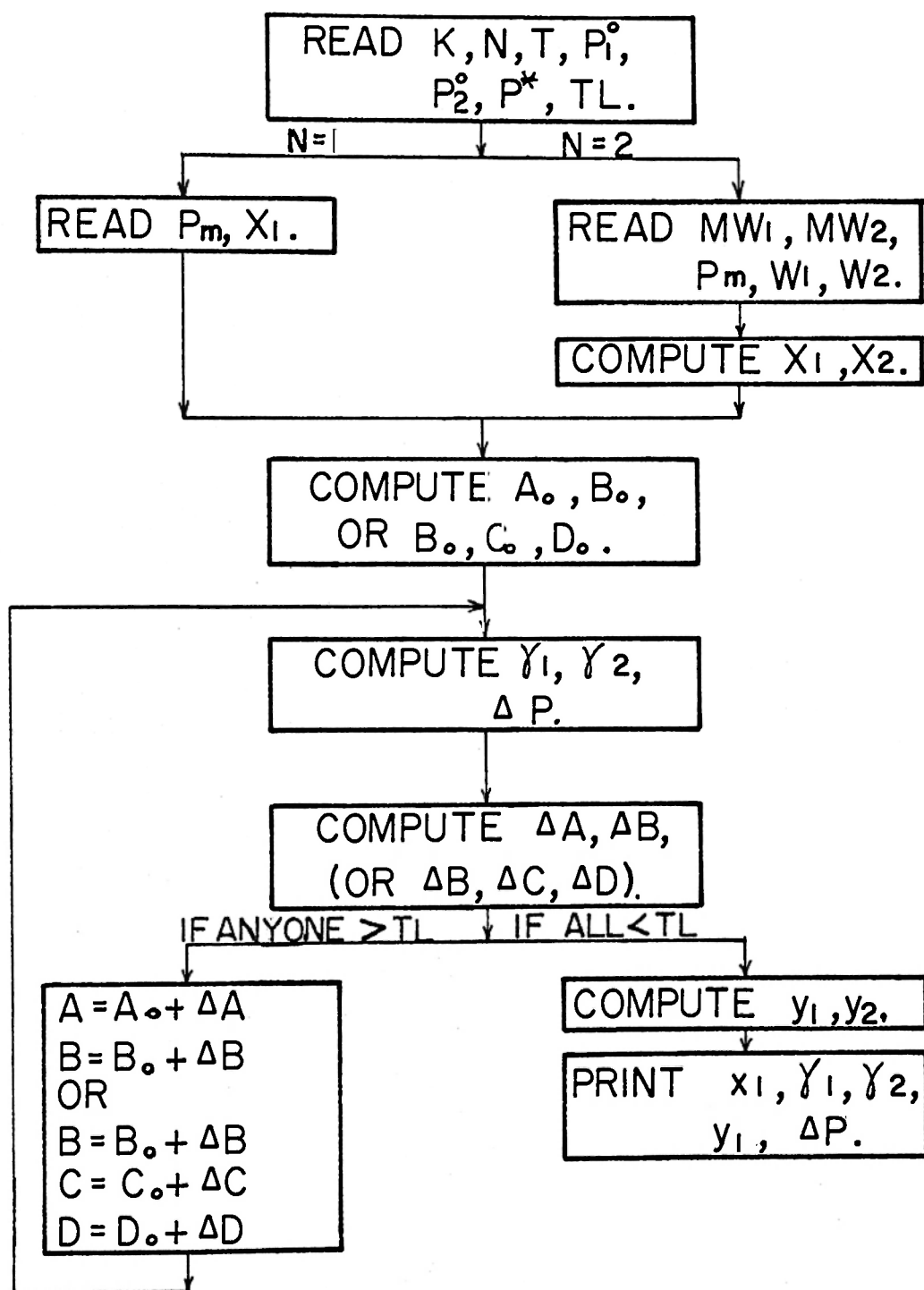
DESCRIPTION OF COMPUTER FLOW DIAGRAM

The flow diagram shown in the next page was designed for two different kinds of data input; when $N=1$, the data input was pressure-liquid mole fraction; when $N=2$, the data input was pressure-liquid weight. Also if the Wohl activity coefficient equations were used, the choice of Margules, van Laar, or Scatchard-Hammer equations were made by controlling the computer switches immediately after the computation of A_0 and B_0 .

