THE CORRELATION OF TERNARY LIQUID-LIQUID EQUILIBRIA USING THE REDLICH-KISTER EQUATIONS

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PREFACE

The purpose of this work was two fold; first to correlate ternary liquid-liquid equilibrium compositions using the Redlich-Kister equations; second, to study the effect of temperature on Redlich-Kister constants. The application of Redlich-Kister equations to the IBM 650 computer was developed. Linear relationships between Redlich-Kister constants and the inverse of absolute temperature were found. These relationships can be used in extending the prediction of liquid-liquid equilibrium compositions to temperatures at which no experimental data are available.

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CHAPTER I

INTRODUCTION

The prediction of liquid-liquid equilibrium data is of great importance for the design of solvent extraction processes. The increasing use of liquid-liquid extraction as a means of separating the components of solutions has made it necessary to have a large amount of solubility data and equilibrium data for ternary liquid systems. Unfortunately, the required data are frequently not available, and the experimental determination of equilibrium data is ordinarily laborious. Therefore, there is a need for methods of predicting accurately equilibrium data for liquid-liquid systems.

Several methods for the correlation of liquid-liquid equilibrium data are of particular interest. Hopp and Smith (14) introduced an algebraic approach to the calculation of solvent extraction in complex mixtures. Empirical equations were found to relate the distribution coefficients of the components and solvent. The three simultaneous nonlinear equations resulting were solved using the Newton-Raphson method.

Redlich and Kister (27) derived semi-theoretical equations for relating activity coefficients with solution composition. Thus, the conjugated phase composition can be calculated from these relationships. Another semi-theoretical method was proposed by Black (4). This method was developed from the consideration of physical interactions between molecules. Modified van Laar type equations were derived which are suitable for use with solutions containing highly associating components. From the standpoint of convenience and flexibility, Redlich and Kister's proposal was selected as a basis for correlation of ternary liquid-liquid equilibrium data in this work.

Recently, Scheibel (30) applied the Redlich-Kister equations to the calculation of liquid-liquid equilibria. The methods for evaluating Redlich-Kister constants and correlation of activity coefficients with solvent concentration were illustrated. He also found empirical relationships between the Redlich-Kister constants and the number of carbon atoms for the aromatic hydrocarbons in paraffin-diethylene glycol.

Techo (33) has studied the applicability of several mathematical models for the Gibbs free energy function such as Margules (17), van Laar (36) and Scatchard-Hamer (29) equations to the prediction of equilibrium state of ternary liquid mixtures. Due to the small number of constants he used, his results show large deviations from the experimental data.

Boberg (5) studied the correlation of liquid-liquid equilibria for systems of homologous series from both binary and ternary data by using Redlich-Kister equations. He tried to correlate the Redlich-Kister constants as simple functions of the boiling point for the homologous series, and he concluded that the boiling point is not a suitable correlating property to use when it is desired to predict the equilibrium compositions of series of systems including isomers. Boberg suggested that the effect of temperature on the correlation of liquid-liquid equilibrium be studied.

Following Boberg's recommendations, the correlation of Redlich-Kister constants with temperature and the prediction of ternary liquid-liquid equilibrium compositions at different temperatures have been studied. Solubility and tie-line data for ternary systems were used as basic information. The Redlich-Kister constants were obtained by a least squares method.

The equilibrium compositions can be solved from Redlich-Kister equations if the constants are known. Furthermore, if general relationships for the temperature behavior of the Redlich-Kister constants could be developed, the prediction of equilibrium compositions could be extended to any desired temperature even though sufficient experimental data are not available.

In summary, the object of this work was two fold: to study the prediction of the equilibrium compositions for a number of ternary liquid systems at different temperatures by the use of Redlich-Kister equations. Second, to study the temperature effect on the Redlich-Kister constants. The predicted equilibrium compositions were compared with the experimental data. IBM 650 computer programs have been developed for the evaluation of Redlich-Kister constants and the correlation of equilibrium compositions.

CHAPTER II

REVIEW OF LITERATURE

Correlation of Liquid-Liquid Equilibrium Data

A general theoretical treatment of ternary liquid-liquid equilibrium systems has not been thoroughly accomplished. Almost all equations and methods for correlating equilibrium are empirical. In general, the methods may be separated into two categories; those methods which utilize graphical interpolation or extrapolation, and those which employ empirical or semi-empirical equations.

A graphical interpolation of tie-line data has been devised by Sherwood (31). Lines are drawn from the ends of each tie-line parallel to the base and one side of the triangle respectively. By connecting several intersection points of these two lines, a conjugated curve is obtained. Thus, tie-lines can be interpolated from this conjugated curve. This method has been commonly adopted, but the conjugated curve may have great curvature, thereby lessening its accuracy unless a large number of data points are available.

Bachman (1) found the following relation

$$x_3'' = a + b(x_3''/x_2') \qquad (1)$$

where a and b are constants. A plot of x_3'' against x_3''/x_2' will give a straight line. This method would not be applied to ternary systems of two liquid phases containing two or three solubility curves (1).

Othmer and Tobias (21) in analyzing equilibrium data obtained the following relation

$$\log \frac{1-x_3''}{x_3''} = A \log \frac{1-x_2'}{x_2'} + B \qquad (2)$$

The above two methods suffer from the fact that the concentration of the solute is not indicated in the coordinates (35). Hand (10) showed that a log-log plot of x_1''/x_3'' against x_1''/x_2' gives a straight line. However, several cases are not representated by straight lines, expecially those systems where the direction of the tie-line slope changes greatly with changes in concentration (30).

Hildebrand (12) proposed a graphical method for predicting ternary liquid-liquid equilibrium from activity coefficients of binary solutions. A plot of $x_1'\gamma_1'$ vs. x_1' and $x''\gamma_1''$ vs. x_1'' is made using a common ordinate. At equal values of $x_1'\gamma_1'$ and $x_1''\gamma_1''$ the corresponding values of x_1' and x_1'' are read. The principal advantage of this method lies in the fact that no previous knowledge of the nature of the ternary diagram is necessary. Hildebrand's principle ignores the mutual solubility of two partial miscible solvents. Consequently, the method becomes an approximation when the mutual solubility of the two solvents becomes appreciable (35).

Margules (17) integrated the Gibbs-Duhem equation in terms of composition and empirical constants. He assumed that activity coefficients could be represented by the expressions:

$$\log \gamma_1 = ax_2 + bx_2^2 + cx_2^3 + \ldots \qquad (3)$$

$$\log \gamma_2 = a'x_1 + b'x_1^2 + c'x_1^3 + \ldots \qquad (4)$$

Carlson and Colburn (8) rearranged the equations into the form:

$$\log \gamma_1 = x_2^2 \left[A + 2x_1 (B-A) \right] \tag{5}$$

$$\log \gamma_2 = x_1^2 \left[B + 2x_2 (A-B) \right] \tag{6}$$

This model is the third-order Margules equation for binary system. When the third-order Margules equation does not represent adequately a set of data, a fourth-order equation is sometimes used. The fourth-order equation results from including an additional term in the original expression. If desired, still more terms could be added to the Margules equations, but adding additional terms makes the equations unwieldy (11). The Margules equations for a ternary system are shown in Appendix A. Margules equations are suited for symmetrical systems, that is, systems for which the curves of $\log \gamma_1$ and $\log \gamma_2$ with respect to composition are symmetrical. This condition corresponds to the two Margules constants being nearly the same. On the basis of Techo's results, it was observed that for non-ideal miscible systems the Margules three constants equations gave the best fit of activity coefficient data. Techo also concluded that the Margules model is slightly better than van Laar model for ternary systems containing two partially miscible binary pairs and an ideal binary pair, such as Furfural-n-heptane-cyclohexane, or Aniline-n-heptane-cyclohexane.

Van Laar developed semi-theoretical equations based on the van der Waals equation of state. The van Laar equations for a ternary system are shown in Appendix A. These equations are suited for unsymmetrical systems but they are not satisfactory for solutions of associating components (4). Both the van Laar and the Margules equations have the advantage that the two binary constants can be evaluated from binary vapor-liquid equilibrium data by extrapolating the $\log\gamma_1$ vs. x_1 and $\log\gamma_2$ vs. x_2 to the terminal values respectively.

Scatchard and Hamer (29) extended the methods of van Laar to obtain equations which for a binary system can be represented as follows:

$$\log\gamma_1 = A_{12}\left(\frac{2A_{21}V_1}{A_{12}V_2} - 1\right)z_2^2 - 2A_{12}\left(\frac{A_{21V1}}{A_{12}V_2} - 1\right)z_2^3 \qquad (7)$$

$$\log\gamma_2 = A_{21}\left(\frac{2A_{12}V_2}{A_{21}V_1} - 1\right)z_1^2 - 2A_{21}\left(\frac{A_{12}V_2}{A_{21}V_1} - 1\right)z_1^3 \qquad (8)$$

where $V_1 =$ molar volumes

$z_1 =$ volume fraction of the component

This method is applicable to the equilibria between two liquid or two solid phases of partially miscible solutions and to vapor-liquid systems. Their equations approximate the experimental data for all hydrocarbon systems except those containing benzene (35).

The Redlich and Kister (27) equations were based on representations of the molar excess free energy with the same form as the Margules equations. The development of these equations will be shown in the next chapter and in Appendix A. Methods for evaluating the Redlich-Kister constants from vapor pressure and the azeotropic point of the binary systems were proposed (27). Chao (9) modified the Redlich-Kister equations for application to isobaric data. Boberg concluded that the Redlich-Kister equations are capable of representing a large majority of cases of ternary liquid-liquid equilibria. He found that systems having one partially miscible region can be fitted more accurately than systems having two partially miscible binary pairs. Boberg proposed that the Redlich-Kister constants obtained for a homologous series of systems are simple functions of the boiling point or some other property of the variable component.

Hopp and Smith (14) proposed an algebraic method for the extraction calculations. They found from experimental data that the following empirical equations related adequately the distribution coefficients to the difference in solvent concentration for the two phases.

$$\begin{aligned} \log K_1 &= A_1(x_3'' - x_3') \\ \log K_2 &= A_2(x_3'' - x_3') \\ \log K_3 &= A_3(x_3'' - x_3') \end{aligned} \qquad (9)$$

K_i is the distribution coefficient defined by

$$K_i = x_i''/x_i' \qquad (10)$$

This method has the advantage that compositions of both phases can be evaluated at same time without using a solubility curve.

Black (4) pointed out that the ordinary van Laar equation indicates that plotting $\log\gamma_1^{\frac{1}{2}}$ against $\log\gamma_2^{\frac{1}{2}}$ should give a straight line. As some systems deviate from this relationship, Black has suggested that such deviations occur when the molecules of one or both of the liquids associate or interassociate. To account for such deviations from linearity, Black added an empirical correction term to the van Laar equations that would give the straight line.

$$\log\gamma_i = \text{van Laar value} + E_i$$

in which

$$E_i = \left\{ x_j(x_i - x_j)\left[3(x_i - x_j)(1 - x_j) - 2x_j\right]\right\} C_{ij} \qquad (11)$$

The term C_{ij} is an empirical constant. Thus, when the Black relationship is used, three empirical constants must be determined, two van Laar constants and C_{ij}. The Black equations for both binary and ternary systems are shown in Appendix A.

Scheibel (30) demonstrated a method for estimating distribution coefficients and calculating extraction stages. He suggested both graphical and analytical methods for estimating the Relich-Kister constants. Also, he proposed some simple relations of the Redlich-Kister constants with the numbers of carbon in the solvent for some systems used in petroleum refining industry.

Ishia (16) proposed the following semi-empirical equations:

$$\log(E''/S'') = n \log(x_1/x_3) + K \tag{12}$$

and

$$x_1/x_3 = \omega/kT - 2 \tag{13}$$

where

$$\omega/kT = (X''_2/X''_3 + 1) \ln(X''_2/X''_3)/(X''_2/X''_3 - 1) \tag{14}$$

x = a transferred value corresponding to X composition

ω/kT = parameter related with interaction energy and mutual solubility

K = empirical constant

E'' = mole fraction of solute in extract phase

S'' = mole fraction of solvent in extract phase

and subscripts

1 = solute

2 = raffinate solvent

3 = extract solvent

Ishia gave an example for the calculation of the equilibrium compositions. Based on his results, it was observed that the calculated tie-lines have deviated considerably from the experimental data, and that there is disagreement on the solubility curve near the plait point.

Recently, Otterstedt and Missen (22) proposed a representation of Gibbs free energy change in square root form.

$$\Delta G^E = x_1 x_2 \sum_{k=1}^{n} c_k x_1^{(k-2)/2} \tag{15}$$

where the c are constants. The advantages of square root equation are that: it provides a term $x_1^{-\frac{1}{2}}$ which allows $\Delta G^E/x_1x_2$ to rise steeply as x_1 becomes small; it allows the excess free energy to change sign. Thus, it should be useful in some cases where the Margules and van Laar equations are unsuitable.

Besides the above proposals, there is a theoretical approach to the prediction of solution behavior suggested by Prausnitz and Anderson (26). They proposed that the solvent selectivity for hydrocarbons at infinite dilution can be expressed as a function of physical and chemical properties of the solvent and the non-polar hydrocarbons. This selectivity relation can be used as an aid for correlation of equilibrium data.

Temperature Effects

Little information concerning the effect of temperature on the Redlich-Kister constants could be found. However, a simple linear relationship of the Redlich-Kister constants with 1/T has been developed by Redlich and Kister (28). This relation can be expressed as follows:

$$\frac{\partial B_{12}}{\partial (1/T)} = \frac{b_{12}}{2.303\ R}$$

$$\frac{\partial C_{12}}{\partial (1/T)} = \frac{c_{12}}{2.303\ R} \qquad (16)$$

where b_{12} and c_{12} are constants related with heat of mixing. The detailed derivation of equations (16) will be shown in the next chapter. Other than Redlich and Kister's work, it might be of interest to note that Nord (20) obtained straight line relationships by plotting 2B-A, 2A-B and 2(A-B) with respect to 1/T for Ethanol-chloroform system. Merters and Colburn (18) also obtained straight line functions for the Margules constants with 1/T for binary systems of Isobutane, n-butane and 1-butane with furfural. A simple function was developed:

$$\bar{H}^{o} = 2.303\ RTA_{12} \qquad (17)$$

where $\bar{H}^{o}$ = partial molar heat absorbed on solution at infinite dilution.

$A_{12} = \text{Limit } \log \gamma_1 \ (x_1 \rightarrow 0)$

Margules constants for a large number of systems at different temperatures have been collected by Perry (24).

Berg and McKinnis (3) derived an empirical equation to correlate activity coefficients with temperature. Their equation is

$$\log \gamma = K(1-T_R)^{0.43}/T_R \qquad (18)$$

Vapor-liquid equilibrium data for the systems acetylene-ethane and ethane-H_2O at different compositions were tested and the plots of $\log \gamma$ against $(1-T_R)^{0.43}/T_R$ appeared as good straight lines.

Solubility Diagrams For Ternary Liquid Systems

Surveys of solubility diagrams and tie-line data for ternary liquid systems were collected by Perry (25) and Smith (32). Surveys also appeared each year in Extraction section of the Unit Operations Review in Industrial and Engineering Chemistry from the period of 1948 to 1959, but has not been included since 1960. A booklet was compiled by Himmelblau *et al.* (13). This booklet covers the references of the experimental data published up to 1957.

CHAPTER III

THERMODYNAMIC ASPECTS OF TERNARY PHASE EQUILIBRIA

Phase Equilibria

When two phases are in equilibrium the fugacity of a component in each phase is the same.

$$f_i' = f_i'' \tag{19}$$

The activity is defined as:

$$a_i = f_i/f_i^o \tag{20}$$

where f is fugacity at the system temperature and pressure and f^o is the fugacity at standard state.

According to equations (19) and (20), the activity of a component in each phase is the same when referred to the same standard state.

$$a_i' = a_i'' \tag{21}$$

The activity coefficient is defined as:

$$\gamma_i = a_i/x_i \tag{22}$$

Substituting equation (22) into equation (21), it follows

$$\gamma_i' x_i' = \gamma_i'' x_i'' \tag{23}$$

or

$$\gamma_i'/\gamma_i'' = x_i''/x_i' \tag{24}$$

The γ_i value in equations (23) and (24) can be substituted by Redlich-Kister equations for correlating equilibrium data. The development of the Redlich-Kister equations will be shown in the following section.

Excess Free Energy of a Solution

When one mole of component i is transferred from its standard state of unit fugacity to a solution at the same temperature and pressure, the change in chemical potential, $\Delta\mu_i^M$, of component i is expressed in terms of fugacity. Thus,

$$(\Delta\mu_i^M)_{T,P} = (\mu_i - \mu_i^o)_{T,P} = RT\ \ln(f_i/f_i^o)_{\ T,P} \qquad (25)$$

For an ideal solution, $f_i^* = x_i f_i^o$

$$\mu^* = RT\ \ln x_i + \mu_i^o \qquad (26)$$

For a non-ideal solution:

$$\mu = RT\ \ln x_i + RT\ \ln \gamma_i + \mu_i^o \qquad (27)$$

The excess free energy G^E is defined as:

$$G_i^E = \mu_i^E = \mu_i(\text{real}) - \mu_i^*(\text{ideal}) = RT\ \ln \gamma_i \qquad (28)$$

Thus the excess free energy per mole of solution becomes:

$$g^E = \sum_{i=1}^{k} x_i \mu_i^E = \sum_{i\ 1}^{k} x_i RT\ \ln \gamma_i \qquad (29)$$

Define $Q = g^E/(2.303RT)$ (30)

Equation (29) becomes

$$Q = \sum_{i=1}^{k} x_i \log \gamma_i \tag{31}$$

The excess free energy permits a direct representation of the deviations from the laws of ideal solution. An ideal solution is one which follows Raoult's law and does not change enthalpy and entropy on mixing.

Redlich-Kister Equations

Redlich and Kister (27) introduced a general empirical representation of excess free energy which is related to composition by a series function.

$$Q_{12} = x_1x_2 \left[B_{12}+C_{12}(x_1-x_2)+D_{12}(x_1-x_2)^2+\ldots\ldots \right]_{P,T} \tag{32}$$

For a ternary system;

$$\begin{aligned} Q &= Q_{12}+Q_{23}+Q_{31}+x_1x_2x_3\left[C_1+D_1(x_2-x_3)+D_2(x_3-x_1)+\ldots\ldots\right] \\ &= x_1x_2\left[B_{12}+C_{12}(x_1-x_2)+D_{12}(x_1-x_2)^2+\ldots\ldots\right] \\ &\quad + x_2x_3\left[B_{23}+C_{23}(x_2-x_3)+D_{23}(x_2-x_3)^2+\ldots\ldots\right] \\ &\quad + x_3x_1\left[B_{31}+C_{31}(x_3-x_1)+D_{31}(x_3-x_1)^2+\ldots\ldots\right] \\ &\quad + x_1x_2x_3\left[C_1+D_1x_1+D_2x_2+\ldots\right] \end{aligned} \tag{33}$$

where B_{ij}, C_{ij} are binary constants

and $B_{ij} = B_{ji}$, $D_{ij} = D_{ji}$

but $C_{ij} = -C_{ji}$

and C_1, D_1, D_2 .... are ternary constants.

This series furnishes the most flexible representation. Only the first term is required for a nearly perfect solution (27). For most cases the use of the constants B_{ij} and C_{ij} is sufficient to fit the data (5).

The relationship between activity coefficients for each component and the Q function can be further derived from equation (31) by taking partial derivatives of Q with respect to x.

$$\partial Q/\partial x_r = \log \gamma_r \tag{34}$$

and

$$x_k \partial Q/\partial x_k = x_k \log \gamma_k \tag{35}$$

$$\sum_{k=1}^{n} x_k \partial Q/\partial x_k = \sum_{k=1}^{n} x_k \log \gamma_k = Q \tag{36}$$

where n = number of components

Adding equations (35) and (36), one obtains:

$$\log \gamma_r = Q + \partial Q/\partial x_r - \sum_{k=1}^{n} x_k \partial Q/\partial x_k \tag{37}$$

Performing the operations indicated on equation (33):

$$\begin{aligned}\log \gamma_1 = {} & B_{12}x_2(1-x_1) - B_{23}x_2x_3 + B_{31}x_3(1-x_1) \\ & + C_{31}\left[2x_3(1-x_1)(x_3-x_1) - x_3^2\right] \\ & + D_{31}\left[3x_3(1-x_1)(x_3-x_1)^2 + 2x_3^2(x_3-x_1)\right] \\ & + C_{12}\left[2x_2(1-x_1)(x_1-x_2) + x_2^2\right] \\ & + D_{12}\left[3x_2(1-x_1)(x_1-x_2)^2 + 2x_2^2(x_1-x_2)\right] \\ & + C_{23}\left[-2x_2x_3(x_2-x_3)\right] \\ & + D_{23}\left[-3x_2x_3(x_2-x_3)^2\right] \end{aligned} \tag{38}$$

The detailed derivation of equation (38) is shown in Appendix A.

The equations for the $\log \gamma_2$ and $\log \gamma_3$ are obtained by cycling the subscripts as follows:

$$\begin{tikzcd} & 2 \arrow[dr] & \\ 1 \arrow[ur] & & 3 \arrow[ll] \end{tikzcd}$$

Correlation of Phase Equilibria

Taking the logarithm of both sides of equation (24) gives

$$\log \gamma_i' - \log \gamma_i'' = \log x_i'' - \log x_i' \tag{39}$$

Substituting the values for log γ from equation (38) into equation (39), and rearranging

$$
\begin{aligned}
\log x_1'' - \log x_1' = {} & B_{31}x_3'(1-x_1') + B_{12}x_2'(1-x_1') - B_{23}x_2'x_3' \\
& + C_{31}\left[2x_3'(1-x_1')(x_3'-x_1') - x_3'^{\,2} \right] \\
& + D_{31}\left[3x_3'(1-x_1')(x_3'-x_1')^2 - 2x_2'^{\,2}(x_3'-x_1') \right] \\
& + C_{12}\left[2x_2'(1-x_1')(x_1'-x_2') + x_2'^{\,2} \right] \\
& + D_{12}\left[3x_2'(1-x_1')(x_1'-x_2')^2 + 2x_2'^{\,2}(x_1'-x_2') \right] \\
& + C_{23}\left[-2x_2'x_3'(x_2'-x_3') \right] \\
& + D_{23}\left[-3x_2'x_3'(x_2'-x_3')^2 \right] \\
& - B_{31}x_3''(1-x_1'') - B_{12}(1-x_1'') + B_{23}x_2''x_3'' \\
& - C_{31}\left[2x_3''(1-x_1'')(x_3''-x_1'') - x_3''^{\,2} \right] \\
& - D_{31}\left[3x_3''(1-x_1'')(x_3''-x_1'')^2 - 2x_3''^{\,2}(x_3''-x_1'') \right] \\
& - C_{12}\left[2x_2''(1-x_1'')(x_1''-x_2'') + x_2''^{\,2} \right] \\
& - D_{12}\left[3x_2''(1-x_1'')(x_1''-x_2'')^2 + 2x_2''^{\,2}(x_1''-x_2'') \right] \\
& - C_{23}\left[-2x_2''x_3''(x_2''-x_3'') \right] \\
& - D_{23}\left[-3x_2''x_3''(x_2''-x_3'')^2 \right] \qquad (40)
\end{aligned}
$$

This equation can be written in a general form for components i, j, and k.

$$\begin{aligned}
\log x_i'' - \log x_i' = {} & B_{ki}x_k'(1-x_i')+B_{ij}x_j'(1-x_i')-B_{jk}x_j'x_k' \\
& + C_{ki}\left[2x_k'(1-x_i')(x_k'-x_i')-x_k'^2\right] \\
& + D_{ki}\left[3x_k'(1-x_i')(x_k'-x_i')^2-2x_j'^2(x_k'-x_i')\right] \\
& + C_{ij}\left[2x_j'(1-x_i')(x_i'-x_j')^2+x_j'^2\right] \\
& + D_{ij}\left[3x_j'(1-x_i')(x_i'-x_j')^2+2x_j'^2(x_i'-x_j')\right] \\
& + C_{jk}\left[-2x_j'x_k'(x_j'-x_k')\right] \\
& + D_{jk}\left[-3x_j'x_k'(x_j'-x_k')^2\right] \\
& - B_{ki}x_k''(1-x_k'')-B_{ij}x_j''(1-x_j')+B_{jk}x_i''x_j'' \\
& - C_{ki}\left[2x_k''(1-x_i'')(x_k''-x_i')-x_k''^2\right] \\
& - D_{ki}\left[3x_k''(1-x_i'')(x_k''-x_i'')^2-2x_j''^2(x_k''-x_i'')\right] \\
& - C_{ij}\left[2x_j''(1-x_i'')(x_i''-x_j'')^2+x_j''^2\right] \\
& - D_{ij}\left[3x_j''(1-x_i'')(x_i''-x_j'')^2+2x_j''^2(x_i''-x_j'')\right] \\
& - C_{jk}\left[-2x_j''x_k''(x_j''-x_k'')\right] \\
& - D_{jk}\left[-3x_j''x_k''(x_j''-x_k'')^2\right]
\end{aligned} \qquad (41)$$

The value of x_i'' can be evaluated from the corresponding equilibrium composition, x_i', provided the constants in Redlich-Kister equations are known.