Some notations which are not listed or are different from the nomenclature on page 1 are given below:

- K Number of data points
- N Controlling index
- TL Tolerance used to restrict the size of A and B.
- MW Molecular weight
- W Weight of material

COMPUTER FLOW DIAGRAM



SOURCE PROGRAM 1. CALCULATION OF VAPOR COMPOSITION FROM P-X DATA.
USING THE WOHL ACTIVITY COEFFICIENT EQUATIONS.

```

DIMENSION PM(30),W1(30),W2(30),X1(30),DZA(30),DZB(30),DZAA(30)
DIMENSION DZAB(30),DZBB(30),Y1(30),CP(30),GA(30),GB(30),DL(30)
1 READ 2,K,N,T
2 FORMAT(13,13,E12.6)
PRINT 3
3 FORMAT(41H CALCULATION OF Y FROM P AND X AT CONST. T20X7HR.C.LIN)
READ 4,A1,B1,C1,A2,B2,C2
4 FORMAT(E12.6,E12.6,E12.6,E12.6,E12.6,E12.6)
11 FORMAT(12HNC. ITERATION6X1HA11X1HB1UX4HDA/A8X4HDB/B6X10HAV. SQUARE)
P10=EXP(2.302585*(A1-B1/(C1+T)))
P20=EXP(2.302585*(A2-B2/(C2+T)))
5 FORMAT(E12.6,E12.6)
3 FORMAT(E12.6,E12.6,E12.6)
13 FORMAT(E12.6)
GO TO (50,51),N
50 DO 30 J=1,K
30 READ 6,PM(J),X1(J)
GO TO 54
51 READ 6,WM1,WM2
DO 32 J=1,K
READ 8,PM(J),W1(J),W2(J)
32 XI(J)=W1(J)/WM1/(W1(J)/WM1+W2(J)/WM2)
54 DQBB=0.
R=1.
READ 8,A,B,TL
IF (SENSE SWITCH 1) 80,79
80 DQA=0.
DQB=0.
DQAA=0.
DQAB=0.
DO 34 J=1,K
DZA(J)=0.
DZB(J)=0.
DZAB(J)=0.
DZAA(J)=0.
34 DZBB(J)=0.
IF (SENSE SWITCH 3) 82,83
82 Q=1.
PRINT 5
5 FORMAT(/21H USE MARGULES EQUATION2X4HQ=1.)
PRINT 11
GO TO 55
83 READ 6,V1,V2
Q=V2/V1
PRINT 7
7 FORMAT(/28H USE SCATCHARD-HAMER EQUATION2X7HQ=V2/V1)
17 FORMAT (3HV1=E12.6,2X3HV2=E12.6,2X2HQ=E12.6)
PRINT 17,V1,V2,Q
PRINT 11
GO TO 55
79 PRINT 9
9 FORMAT(/21H USE VAN LAAR EQUATION2X5HQ=0/A)
PRINT 11
81 Q=P/A
DQA=-B/A/A
DQB=1./A
DQAA=2.*B/A/A/A
DQAB=-1./A/A
DO 36 J=1,K
X2=1.-X1(J)
DZA(J)=X1(J)*X2*B/(X1(J)*A+X2*B)/(X1(J)*A+X2*B)
DZB(J)=-DZA(J)/Q
DZAA(J)=-DZA(J)*2.*X1(J)/(X1(J)*A+X2*B)