Effect of Temperature On Redlich-Kister Constants

The activity coefficient is not only a function of composition but also a function of temperature. However, the Redlich-Kister constants are functions of temperature, but not of composition. In order to predict phase equilibria at any temperature, a knowledge of B_{ij} and C_{ij} as functions of temperature is required.

Starting from the basic relation

$$dG = dH - dTS \tag{42}$$

For an infinitesimal change

$$\Delta G = \Delta H - \Delta TS \tag{43}$$

Divide equation (43) by T

$$\Delta G/T = \Delta H/T - \Delta S \tag{44}$$

Partial differential with respect to T

$$\left[\frac{\partial(\Delta G/T)}{\partial T}\right]_P = \frac{1}{T}\left(\frac{\partial \Delta H}{\partial T}\right)_P - \frac{\Delta H}{T^2} - \left(\frac{\partial \Delta S}{\partial T}\right)_P \tag{45}$$

Substituting the relation

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = T\left(\frac{\partial \Delta S}{\partial T}\right)_P \tag{46}$$

into equation (45) gives

$$\left(\frac{\partial \Delta G/T}{\partial T}\right)_P = -\frac{\Delta H}{T^2} \tag{47}$$

Rearranging equation (47) gives

$$\left(\frac{\partial \Delta G/T}{-T^2 \partial T}\right)_P = \Delta H \tag{48}$$

Equation (48) can be written as

$$\left(\frac{\partial \Delta G/T}{\partial\ 1/T}\right)_P = \Delta H \tag{49}$$

For the case of mixing

$$\left(\frac{\partial \Delta G^M/T}{\partial\ 1/T}\right)_P = \Delta H^M \tag{50}$$

For one mole of solution, equation (50) can be written as

$$\frac{\partial\,(g^E/2.303RT)}{\partial\ (1/T)} = \frac{\partial\ Q}{\partial\ (1/T)} = \frac{\Delta h^M}{2.303R} \tag{51}$$

A representation of Δh^M has been proposed by Redlich and Kister (28) similar to that for Q. For the ternary case:

$$\begin{aligned} \Delta h^M = {} & x_1x_2\left[b_{12}+c_{12}(x_1-x_2)+d_{12}(x_1-x_2)^2\ \ldots\right] \\ & + x_1x_3\left[b_{13}+c_{31}(x_3-x_1)+d_{31}(x_3-x_1)^2\ \ldots\right] \\ & + \ldots \end{aligned} \tag{52}$$

Differentiating the Q function [equation (33)] with respect to 1/T gives

$$\frac{\partial Q}{\partial (1/T)} = x_1x_2\left[\frac{B_{12}}{(1/T)} + (x_1-x_2)\frac{C_{12}}{(1/T)} + (x_1-x_2)^2\frac{D_{12}}{(1/T)} + \cdots\right]$$

$$+ \cdots\cdots \qquad (53)$$

Comparing equations (52) with (53) term by term, it follows

$$\frac{\partial B_{12}}{\partial (1/T)} = \frac{b_{12}}{2.303R}$$

$$\frac{\partial C_{12}}{\partial (1/T)} = \frac{c_{12}}{2.303R}$$

$$\cdots\cdots \qquad (54)$$

If b_{12} and c_{12} are constants, B_{12} and C_{12} should be linear functions of 1/T.

CHAPTER IV

THE PREDICTION OF TERNARY LIQUID-LIQUID EQUILIBRIA

Calculation of Equilibria Using Redlich-Kister Equations

The procedure for the evaluation of ternary liquid-liquid equilibrium compositions using Redlich-Kister equations can be divided into two major parts:

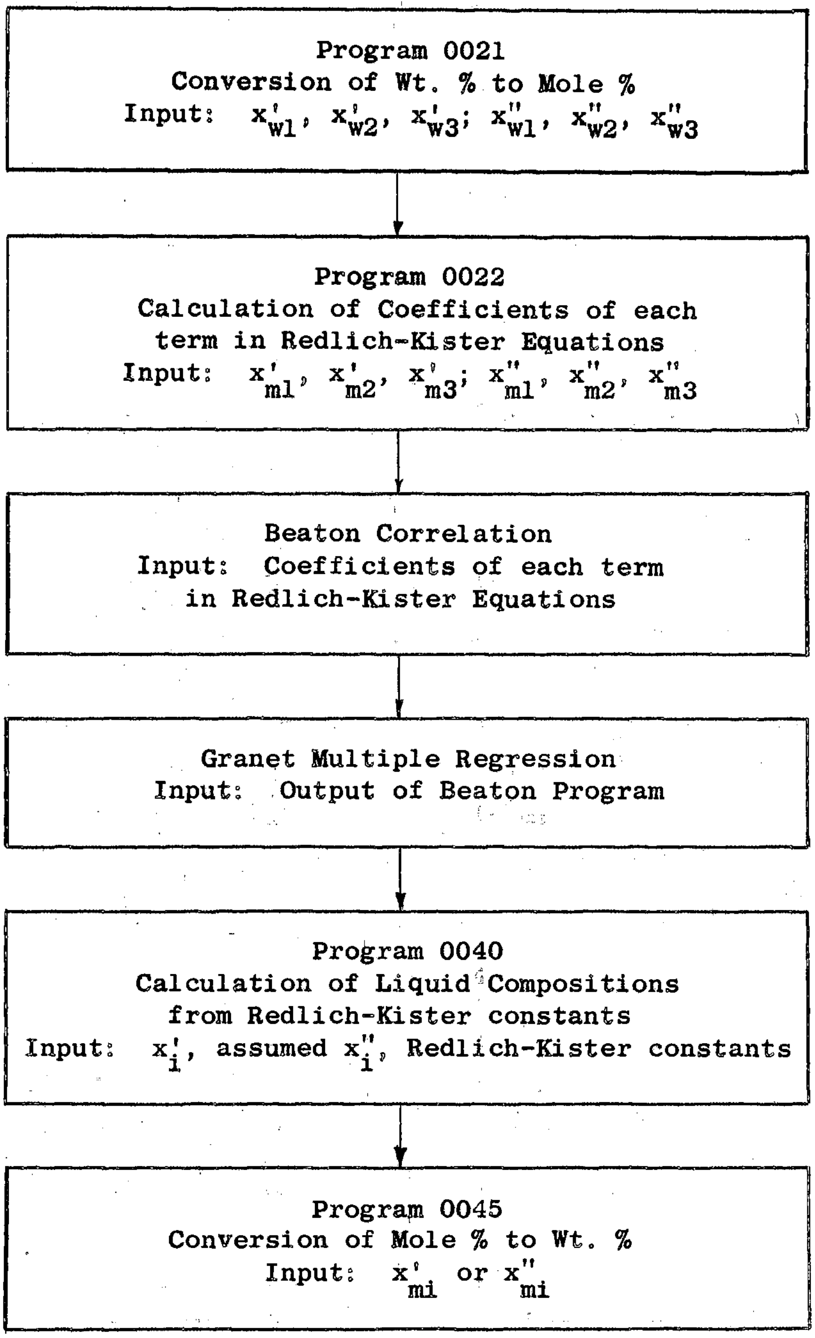
1. Calculation of Relich-Kister constants from experimental data.
2. Calculation of equilibrium compositions, using the Redlich-Kister equations with the obtained constants.

Table I shows the general procedure for computing ternary liquid-liquid tie-lines. The Redlich-Kister constants are evaluated by substituting experimental tie-line data into equation (41). Thus, a set of these equations can be obtained, and the unknown constants can be estimated by the least squares method. Once the constants are known, the conjugate compositions can be calculated by utilizing equation (41) from the Redlich-Kister constants and the composition of one phase. A trial and error method is involved in solving these fourth order equations.

The evaluation of the constants in the Redlich-Kister equations was a most important problem in this work. The success of the application of the Redlich-Kister equations for the correlation of the equilibrium compositions depends on the accuracy of the evaluation of the constants.

TABLE I

PROCEDURE FOR COMPUTING TERNARY LIQUID-LIQUID TIE-LINES USING REDLICH-KISTER EQUATIONS



Generally, the Redlich-Kister constants are evaluated by the method of least squares (15). This method can be easily solved by using a digital computer. The principle of the least squares method is reviewed below.

The Method of Least Squares

The method of least squares (36) is a process for finding the best possible values for a set of k unknowns, say, b_1, b_2, ... b_k, connected by n sets of data. Let the equation to be evaluated be:

$$\hat{y} = b_1X_1 + b_2X_2 + b_3X_3 \ldots + b_kX_k \tag{55}$$

this equation passes through the mean value and is known as the multiple linear regression equation. The variables b_1, b_2 ... b_k, are called partial regression coefficients. A deviation of the experimental data, y, from regression is given by equation (2).

$$d = y - \hat{y} = y - b_1X_1 - \ldots - b_kX_k \tag{56}$$

The least squares criterion is that the independent variables, b_1, b_2, ... b_k, should be chosen so as to make the sum of the squares of the deviation, d, as small as possible.

$$\sum (y - \hat{y})^2 = \text{minimum} \tag{57}$$

or

$$\partial \sum (y - \hat{y})^2 / \partial b_1 = 0$$

$$\partial \sum (y - \hat{y})^2 / \partial b_2 = 0$$

$$\ldots\ldots$$

$$\partial \sum (y - \hat{y})^2 / \partial b_k = 0 \tag{58}$$

Thus we obtain

$$b_1\sum X_1^2 + b_2\sum X_1X_2 + \ldots\ldots + b_k\sum X_1X_k = \sum X_1y$$

$$b_1\sum X_1X_2 + b_2\sum X_2^2 + \ldots\ldots + b_k\sum X_2X_k = \sum X_2y$$

$$\ldots\ldots$$

$$b_1\sum X_kX_1 + b_2\sum X_kX_2 + \ldots\ldots + b_k\sum X_k^2 = \sum X_ky \qquad (59)$$

These equations are called normal equations. The regression matrix is:

$$A = \begin{bmatrix} X_1^2 & X_1X_2 & \ldots\ldots & X_1X_k \\ \sum X_1X_2 & X_2^2 & \ldots\ldots & X_2X_k \\ \ldots\ldots & & & \\ X_kX_1 & X_kX_2 & \ldots\ldots & X_k^2 \end{bmatrix} \qquad (60)$$

A G matrix is defined as:

$$G = \begin{bmatrix} \sum X_1y \\ \sum X_2y \\ \cdot \\ \cdot \\ \cdot \\ \sum X_ky \end{bmatrix} \qquad (61)$$

And a B matrix is defined as:

$$B = \begin{bmatrix} b_1 \\ b_2 \\ \cdot \\ \cdot \\ \cdot \\ b_k \end{bmatrix} \qquad (62)$$

Thus equation (62) can be written in the form:

$$A\ B = G \qquad (63)$$

The variables, b_1, b_2, ... b_k, can be solved by the matrix:

$$B = A^{-1}G \qquad (64)$$

where A^{-1} is the inverse of the regression matrix.

To obtain the regression equation, equation (55), proceed as follows:

1. Compute sums, sums of squares, and sums of cross products for the raw data.
2. Write out the normal equations, equation (59). Thus A and G matrices can be set from the normal equations.
3. Solve A^{-1} and G matrices.
4. Solve B matrix from A^{-1} and G.
5. Obtain the coefficients b_i from B matrix.

Two computer programs, Beaton Correlation and Multiple Regression, were used for this purpose. The first program includes the calculations of sums, sums of squares, sums of cross products, etc.. The second program involves the calculation of the B matrix. Also, two alternative programs Core 4 and Core 4^{-1}were used. Core 4 program corresponds Beaton program, calculating sums of squares and sums of cross products. Core 4^{-1} corresponds to the Regression program, calculating regression coefficients. The Beaton program computes the corrected sum of squares, while the Core 4 program computes the uncorrected sum of squares. The mathematical model for the Beaton and Regression programs is:

$$Y = b_o + b_1X_1 + b_2X_2 + \dots \qquad (65)$$

and that of Core 4 and Core 4^{-1} is:

$$Y = b_1X_1 + b_2X_2 + \dots \qquad (66)$$

The Redlich-Kister equations can be written in the form:

$$\log x_i'' - \log x_i' = \sum B_{ij}[f_1(x_i', x_j', x_k'; x_i'', x_j'', x_k'')]$$
$$+ \sum C_{ij}[f_2(x_i', x_j', x_k'; x_i'', x_j'', x_k'')] + \dots \qquad (67)$$

Comparing this equation with equation (55) or (66), it may be seen that the coefficients b_i in equation (55), corresponding to the Redlich-Kister constants, can be obtained from the regression equation by substituting composition data into equation (67).

CHAPTER V

RESULTS AND DISCUSSION

The application of the Redlich-Kister equations for the prediction of the activity coefficients for two liquid phases in equilibrium has been studied for a number of systems and at several temperatures. The six coefficients retained from the infinite series representation of the excess free energy have been determined, and the equilibrium phase compositions calculated using the Redlich-Kister constants were compared with the experimental data. The variation of the Redlich-Kister constants with temperature was studied and plots of the constants as a function of the reciprocal of absolute temperature are presented.

As described in Chapter IV, linear regression analysis of the Redlich-Kister equations was used to determine the coefficients of the infinite series. In obtaining the Redlich-Kister constants, Beaton and Granet Regression digital computer programs were used. The mathematical model for these programs is of the form:

$$Y = b_o + b_1X_1 + b_2X_2 + \dots . \tag{68}$$

If the b_o is very small, then this analysis can be used to fit the data with an equation of the form:

$$Y = b_1X_1 + b_2X_2 + \dots . \tag{69}$$

Equation (41) can be written as:

$$\log x_i'' - \log x_i' = B_{ki} f_1(x_k', x_i'; x_k'', x_i'') + B_{ij} f_2(x_i', x_j'; x_i'', x_j'')$$

$$+ B_{jk} f_3(x_j', x_k'; x_j'', x_k'') + \ldots. \qquad (70)$$

which is analogous to the form of equation (69). In order to eliminate b_o in equation (68) a value for x_i or the plait point, where $x_i'' - x_i' = 0$, must be taken as a data point. Since the program will overflow for a zero matrix, some small values such as $Y = 0.001$ and $X_1 = 0.001$ must be used instead of zero values. This was done for all calculations reported herein using the Beaton-Granet programs.

Core 4 and Core 4^{-1} programs were found to give comparable results to the Beaton and Regression programs. The mathematical model for Core 4 and Core 4^{-1} programs is in the form of equation (69). The Redlich-Kister constants obtained from each program for the system Methanol-H_2O-Ethyl Acetate at 20°C. are shown in Table II.

TABLE II

COMPARISON OF THE REDLICH-KISTER
CONSTANTS FROM DIFFERENT PROGRAMS

System: Methanol-H_2O-Ethyl Acetate, 20°C.
Number of data: 27 points

	Beaton and Regression	Core 4 and Core 4^{-1}
B_{31}	0.07095	0.0844
B_{12}	- 0.247	- 0.234
B_{23}	1.226	1.236
C_{31}	- 0.0921	- 0.0828
C_{12}	- 0.448	- 0.4498
C_{23}	0.6125	0.609

The predictions of the equilibrium compositions from these two sets of constants are shown in Table V and Figure 1. Compositions predicted by the Core 4 analysis are very close to those predicted by the Beaton-Granet programs, and they are close to the experimental data, except at the upper part of the equilibrium curve where the compositions calculated from the Core 4 are a little higher than those from the Beaton-Granet programs.

The six unknown constants, theoretically can be obtained by solving six simultaneous equations using matrix methods. This method forces the equations to pass through the selected points. The constants obtained from this method failed to give good results for the calculation of equilibrium compositions. Boberg (5) also was unable to obtain satisfactory results using this method. The least squares method has the advantage that more data points can be taken, consequently, it will give the best fit over the whole range.

The data points selected to determine the Redlich-Kister constants should be equally distributed along the whole solubility curve. In cases where a limited amount of tie-line data were available, the conjugate curve was constructed and additional tie-line points were determined. It was easy to interpolate the conjugate curve to obtain the data points on the middle and lower part of the curve; but the accuracy of the extrapolation of the conjugate curve near the plait point, especially for the case where there was no experimental determination of the plait point indicated might be questionable.

It would be desirable to use a minimum amount of data for evaluating Redlich-Kister constants. Unfortunately, no consistent trend of the constants toward limiting values was found when using up to 27 data points in evaluating the Redlich-Kister constants. Thus, while a few data points might suffice to determine the Redlich-Kister constants applicable over a short range of the solubility curve, many data values are required to determine values of the constants applicable over a wide range of the solubility curve. Table III shows the Redlich-Kister constants obtained from 17, 22 and 27 data points for the system Methanol-H_2O-Ethyl Acetate at 20°C.

TABLE III

EFFECT OF THE NUMBER OF DATA POINTS ON REDLICH-KISTER CONSTANTS

Programs: Beaton and Granet Regression

	17 data	22 data	27 data
B_{31}	0.0175	0.0162	0.07095
B_{12}	- 0.226	- 0.226	- 0.247
B_{23}	1.183	1.118	1.226
C_{31}	0.0415	0.0425	- 0.0921
C_{12}	- 0.491	- 0.487	- 0.448
C_{23}	0.677	0.669	0.6125

The comparison of the calculated equilibrium compositions for the system Methanol-H_2O-Ethyl Acetate using Redlich-Kister constants from different programs and number of data taken is shown in Table V. For this system, the calculated compositions for x_1'' from Core 4 correlation with 27 data points shows less deviation ($S_{\bar{d}} = 0.001$) than that from Beaton with 27 data points ($S_{\bar{d}} = 0.00374$), and for x_3'', Beaton correlation shows less deviation (0.00424 compared with 0.0015). Since neither method was clearly superior an arbitrary choice of the Beaton method was selected for studying the use of the Redlich-Kister equations for the correlation of liquid equilibrium.

The system n-Heptane-Benzene-Diethyl Glycol has been studied for the purpose of comparison of the Redlich-Kister constants evaluated in this work with those evaluated by Schiebel (30). These two sets of constants are shown in Table IV.

TABLE IV

REDLICH-KISTER CONSTANTS FOR
N-HEPTANE-BENZENE-DIETHYLENE GLYCOL

$t = 30^{\circ}C.$

	Schiebel	This Work
B_{31}	1.63	1.678
B_{12}	0.20	0.285
B_{23}	0.93	0.988
C_{31}	- 0.05	- 0.0455
C_{12}	- 0.04	- 0.155
C_{23}	0.41	0.201
D_{31}	0.09	---
D_{12}	0	---
D_{23}	0.27	---

Schiebel described an approximate method for determining Redlich-Kister constants by solving simultaneous equations. He obtained the above constants by using the last two tie lines on the lower part of the solubility curve as data points. Thus, the prediction of the equilibrium compositions from Schiebel's constants gave good results at lower part of the curve, but the deviations from experimental data increased in the upper part of the curve. In order to reduce this deviation, more weight should be assigned to data near the plait point when evaluating the Redlich-Kister constants (34).

Techo (33) predicted the equilibrium compositions by use of the Margules equations. The Margules constants were evaluated from binary vapor-liquid equilibrium data. The system Cyclohexane-n-Heptane-Furfural has been studied for the purpose of comparison with Techo's work. In this work, 22 data points were used. Due to the large change of the slope of the tie-lines for this system, the calculated compositions for the high solute concentration showed a large deviation from the experimental data (Figure 3 and Table VII). However, the prediction of the equilibrium compositions gave better results than that using two pair of constants in Margules equations.

The systems Phenol-H_2O-Aniline and Acetone-H_2O-Benzene were taken for the study of temperature effect on the correlation of the equilibrium compositions. Equilibrium data at three different temperatures for the system Acetone-H_2O-Benzene and five different temperatures for Phenol-H_2O-Aniline have been studied. The solubility curve of the system Acetone-H_2O-Benzene is the most common Type I systems (Figures 17-19). The solubility curve of Phenol-H_2O-Aniline at low temperature is that of a Type II system (Figures 4, 5, 6, 8), and at high temperature is that of a Type I (Figure 7) system.

Plots of Redlich-Kister constants against the reciprocal of absolute temperature resulted in almost linear relationships. For Phenol-H_2O-Aniline, the plots showed slight curvatures at high temperature. The Redlich-Kister constants at 48°C. for this system were estimated by interpolation of their temperature correlations by linear relationships.

The predicted compositions from the constants interpolated from the straight line relations gave an average 1.5% deviation from that of smooth curvatures.

A homologous series of Alcohol-H_2O-Ethyl Acetate has been studied for the purpose of finding some generalized correlations of the Redlich-Kister constants with temperature. The solubility curves for the Methanol, Ethanol and Propanol series belong to Type I, while for n-Butanol the solubility curve is of Type II. The area of the two phase region at 20°C. is less than that at 0°C. and the tie lines at 20°C. have higher slopes than that of at 0°C. for all systems. The plots of reduced temperature (i.e. the temperature of the system divided by the critical temperature) of the alcohol with Redlich-Kister constants produced approximate straight line relationships. B_{23} and C_{23} are almost constant, while B_{31}, B_{12} and C_{12} spread widely along the line. The accuracy of equilibrium compositions calculated using Redlich-Kister constants estimated from this type of correlation was not studied, and should be a part of a further study. It is also possible that critical solution temperatures might be used for a correlation of this type.

TABLE V

THE SYSTEM METHANOL-H_2O-ETHYL ACETATE AT 20°C.

Raffinate Phase Composition-Mole Fract.		Extract Phase Composition Mole Fraction							
Experimental Data		Experimental Data		Calculated Using Beaton-Granet Analysis				Calculated Using Core 4 Analysis	
				17 data		27 data		27 data	
x'_1	x'_3	x''_1	x''_3	x''_1	x''_3	x''_1	x''_3	x''_1	x''_3
0.026	0.957	0.0241	0.830	0.0387	0.8166	0.0385	0.8168	0.0387	0.817
0.054	0.9268	0.0698	0.758	0.0760	0.752	0.0736	0.7542	0.0736	0.754
0.0754	0.902	0.111	0.674	0.1062	0.6788	0.1011	0.6839	0.1012	0.6837
0.0998	0.875	0.1278	0.645	0.1316	0.6414	0.1244	0.6486	0.1247	0.6483
0.1434	0.820	0.175	0.506	0.1919	0.4901	0.1791	0.5029	0.1802	0.5018
0.1818	0.758	0.207	0.391	0.2317	0.3659	0.2190	0.3790	0.2204	0.375
			$\bar{d}$	0.0102	0.00985	0.0035	0.00144	0.00385	0.004
			$S_{\bar{d}}$	0.0326	0.0234	0.00374	0.00424	0.001	0.0215