```

```

36 DZAB(J)=DZA(J)/(X1(J)*A+X2*B)/Q*(X1(J)*A-X2*B)
35 DZBB(J)=-DZB(J)*2.*X2/(X1(J)*A+X2*B)
ABF1=Q.
ABF2=Q.
DFA=Q.
DFB=Q.
DF3=Q.
SQ=Q.
38 J=1,K
X2=1.-X1(J)
Z1=X1(J)/(X1(J)+X2*Q)
Z2=1.-Z1
AZB=A+2.*Z1*(B/Q-A)
BZA=B+2.*Z2*(A*Q-B)
G1=EXP(2.302585*Z2*Z2*AZB)
G2=EXP(2.302585*Z1*Z1*BZA)
PC=X1(J)*P10*G1+X2*P20*G2
Y1(J)=X1(J)*P10*G1/PC
DP=PM(J)-PC
SQ=SQ+DP*DP
G11=1.+2.*(B/Q-A)*DZA(J)-2.*Z1*(B/Q/Q*DQA+1.)
G21=1.-2.*DZB(J)*(A*Q-B)+2.*Z2*(A*DQB-1.)
G1B=DZB(J)*(B/Q-A)+Z1*(1./Q-Q/Q*DQB)
G2A=-DZA(J)*(A*Q-B)+Z2*(Q+A*DQA)
DG1A=2.302585*G1*Z2*(Z2*G11-2.*DZA(J)*AZB)
DG1B=2.302585*G1*2.*Z2*(Z2*G1B-DZB(J)*AZB)
DG2A=4.6J517*G2*Z1*(DZA(J)*BZA+Z1*G2A)
DG2B=2.302585*Z1*G2*(2.*DZB(J)*BZA+Z1*G21)
AF1=X1(J)*P10*DG1A+X2*P20*DG2A
BF2=X1(J)*P10*DG1B+X2*P20*DG2B
ABF1=ABF1+DP*AF1
ABF2=ABF2+DP*BF2
G1AA=(B/Q-A)*DZAA(J)-(B/Q/Q*DQAA+1.)*DZA(J)*2.
G1AA=G1AA-Z1*(B/Q/Q*DQAA-2.*B/Q/Q/Q*DQA*DQA)
DG1AA=AZB*(G1*DZA(J)*DZA(J)-DG1A*Z2*DZA(J)-G1*Z2*DZAA(J))
DG1AA=DG1AA+G11*(Z2*Z2*DG1A/2.-G1*Z2*DZA(J)-G1*Z2*DZAA(J))
DG1AA=(DG1AA+G1AA*Z2*Z2*G1)*4.60517
G1BB=DZBB(J)*(B/Q-A)+DZB(J)*(1./Q-Q/Q*DQB)*2.
G1BB=G1BB-Z1*(2.*(Q-B*DQB)/Q/Q/Q*DQB+B/Q/Q*DQB)
DG1BB=AZB*(G1*DZB(J)*DZB(J)-DG1B*Z2*DZB(J)-G1*Z2*DZBB(J))
DG1BB=DG1BB+G1B*(DG1B*Z2*Z2-G1*Z2*DZB(J)*2.-G1*2.*Z2*DZB(J))
DG1BB=(DG1BB+G1*Z2*Z2*G1BB)*4.60517
G1AB=(1.-B/Q*DQB)/Q*DZA(J)+(B/Q-A)*DZAB(J)-(B/Q/Q*DQA+1.)*DZB(J)
G1AB=G1AB-Z1*(B/Q/Q*DQAB+(Q-2.*B*DQB)/Q/Q/Q*DQA)
DG1AB=AZB*(G1*DZB(J)*DZA(J)-DG1B*Z2*DZA(J)-G1*Z2*DZAB(J))
DG1AB=DG1AB-Z2*G1*DZA(J)*2.*G1B-(G1*DZB(J)-Z2*DG1B/2.)*Z2*G11
DG1AB=(DG1AB+G1AB*Z2*Z2*G1)*4.60517
G2AA=Z2*(DQA*2.+A*DQAA)-DZAA(J)*(A*Q-B)-DZA(J)*(Q+A*DQA)*2.
DG2AA=BZA*DZA(J)*(DG2A*Z1+G2*DZA(J))+G2*Z1*DZAA(J)*BZA
DG2AA=DG2AA+G2A*(4.*G2*Z1*DZA(J)+Z1*Z1*DG2A)
DG2AA=(DG2AA+Z1*Z1*G2*G2AA)*4.60517
G2BB=Z2*A*DQBB-DZBB(J)*(A*Q-B)-2.*DZB(J)*(A*DQB-1.)
DG2BB=BZA*(DZB(J)*G2*DZB(J)+Z1*DG2B*DZB(J)+Z1*G2*DZBB(J))
DG2BB=DG2BB+G21*(Z1*G2*DZB(J)+DG2B*Z1*Z1/2.+G2*Z1*DZB(J))
DG2BB=(DG2BB+G2*Z1*Z1*G2BB)*4.60517
G2AB=-DZAB(J)*(A*Q-B)-DZA(J)*(A*DQB-1.)-DZB(J)*(Q+A*DQA)
G2AB=G2AB+Z2*(DQB+A*DQAB)
DG2AB=BZA*(DG2B*Z1*DZA(J)+G2*DZB(J)*DZA(J)+G2*Z1*DZAB(J))
DG2AB=DG2AB+Z1*(G2*DZA(J)*G21+2.*G2*DZB(J)*G2A+Z1*DG2B*G2A)
DG2AB=(DG2AB+Z1*Z1*G2*G2AB)*4.60517
DF1=X1(J)*P10*DG1AA+X2*P20*DG2AA
DF2=X1(J)*P10*DG1AB+X2*P20*DG2AB
DF3=X1(J)*P10*DG1BB+X2*P20*DG2BB
DFA=DFA-AF1*AF1+DP*DF1
38 DFB=DFB-AF1*BF2+DP*DF2
DF3=DF3-BF2*BF2+DP*DF3
DTM=DFA*EFB-DFB*DFB
DTA=ABF2*DFB-ABF1*EFB
DTB=DFB*ABF1-DFA*ABF2
DA=DTA/DTM

```

```

DB=DTB/DTM
ACA=DA/A
ACB=DB/B
S=K
ASQ=SQ/S
PRINT 4,R,A,B,ACA,ACB,ASQ
IF (ACA) 90,91,91
90 ACA=-ACA
91 IF (TL-ACA) 99,92,92
92 IF (ACB) 93,94,94
93 ACB=-ACB
94 IF (TL-ACB) 99,100,100
99 A=A+DA
   B=B+DB
   R=R+1.
   IF (SENSE SWITCH 1)55,81
100 PRINT 12,T,TL
12  FORMAT(12HTEMPERATURE=E12.6,2X10HTCLERENCE=E12.6)
   PRINT 13,A,B
13  FORMAT(17HACTIVITY COEF. A=E12.6,2X2HB=E12.6)
   PRINT 14
14  FORMAT(5X2HPM10X2HX110X2HPC10X2HG110X2HG210X2HY110X2HDP)
16  FORMAT(E12.6,E12.6,E12.6,E12.6,E12.6,E12.6,E12.6)
   DO 40 J=1,K
   X2=1.-X1(J)
   Z1=X1(J)/(X1(J)+X2*Q)
   Z2=1.-Z1
   AZB=A+2.*Z1*(B/Q-A)
   BZA=B+2.*Z2*(A*Q-B)
   GA(J)=EXP(2.302585*Z2*Z2*AZB)
   GB(J)=EXP(2.302585*Z1*Z1*BZA)
   CP(J)=X1(J)*P10*GA(J)+X2*P20*GB(J)
40  DL(J)=PM(J)-CP(J)
   DO 42 J=1,K
42  PRINT 16,PM(J),X1(J),CP(J),GA(J),GB(J),Y1(J),DL(J)
   READ 18,M
18  FORMAT(I3)
   GC TC (45,46),M
46  DO 44 J=1,K
   READ 10,W1(J)
44  W2(J)=(Y1(J)-W1(J))/W1(J)
   PRINT 19
19  FORMAT(5X3HY1M10X2HY110X3HPDY)
   DO 43 J=1,K
43  PRINT 8,W1(J),Y1(J),W2(J)
45  PRINT 15
15  FORMAT(17HSOLUTION COMPLETE)
   GC TC 1
   END