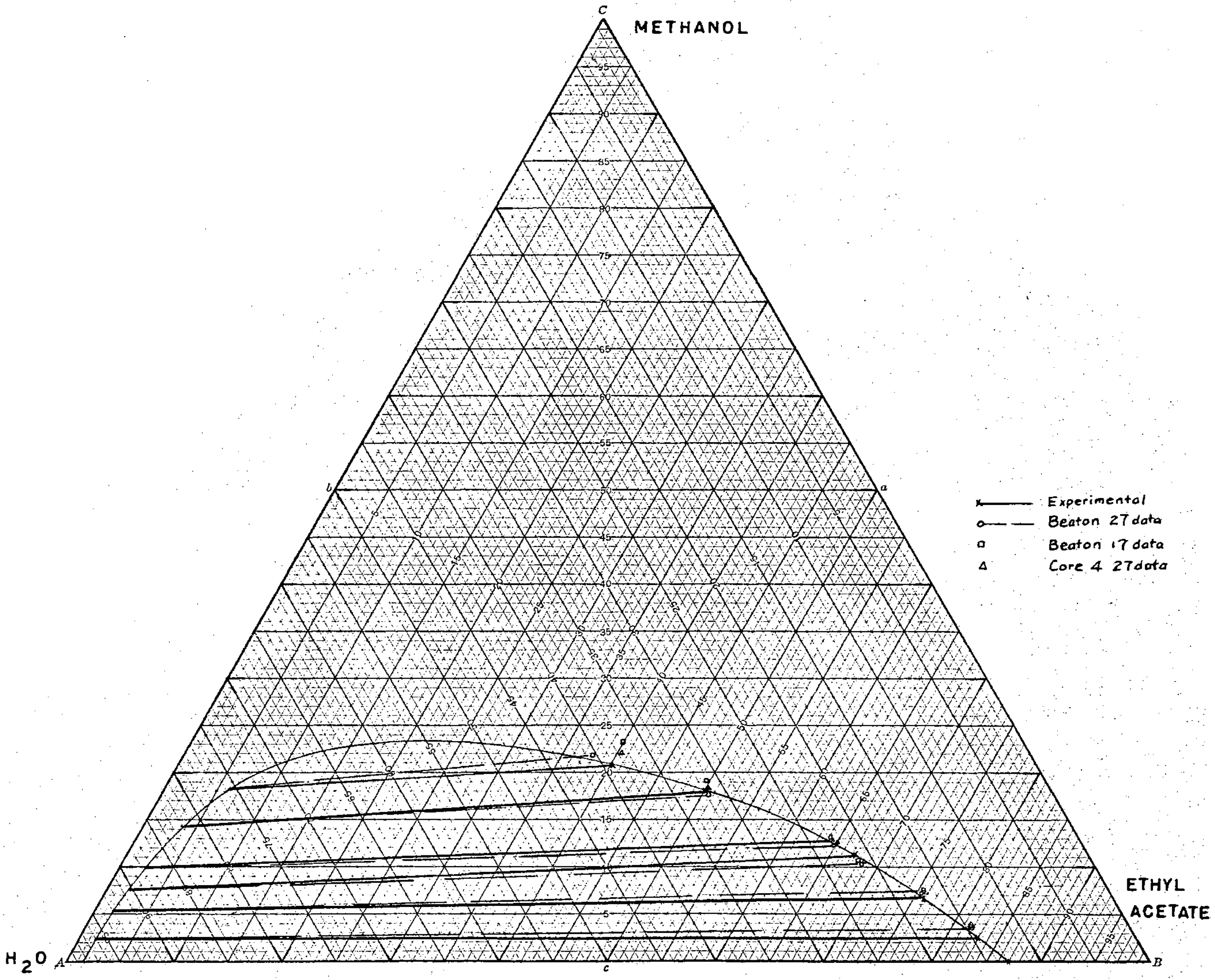


Fig. 1. The System Methanol-H_2O-Ethyl Acetate at 20°C

TABLE VI

THE SYSTEM BENZENE-HEPTANE-DIETHYLENE GLYCOL AT 150°C. (30)

Raffinate Phase Composition-Mole Fract.		Extract Phase Composition Mole Fraction					
Experimental Data		Experimental Data		From the Constants Evaluated by Schiebel		This Work Beaton-Granet Analysis	
x_2'	x_3'	x_2''	x_3''	x_2''	x_3''	x_2''	x_3''
0.047	0.025	0.013	0.963	0.0126	0.963	0.0157	0.958
0.089	0.027	0.028	0.943	0.0248	0.949	0.032	0.940
0.187	0.028	0.044	0.928	0.0560	0.918	0.055	0.916
0.344	0.036	0.094	0.876	0.117	0.850	0.108	0.865
0.521	0.059	0.203	0.760	0.202	0.734	0.202	0.752
0.280	0.030	---	---	0.098	0.828	0.0781	0.899
0.430	0.045	---	---	0.157	0.810	0.160	0.800
0.560	0.070	---	---	0.234	0.720	0.246	0.717
			$\bar{d}$	0.0058	0.0112	0.0035	0.009
			$S_{\bar{d}}$	0.00551	0.00659	0.00276	0.00127

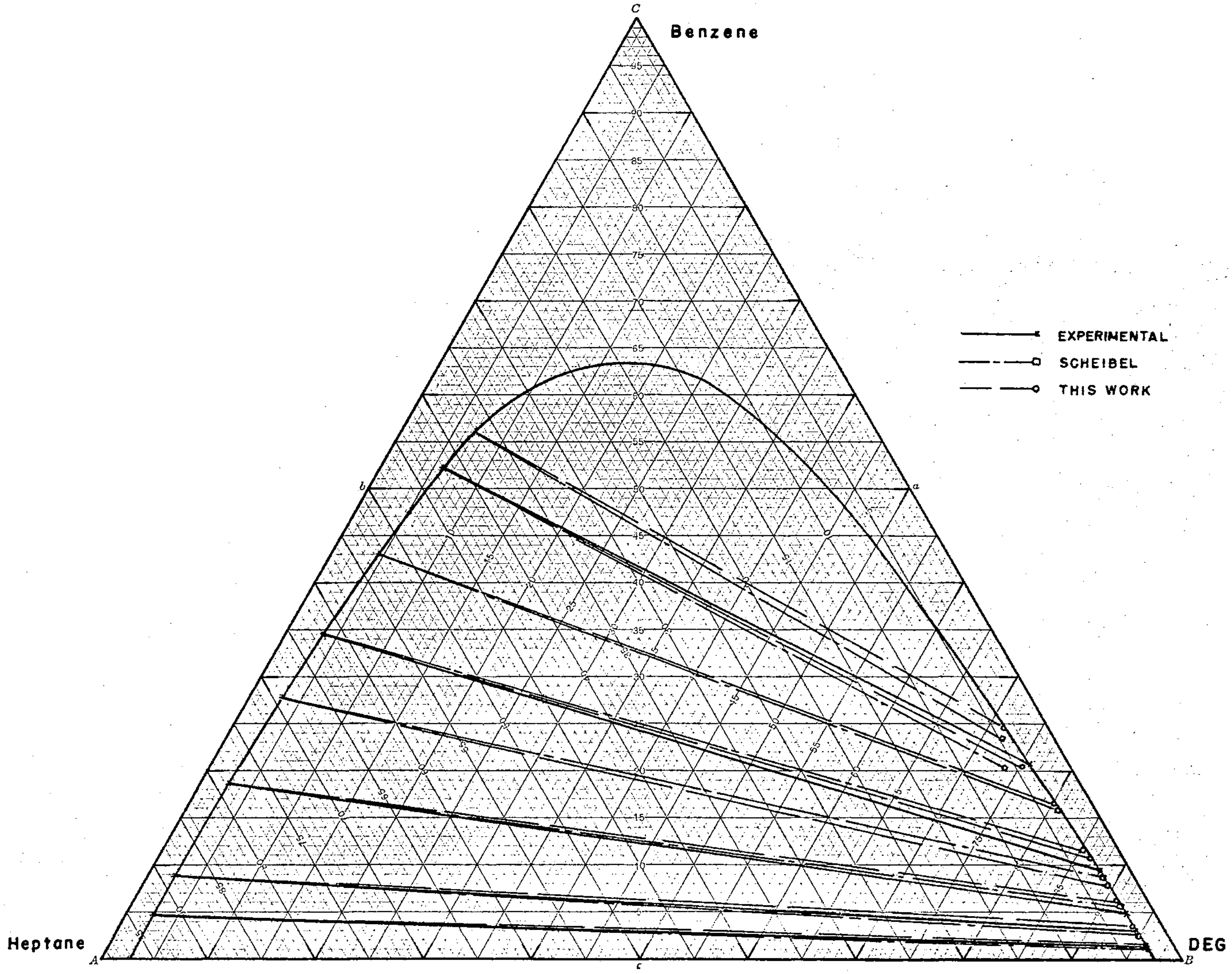


Fig. 2. The System Benzene-H_2O-Diethylene Glycol at 150°C

TABLE VII

THE SYSTEM CYCLOHEXANE-N-HEPTANE-FURFURAL AT 30°C. (23)

Raffinate Phase Composition-Mole Fract.		Extract Phase Composition Mole Fraction									
Experimental		Experimental		Techo's Results (33)				Beaton-Granet Analysis			
x_2''	x_3''	x_2'	x_3'	x_2'	x_3'	$\Delta x_2'$	$\Delta x_3'$	x_2'	x_3'	$\Delta x_2'$	$\Delta x_3'$
0.05	0.93	0.745	0.061	0.780	0.06	0.035	- 0.001	0.768	0.060	0.023	- 0.001
0.0498	0.0922	0.7106	0.060	0.705	0.06	- 0.0056	---	0.718	0.060	- 0.0074	---
0.0441	0.915	0.6184	0.063	0.640	0.06	0.0216	- 0.003	0.639	0.061	0.0106	- 0.002
0.0353	0.903	0.4727	0.064	0.500	0.06	0.0273	- 0.004	0.491	0.061	0.0183	- 0.003
0.016	0.869	0.1800	0.059	0.130	0.06	- 0.05	0.001	0.219	0.061	0.039	0.002
					$\bar{d}$	0.00566	0.0014			0.0165	0.001
					$S_{\bar{d}}$	0.0158	0.00116			0.0112	0.00095

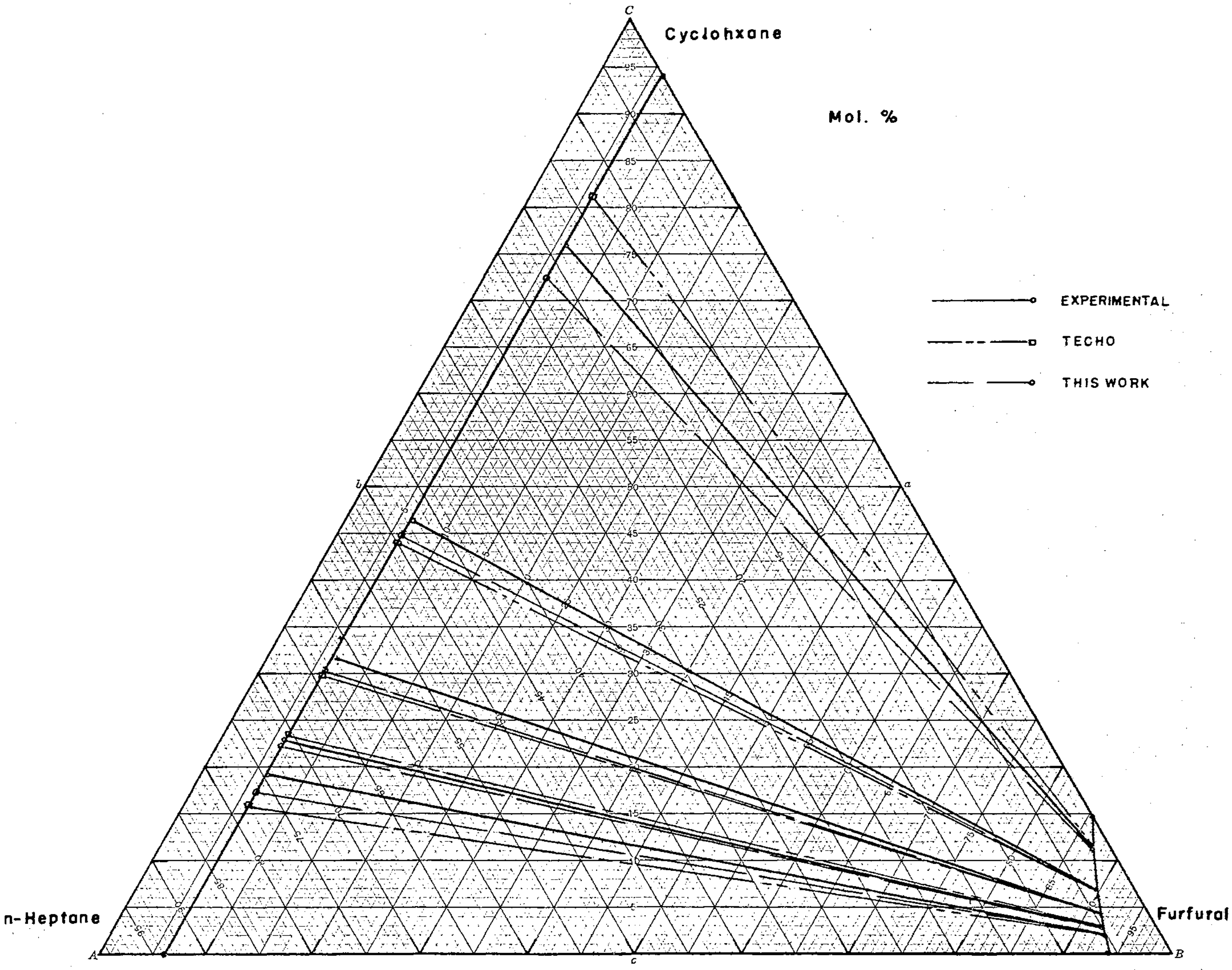


Fig. 3. The System Cyclohexane-n-Heptane-Furfural at 30°C

TABLE VIII

THE SYSTEM PHENOL-H_2O-ANILINE AT 8.6°C. (7)

Raffinate Phase Composition Weight Fraction			Extract Phase Composition Weight Fraction					
Experimental			Experimental			Calculated		
x'_1	x'_2	x'_3	x''_1	x''_2	x''_3	x''_1	x''_2	x''_3
0.004	0.960	0.036	0.102	0.053	0.845	0.097	0.055	0.848
0.009	0.963	0.026	0.257	0.046	0.697	0.250	0.050	0.700
0.011	0.962	0.029	0.293	0.042	0.665	0.281	0.050	0.669
0.025	0.955	0.020	---	---	---	0.388	0.042	0.570
0.035	0.950	0.015	---	---	---	0.495	0.044	0.461
0.044	0.946	0.010	0.630	0.390	0.331	0.602	0.058	0.340
0.055	0.939	0.006	0.700	0.090	0.210	0.730	0.154	0.116
					$\bar{d}$	0.0044	0.0194	0.015
					$S_{\bar{d}}$	0.00975	0.0145	0.0212

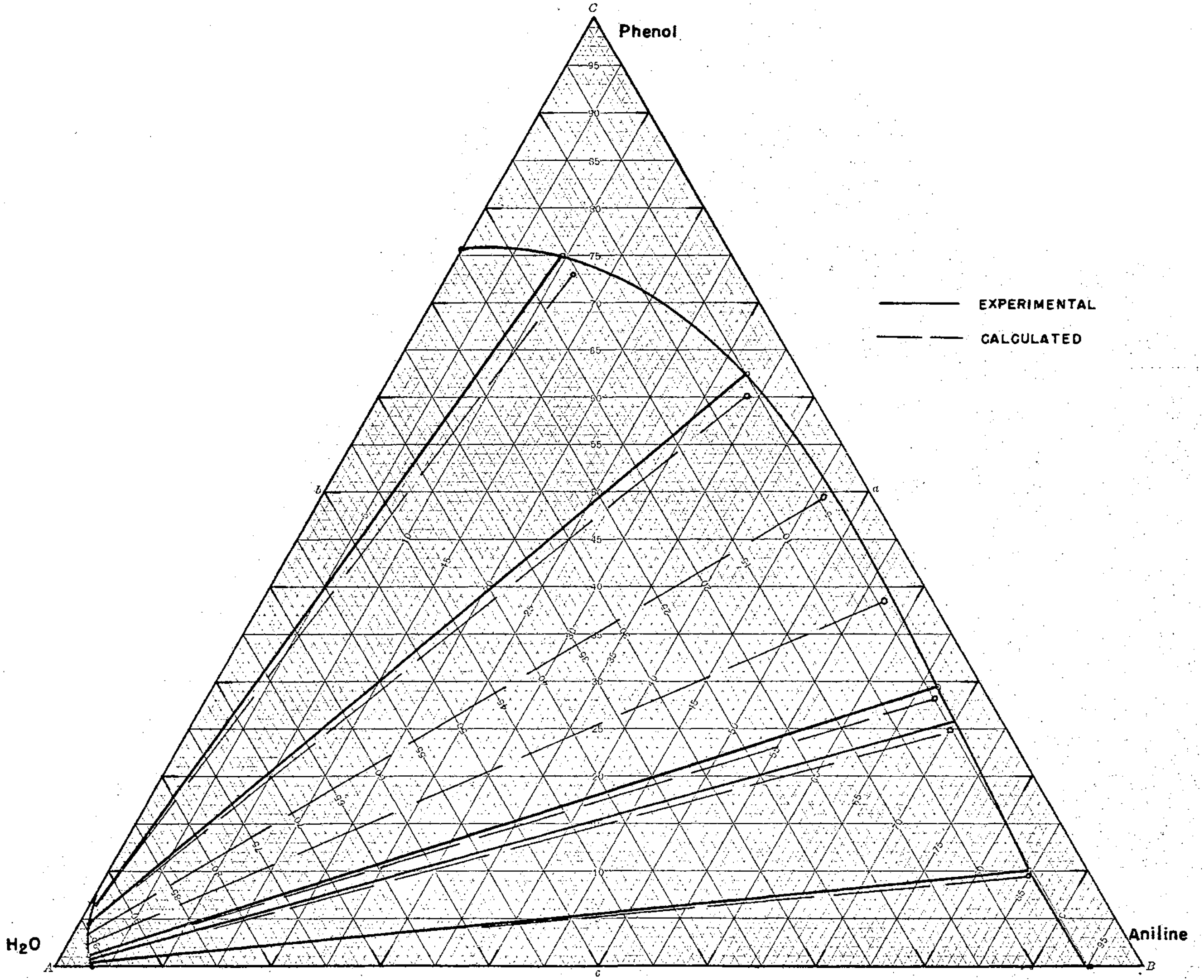


Fig. 4. The System Phenol-H_2O-Aniline at 8.6°C

TABLE IX

THE SYSTEM PHENOL-H_2O-ANILINE AT 25.4°C. (7)

Raffinate Phase Composition Weight Fraction			Extract Phase Composition Weight Fraction					
Experimental			Experimental			Calculated		
x'_1	x'_2	x'_3	x''_1	x''_2	x''_3	x''_1	x''_2	x''_3
0.002	0.964	0.034	0.084	0.066	0.850	0.080	0.060	0.860
0.007	0.968	0.025	0.210	0.065	0.725	0.201	0.061	0.738
0.012	0.967	0.021	0.317	0.056	0.627	0.320	0.065	0.615
0.020	0.962	0.018	---	---	---	0.396	0.066	0.538
0.033	0.954	0.013	0.504	0.071	0.425	0.498	0.070	0.432
0.067	0.945	0.008	0.662	0.085	0.253	0.661	0.095	0.244
0.061	0.935	0.004	0.728	0.140	0.132	0.722	0.130	0.148
0.065	0.933	0.002	0.750	0.185	0.065	0.745	0.170	0.085
0.074	0.926	---	0.732	0.239	0.029	0.747	0.218	0.035
					$\bar{d}$	0.0021	0.0034	0.0025
					$S_{\bar{d}}$	0.0023	0.0082	0.00411

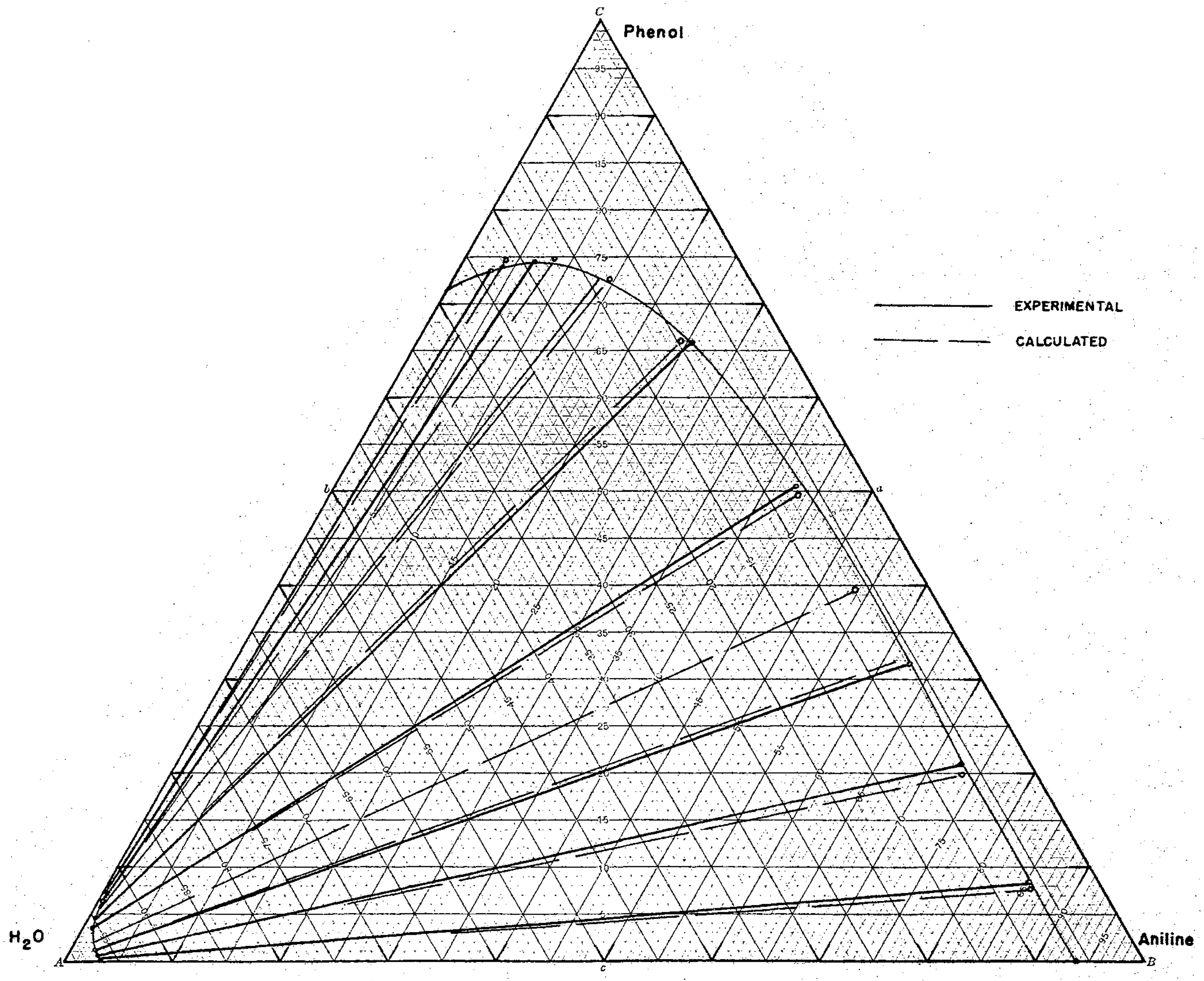


Fig. 5. The System Phenol-H_2O-Aniline at 25.4°C

TABLE X

THE SYSTEM PHENOL-H_2O-ANILINE AT 66.3°C. (7)

Raffinate Phase Composition Weight Fraction			Extract Phase Composition Weight Fraction					
Experimental			Experimental			Calculated		
x_1'	x_2'	x_3'	x_1''	x_2''	x_3''	x_1''	x_2''	x_3''
0.006	0.954	0.040	0.098	0.082	0.820	0.097	0.0823	0.821
0.012	0.952	0.036	0.179	0.096	0.725	0.180	0.0982	0.721
0.020	0.952	0.027	0.298	0.107	0.595	0.290	0.105	0.605
0.028	0.945	0.027	0.330	0.117	0.553	0.332	0.118	0.550
0.045	0.935	0.027	0.487	0.134	0.379	0.480	0.130	0.390
0.053	0.932	0.015	0.537	0.154	0.309	0.540	0.162	0.298
0.071	0.918	0.011	0.603	0.223	0.175	0.598	0.219	0.183
0.108	0.885	0.007	0.613	0.300	0.087	0.610	0.290	0.100
0.149	0.846	0.005	0.580	0.389	0.031	0.579	0.396	0.025
0.158	0.839	0.003	---	---	---	0.555	0.425	0.020
0.178	0.819	0.003	0.520	0.471	0.009	0.498	0.497	0.005
					$\bar{d}$	0.0018	0.0033	0.0027
					$S_{\bar{d}}$	0.00258	0.0091	0.00268