```

SOURCE PROGRAM 2. CALCULATION OF VAPOR COMPOSITION FROM P-X DATA.
USING THE REDLICH-KISTER ACTIVITY COEFFICIENT EQUATIONS.

```

DIMENSION PM(50),X1(50),W1(50),W2(50),GA(50),GB(50),Y1(50),CP(50)
DIMENSION PD(50)
2  FORMAT (I3,I3,E12.6,E12.6,E12.6,E12.6,E12.6,E12.6)
3  FORMAT(41HCALCULATION OF Y FROM P AND X AT CONST. T20X7HR.C.LIN)
4  FORMAT(/31H USING REDLICH KISTER EQUATION.)
5  FORMAT(E12.6,E12.6)
6  FORMAT(E12.6,E12.6,E12.6)
7  FORMAT(E12.6,E12.6,E12.6,E12.6,E12.6,E12.6,E12.6)
8  FORMAT(/76X1HB11X1HC11X1HD11X1HE11X1HF11X1HG11X1HH11X1HI11X1HJ11X1HK11X1HL11X1HM11X1HN11X1HO11X1HP11X1HQ11X1HR11X1HS11X1HT11X1HU11X1HV11X1HW11X1HX11X1HY11X1HZ11X1IA11X1IB11X1IC11X1ID11X1IE11X1IF11X1IG11X1IH11X1II11X1IJ11X1IK11X1IL11X1IM11X1IN11X1IO11X1IP11X1IQ11X1IR11X1IS11X1IT11X1IU11X1IV11X1IW11X1IX11X1IY11X1IZ11X1JA11X1JB11X1JC11X1JD11X1JE11X1JF11X1JG11X1JH11X1JI11X1JJ11X1JK11X1JL11X1JM11X1JN11X1JO11X1JP11X1JQ11X1JR11X1JS11X1JT11X1JU11X1JV11X1JW11X1JX11X1JY11X1JZ11X1KA11X1KB11X1KC11X1KD11X1KE11X1KF11X1KG11X1KH11X1KI11X1KJ11X1KK11X1KL11X1KM11X1KN11X1KO11X1KP11X1KQ11X1KR11X1KS11X1KT11X1KU11X1KV11X1KW11X1KX11X1KY11X1KZ11X1LA11X1LB11X1LC11X1LD11X1LE11X1LF11X1LG11X1LH11X1LI11X1LJ11X1LK11X1LL11X1LM11X1LN11X1LO11X1LP11X1LQ11X1LR11X1LS11X1LT11X1LU11X1LV11X1LW11X1LX11X1LY11X1LZ11X1MA11X1MB11X1MC11X1MD11X1ME11X1MF11X1MG11X1MH11X1MI11X1MJ11X1MK11X1ML11X1MN11X1MO11X1MP11X1MQ11X1MR11X1MS11X1MT11X1MU11X1MV11X1MW11X1MX11X1MY11X1MZ11X1NA11X1NB11X1NC11X1ND11X1NE11X1NF11X1NG11X1NH11X1NI11X1NJ11X1NK11X1NL11X1NM11X1NO11X1NP11X1NQ11X1NR11X1NS11X1NT11X1NU11X1NV11X1NW11X1NX11X1NY11X1NZ21X1OA11X1OB11X1OC11X1OD11X1OE11X1OF11X1OG11X1OH11X1OI11X1OJ11X1OK11X1OL11X1OM11X1ON11X1OO11X1OP11X1OQ11X1OR11X1OS11X1OT11X1OU11X1OV11X1OW11X1OX11X1OY11X1OZ21X1PA11X1PB11X1PC11X1PD11X1PE11X1PF11X1PG11X1PH11X1PI11X1PJ11X1PK11X1PL11X1PM11X1PN11X1PO11X1PP11X1PQ11X1PR11X1PS11X1PT11X1PU11X1PV11X1PW11X1PX11X1PY11X1PZ21X1QA11X1QB11X1QC11X1QD11X1QE11X1QF11X1QG11X1QH11X1QI11X1QJ11X1QK11X1QL11X1QM11X1QN11X1QO11X1QP11X1QQ11X1QR11X1QS11X1QT11X1QU11X1QV11X1QW11X1QX11X1QY11X1QZ21X1RA11X1RB11X1RC11X1RD11X1RE11X1RF11X1RG11X1RH11X1RI11X1RJ11X1RK11X1RL11X1RM11X1RN11X1RO11X1RP11X1RQ11X1RR11X1RS11X1RT11X1RU11X1RV11X1RW11X1RX11X1RY11X1RZ21X1SA11X1SB11X1SC11X1SD11X1SE11X1SF11X1SG11X1SH11X1SI11X1SJ11X1SK11X1SL11X1SM11X1SN11X1SO11X1SP11X1SQ11X1SR11X1SS11X1ST11X1SU11X1SV11X1SW11X1SX11X1SY11X1SZ21X1TA11X1TB11X1TC11X1TD11X1TE11X1TF11X1TG11X1TH11X1TI11X1TJ11X1TK11X1TL11X1TM11X1TN11X1TO11X1TP11X1TQ11X1TR11X1TS11X1TT11X1TU11X1TV11X1TW11X1TX11X1TY11X1TZ21X1UA11X1UB11X1UC11X1UD11X1UE11X1UF11X1UG11X1UH11X1UI11X1UJ11X1UK11X1UL11X1UM11X1UN11X1UO11X1UP11X1UQ11X1UR11X1US11X1UT11X1UU11X1UV11X1UW11X1UX11X1UY11X1UZ21X1VA11X1VB11X1VC11X1VD11X1VE11X1VF11X1VG11X1VH11X1VI11X1VJ11X1VK11X1VL11X1VM11X1VN11X1VO11X1VP11X1VQ11X1VR11X1VS11X1VT11X1VU11X1VV11X1VW11X1VX11X1VY11X1VZ21X1WA11X1WB11X1WC11X1WD11X1WE11X1WF11X1WG11X1WH11X1WI11X1WJ11X1WK11X1WL11X1WM11X1WN11X1WO11X1WP11X1WQ11X1WR11X1WS11X1WT11X1WU11X1WV11X1WW11X1WX11X1WY11X1WZ21X1XA11X1XB11X1XC11X1XD11X1XE11X1XF11X1XG11X1XH11X1XI11X1XJ11X1XK11X1XL11X1XM11X1XN11X1XO11X1XP11X1XQ11X1XR11X1XS11X1XT11X1XU11X1XV11X1XW11X1XX11X1XY11X1XZ21X1YA11X1YB11X1YC11X1YD11X1YE11X1YF11X1YG11X1YH11X1YI11X1YJ11X1YK11X1YL11X1YM11X1YN11X1YO11X1YP11X1YQ11X1YR11X1YS11X1YT11X1YU11X1YV11X1YW11X1YX11X1YY11X1YZ21X1ZA11X1ZB11X1ZC11X1ZD11X1ZE11X1ZF11X1ZG11X1ZH11X1ZI11X1ZJ11X1ZK11X1ZL11X1ZM11X1ZN11X1ZO11X1ZP11X1ZQ11X1ZR11X1ZS11X1ZT11X1ZU11X1ZV11X1ZW11X1ZX11X1ZY11X1ZZ)
9  FORMAT(/13H TEMPERATURE=E12.6)
10 FORMAT(/12HTEMPERATURE=E12.6,2X10HTOLERANCE=E12.6)
11 FORMAT(I3)
12 FORMAT(E12.6)
13 FORMAT(/5X3HY1M10X2HY110X3HPDY)
14 FORMAT(5X2HPM10X2HX110X2HPC10X2HG110X2HG210X2HY110X2HDP)
15 FORMAT(17HSOLUTION COMPLETE)
35 READ 2,K,N,T,P1C,P2C,PEG,TL
PRINT 3
PRINT 4
PRINT 8
GO TO (40,50),N
40 DO 41 J=1,K
41 READ 5,PM(J),X1(J)
GO TO 52
50 READ 5,WM1,WM2
DO 51 J=1,K
READ 6,PM(J),W1(J),W2(J)
51 X1(J)=W1(J)/WM1/(W1(J)/WM1+W2(J)/WM2)
52 R=1.
C=0.0000001
D=0.0000001
B=4.*LCG(2.*PEG/(P1C+P2C))
55 Q1=0.
Q2=0.
Q3=0.
A1=0.
A2=0.
A3=0.
A5=0.
A6=0.
A9=0.
SQ=0.
DO 60 J=1,K
X2=1.-X1(J)
G1=EXP(X2**2.*(B+C*(4.*X1(J)-1.)+D*(2.*X1(J)-1.)*(6.*X1(J)-1.)))
G2=X1(J)**2.*(B+C*(4.*X1(J)-3.)+D*(2.*X1(J)-1.)*(6.*X1(J)-5.))
G2=EXP(G2)
PC=X1(J)*G1*P1C+X2*G2*P2C
DP=PM(J)-PC
SQ=SQ+DP*DP
DG1B=G1*X2*X2
DG1C=G1*X2*X2*(4.*X1(J)-1.)
DG1D=G1*X2*X2*(2.*X1(J)-1.)*(6.*X1(J)-1.)
DG2B=G2*X1(J)**2.
DG2C=G2*X1(J)**2.*(4.*X1(J)-3.)
DG2D=G2*X1(J)**2.*(2.*X1(J)-1.)*(6.*X1(J)-5.)
DG1BB=DG1B**2.
DG1BC=DG1B*DG1C/G1
DG1BD=DG1B*DG1D/G1
DG1CD=DG1C*DG1D/G1
DG1CC=DG1C**2.
DG1DD=DG1D**2.
DG2BB=DG2B**2.