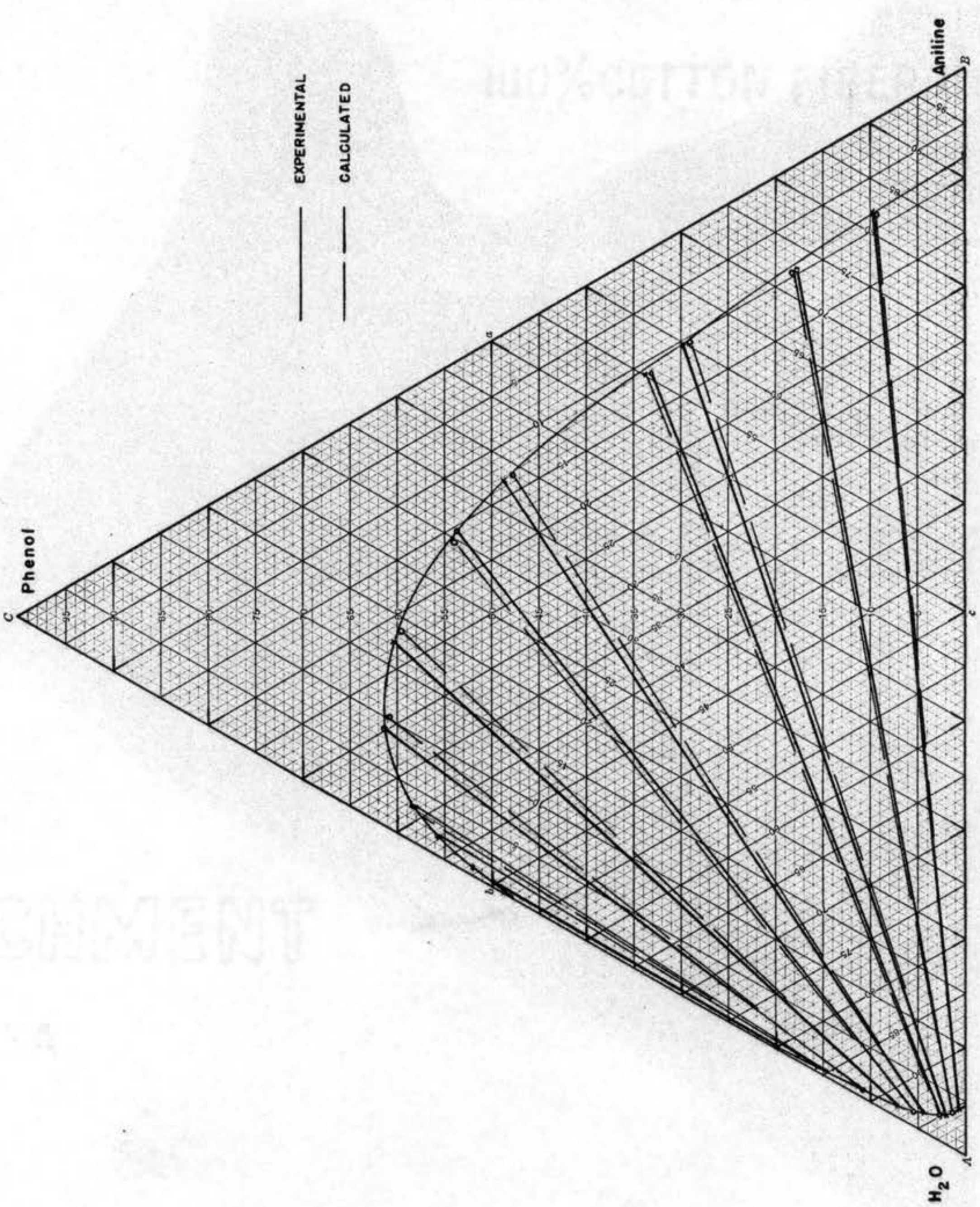


Fig. 6. The System Phenol-H_2O-Aniline at 66.3°C

TABLE XI

THE SYSTEM PHENOL-H_2O-ANILINE AT 97.6°C. (7)

Raffinate Phase Composition Weight Fraction			Extract Phase Composition Weight Fraction					
Experimental			Experimental			Calculated		
x_1'	x_2'	x_3'	x_1''	x_2''	x_3''	x_1''	x_2''	x_3''
0.005	0.927	0.068	0.173	0.138	0.689	0.170	0.130	0.700
0.015	0.930	0.055	---	---	---	0.231	0.141	0.628
0.025	0.925	0.050	0.282	0.144	0.574	0.272	0.150	0.578
0.035	0.925	0.040	---	---	---	0.335	0.165	0.500
0.040	0.924	0.036	0.379	0.171	0.450	0.369	0.175	0.456
0.067	0.906	0.027	0.415	0.192	0.393	0.420	0.191	0.389
0.086	0.888	0.026	0.482	0.222	0.296	0.469	0.220	0.311
0.136	0.842	0.022	0.524	0.322	0.153	0.514	0.327	0.159
0.218	0.769	0.023	0.492	0.438	0.070	0.509	0.405	0.076
					$\bar{d}$	0.00657	0.00557	0.00486
					$s_{\bar{d}}$	0.00383	0.00541	0.00295

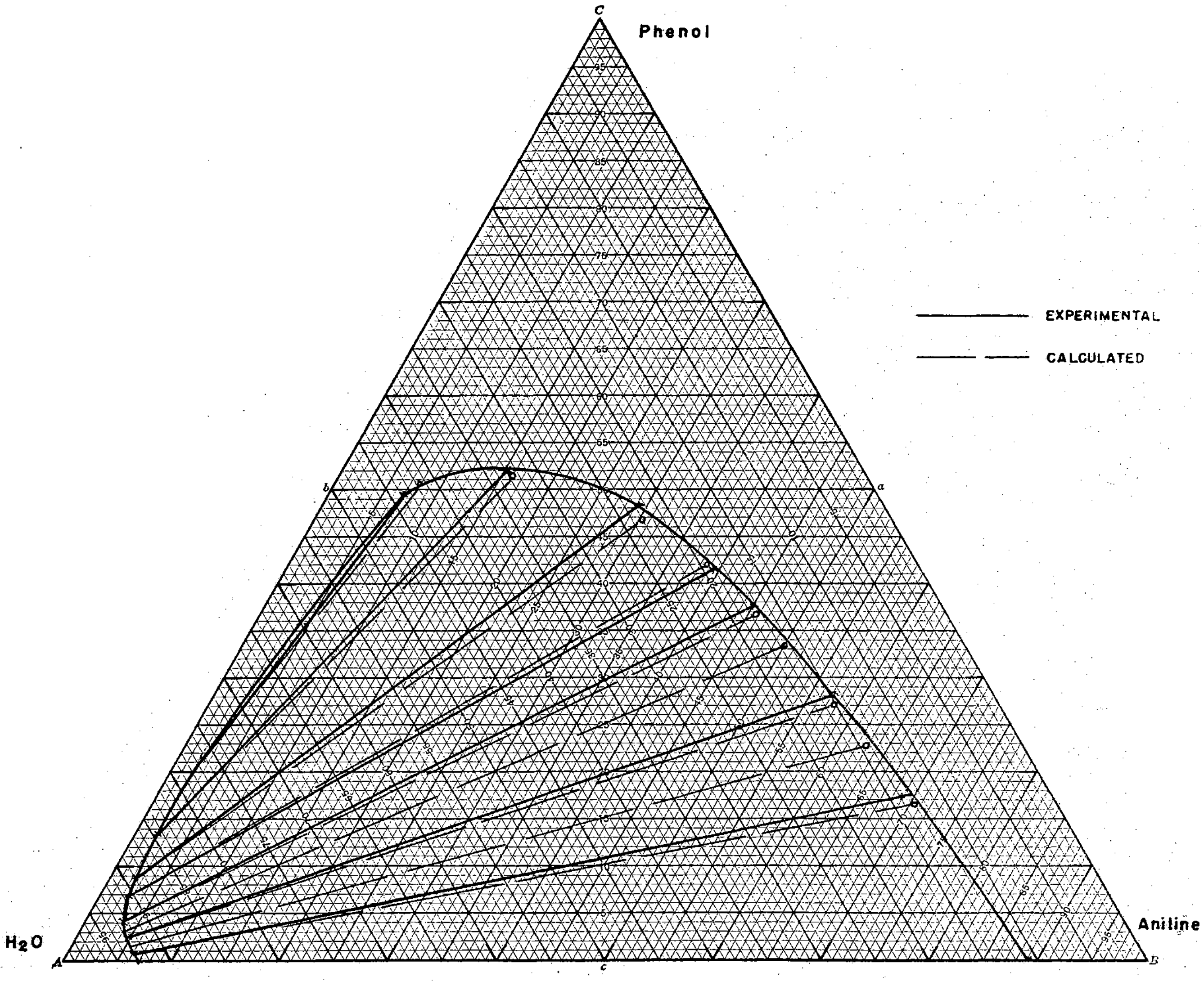


Fig. 7. The System Phenol-H_2O-Aniline at 96.7°C

TABLE XII

THE SYSTEM PHENOL-H_2O-ANILINE AT 48°C. (7)

Raffinate Phase Composition Weight Fraction			Extract Phase Composition Weight Fraction					
Experimental			Experimental			Predicted		
x_1'	x_2'	x_3'	x_1	x_2	x_3	x_1	x_2	x_3
0.003	0.959	0.038	0.088	0.062	0.850	0.094	0.070	0.836
0.014	0.960	0.026	0.272	0.050	0.678	0.248	0.061	0.691
0.034	0.948	0.018	0.472	0.086	0.442	0.468	0.079	0.452
0.052	0.931	0.017	0.590	0.093	0.317	0.608	0.091	0.301
0.074	0.917	0.009	0.690	0.162	0.147	0.674	0.150	0.176
0.087	0.910	0.003	0.685	0.253	0.062	0.678	0.237	0.0842
					$\bar{d}$	0.0105	0.003	0.01736
					$S_{\bar{d}}$	0.00871	0.00424	0.00814

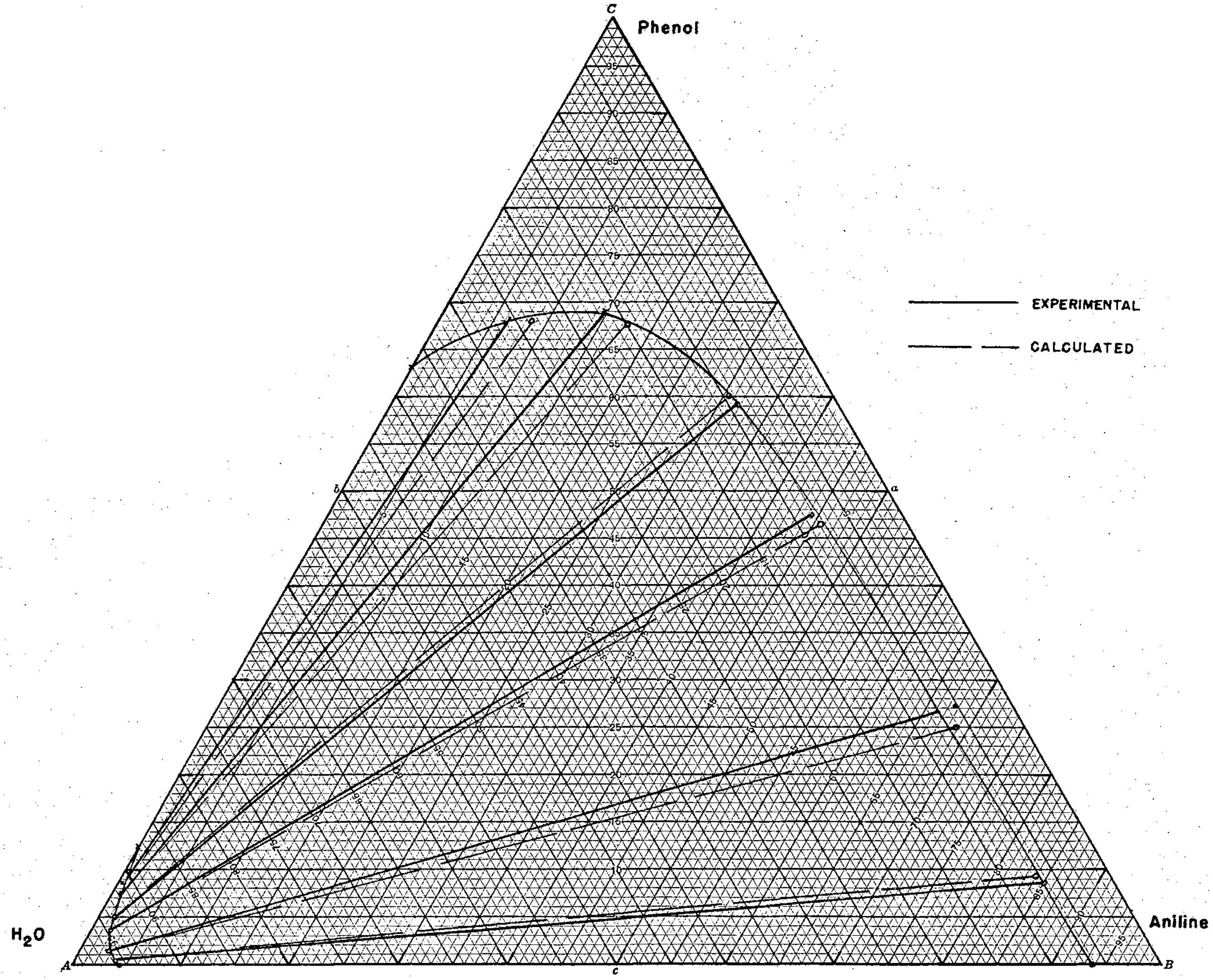


Fig. 8. The System Phenol-H_2O-Aniline at 48°C

TABLE XIII

EFFECT OF TEMPERATURE ON REDLICH-KISTER CONSTANTS (BEATON CORRELATION)