```

```

DG2CC=DG2C*DG2C/G2
DG2DD=DG2D*DG2D/G2
DG2BC=DG2B*DG2C/G2
DG2BD=DG2B*DG2D/G2
DG2CD=DG2C*DG2D/G2
PCB=X1(J)*P1C*DG1B+X2*P2C*DG2B
PCC=X1(J)*P1C*DG1C+X2*P2C*DG2C
PCD=X1(J)*P1C*DG1D+X2*P2C*DG2D
Q1=Q1+DP*PCB
Q2=Q2+DP*PCC
Q3=Q3+DP*PCD
A1=A1-PCB*PCB+DP*(X1(J)*P1C*DG1BB+X2*P2C*DG2BB)
A2=A2-PCB*PCC+DP*(X1(J)*P1C*DG1BC+X2*P2C*DG2BC)
A3=A3-PCB*PCD+DP*(X1(J)*P1C*DG1BD+X2*P2C*DG2BD)
A5=A5-PCC*PCC+DP*(X1(J)*P1C*DG1CC+X2*P2C*DG2CC)
A6=A6-PCC*PCD+DP*(X1(J)*P1C*DG1CD+X2*P2C*DG2CD)
60 A9=A9-PCD*PCD+DP*(X1(J)*P1C*DG1DD+X2*P2C*DG2DD)
DTM=A1*A5*A9+A2*A6*A3+A2*A6*A3-A2*A3*A5-A2*A2*A9-A1*A6*A6
DTB=Q1*A6*A6+Q2*A2*A9+Q3*A3*A5-Q1*A5*A9-Q2*A3*A6-Q3*A2*A6
DTC=Q2*A3*A3+Q1*A2*A9+Q3*A1*A6-Q2*A1*A9-Q1*A6*A3-Q3*A3*A2
DTD=Q1*A3*A5+Q2*A6*A1+Q3*A2*A2-Q3*A1*A5-Q2*A2*A3-Q1*A2*A6
DB=DTB/DTM
DC=DTC/DTM
DD=DTD/DTM
ACB=DB/B
ACC=DC/C
ACD=DD/D
S=K
ASQ=SQ/S
PRINT 7,B,C,D,ACB,ACC,ACD,ASQ
IF (ACB)70,71,71
70 ACB=-ACB
71 IF (TL-ACB)90,73,73
73 IF (ACC)74,75,75
74 ACC=-ACC
75 IF (TL-ACC)90,76,76
76 IF (ACD)77,78,78
77 ACD=-ACD
78 IF (TL-ACD)90,92,92
90 B=B+DB
C=C+DC
D=D+DD
R=R+1.
IF (SENSE SWITCH 3)91,55
91 PRINT 9,T
GO TO 93
92 PRINT 10,T,TL
93 PRINT 14
DC 94 J=1,K
X2=1.-X1(J)
G1=X2**2.*(B+C*(4.*X1(J)-1.)+D*(2.*X1(J)-1.)*(6.*X1(J)-1.))
GA(J)=EXP(G1)
G2=X1(J)**2.*(B+C*(4.*X1(J)-3.)+D*(2.*X1(J)-1.)*(6.*X1(J)-5.))
GB(J)=EXP(G2)
CP(J)=X1(J)*GA(J)*P1C+X2*GB(J)*P2C
Y1(J)=X1(J)*P1C*GA(J)/CP(J)
94 PD(J)=PM(J)-CP(J)
DC 95 J=1,K
95 PRINT 7,PM(J),X1(J),CP(J),GA(J),GB(J),Y1(J),PD(J)
READ 11,M
GO TO (105,100),M
100 DC 101 J=1,K
READ 12,W1(J)
101 W2(J)=(Y1(J)-W1(J))/W1(J)*100.
PRINT 13

```



```
      DO 102 J=1,K
102  PRINT 6,W1(J),Y1(J),W2(J)
105  PRINT 15
      GO TO 35
      END
```

Table 1. Temperature-Total Pressure Data Measured With Still A.

System: n-hexane-iso-octane

Mole fraction of n-hexane in charged liquid	Total Pressure mm Hg.	Temperature °C
0.000	240.1	62.889
	298.6	69.069
	345.0	73.280
0.199	297.0	61.501
	347.0	65.942
	393.6	69.677
0.526	497.9	66.780
	554.2	70.040
	593.5	72.268
0.778	551.8	63.300
	604.5	65.988
	682.1	70.107
1.000	695.1	65.830
	748.7	68.110
	791.2	69.791

Table 2. Temperature-Total Pressure data Measured with Still B.

System: n-hexane-iso-octane

Mole fraction of n-hexane in charged liquid	Total pressure mm Hg.	Temperature °C
0.000	262.5	65.397
	347.4	73.480
	363.6	74.846
0.253	385.7	67.644
	450.2	72.178
	487.0	74.622
0.466	414.8	62.592
	508.8	68.956
	593.9	73.906
0.705	544.9	64.896
	613.5	68.527
	682.1	71.999
1.000	640.0	63.163
	727.7	67.304
	794.2	70.197

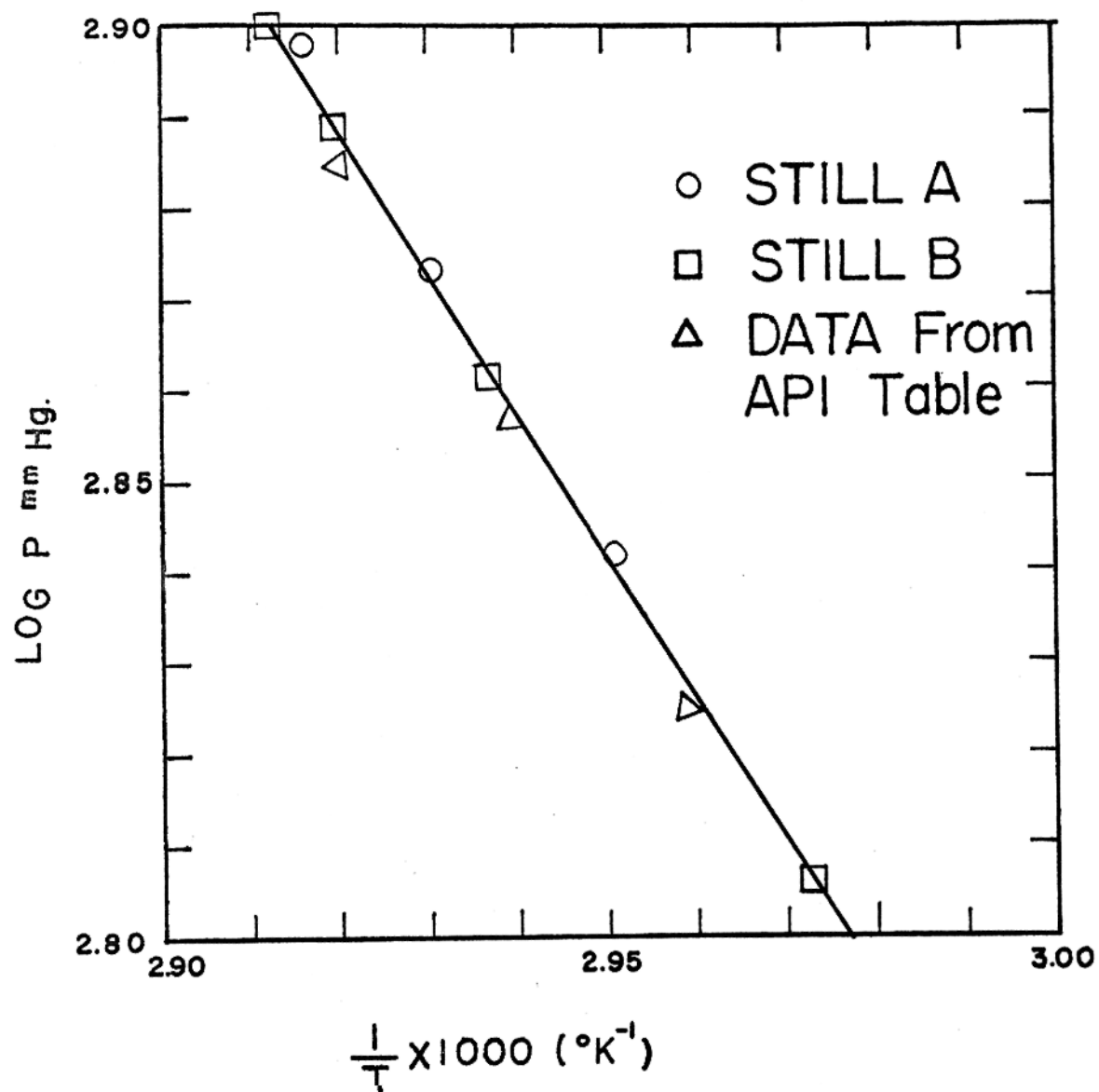


FIG. 1. Interpolation of P-T Data for n-hexane

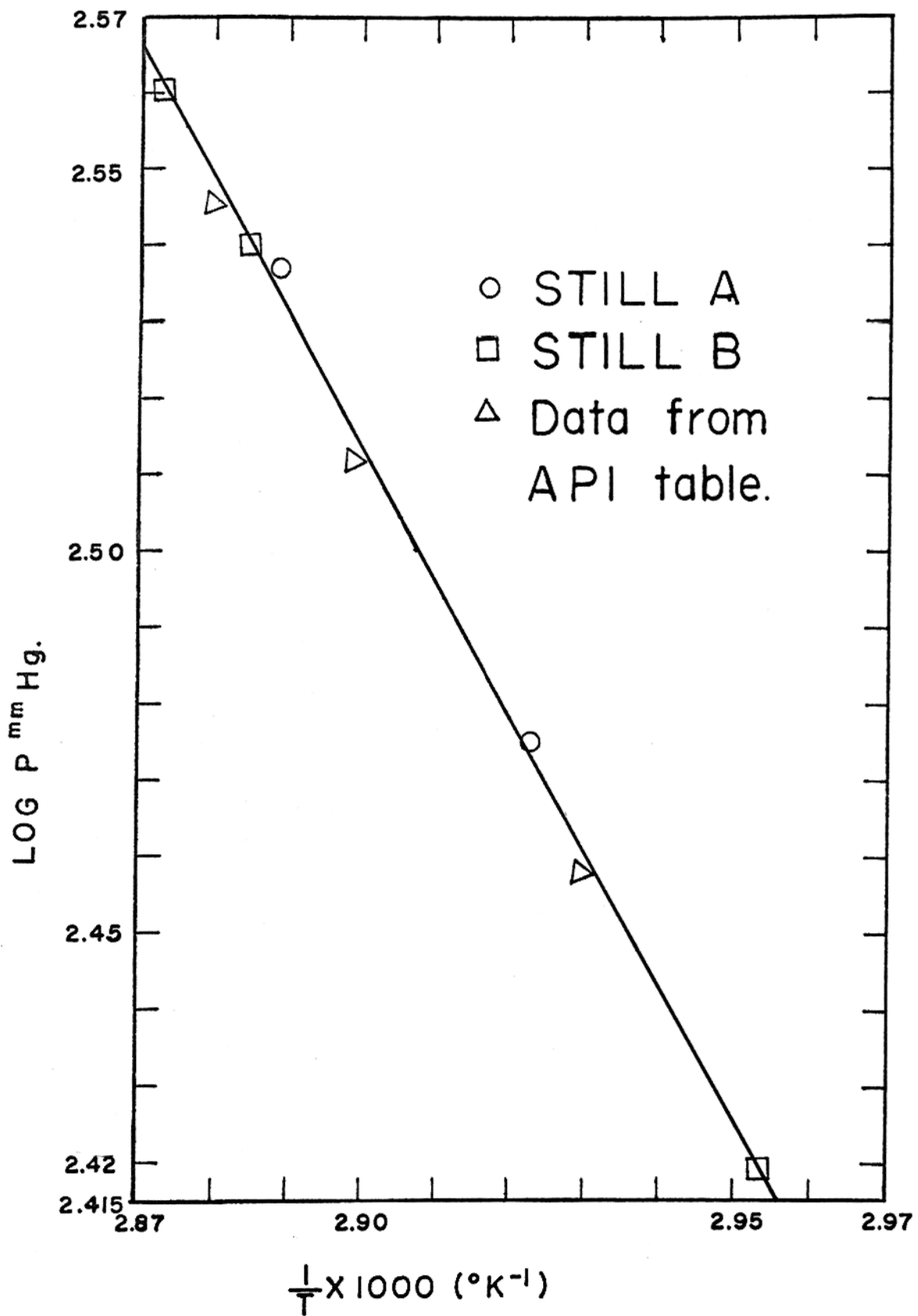


FIG. 2. Interpolation of P-T Data for iso-octane

EVALUATION OF TOTAL PRESSURE METHOD
FOR DETERMINING VAPOR-LIQUID EQUILIBRIA

by

RONG-CHANG LIN

B. S., NATIONAL TAIWAN UNIVERSITY, 1960

AN ABSTRACT OF A MASTER'S THESIS

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requirements for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1963

The purpose of this work was to investigate the feasibility of calculating binary vapor-liquid equilibria from total pressure-liquid composition data without the analysis of the equilibrium liquid and vapor compositions. The Wohl and the Redlich-Kister activity coefficient equations were used to relate the activity coefficients to the liquid compositions. The procedure was first to determine the constants in the activity coefficient equations from the total pressure-liquid composition data by using the least squares method to minimize the differences between the measured pressures and the pressures calculated from the activity coefficient equations. The activity coefficient equations were then used to calculate the equilibrium vapor compositions. Two IBM 1620 Fortran computer programs were developed for this calculation.

To avoid the composition analysis work in obtaining the experimental P-x data, an attempt was made to obtain the equilibrium liquid compositions by weighing the pure components. This can be done by designing an apparatus to bring the charged liquid mixture into an equilibrium state by producing only a negligible changes in the liquid compositions, so that the equilibrium liquid composition can be regarded as equal to the charged liquid composition, which can be previously determined by weighing suitable amount of pure components. Two dynamic equilibrium stills designed for this purpose were investigated and it was found that due to the effects of the fractional vaporization of the circulating stream and the material hold

up in the vapor space, the changes in liquid compositions were considerable. Hence it was concluded that a static equilibrium apparatus would be more desirable than the dynamic apparatus because it eliminates the effect of fractional vaporization of the circulating stream and reduces the effect of material hold up in the vapor space.