System	t°C.	1/T °K.	B_{31}	B_{12}	B_{23}	C_{31}	C_{12}	C_{23}
Acetone-H_2O-Benzene	15.0	0.00347	2.167	1.211	1.701	- 0.773	- 0.342	0.602
	30.0	0.00330	1.860	1.382	1.642	- 0.801	- 0.389	0.481
	45.0	0.00314	1.432	1.201	1.460	- 0.8897	- 2.880	0.183
Phenol-H_2O-Aniline	8.6	0.00355	- 1.850	- 1.212	1.258	0.678	- 0.0258	0.560
	25.4	0.00335	- 1.950	- 1.371	1.132	0.524	- 0.203	0.520
	66.3	0.00295	- 2.245	- 1.687	1.245	0.567	- 0.3854	0.4257
	97.6	0.00271	- 2.281	- 2.050	1.091	0.503	- 0.827	0.281
Methanol-H_2O-Butanol	----	0.00366	2.994	2.416	1.011	- 0.798	0.066	0.763
	15.0	0.00347	2.682	2.402	1.220	- 0.802	0.066	0.861
	30.0	0.00330	2.503	2.430	1.256	- 0.794	+ 0.064	0.670
	60.0	0.00300	2.466	2.289	0.904	- 0.766	0.060	0.552

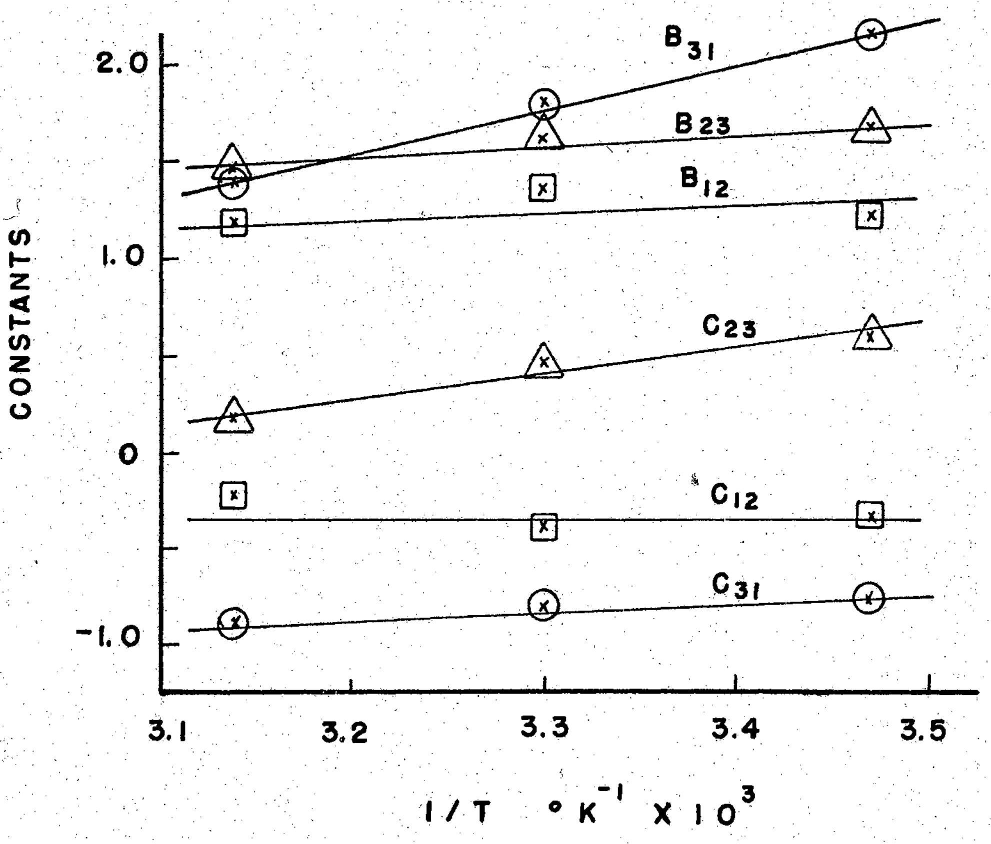


FIG. 9. TEMPERATURE CORRELATION FOR ACETONE-H_2O-BENZENE

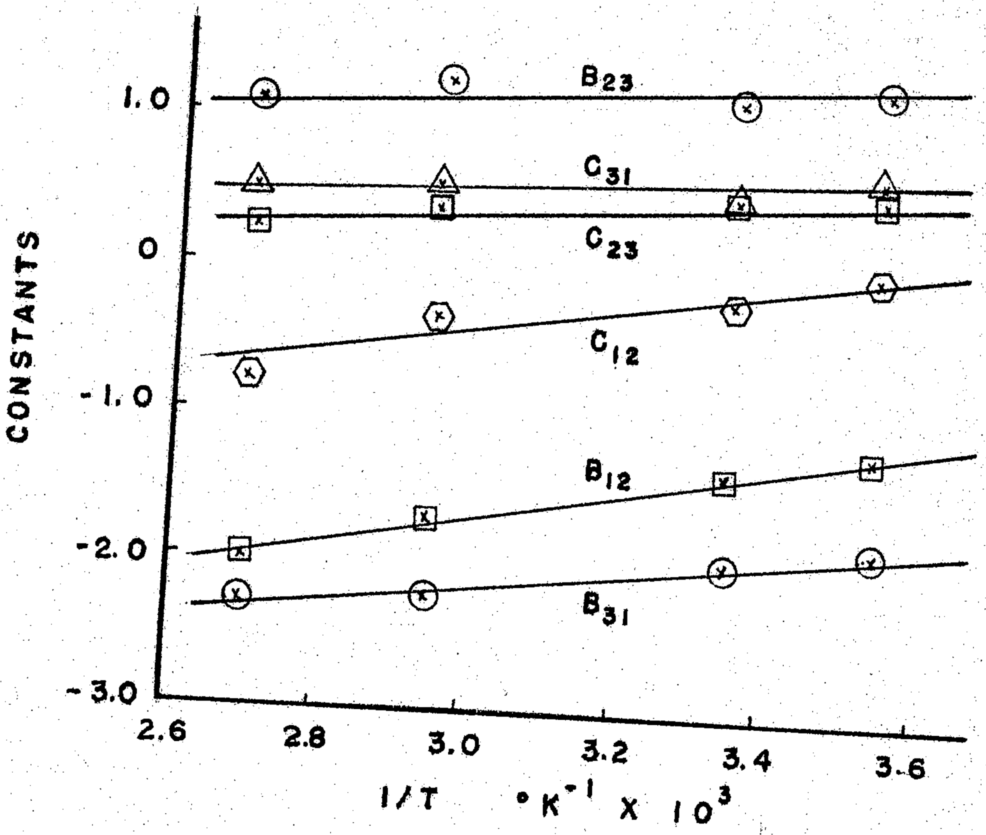


FIG.10. TEMPERATURE CORRELATION FOR PHENOL-H_2O-ANILINE

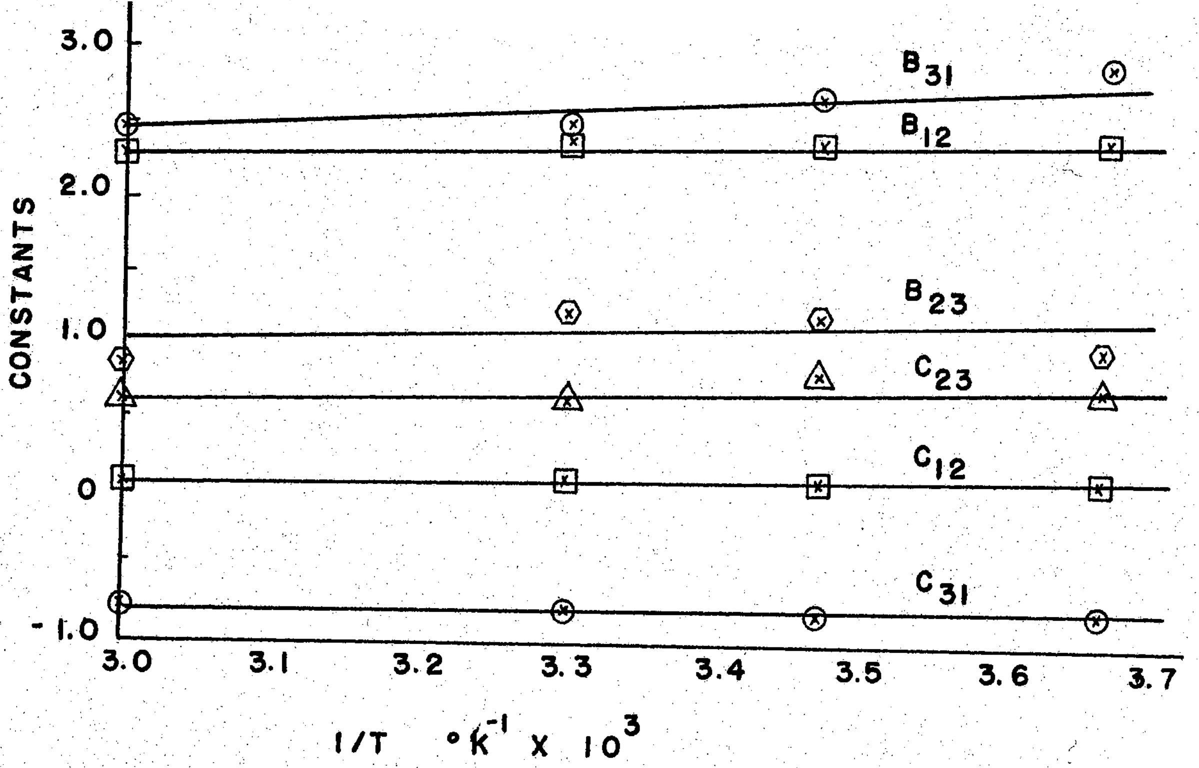


FIG. 11. TEMPERATURE CORRELATION FOR METHANOL- H_2O - n-BUTANOL

TABLE XIV

TEMPERATURE CORRELATION FOR THE ALCOHOL-H_2O-ETHYL ACETATE (BEATON PROGRAM)

Alcohol	T_c °K.	t°C.	1/T	B_{31}	B_{12}	B_{23}	C_{31}	C_{12}	C_{23}
Methanol	513.2	20	1.750	0.07095	-0.247	1.226	- 0.0921	- 0.448	0.6125
		0	1.879	0.0978	0.0887	1.325	- 0.035	- 0.278	0.6120
Ethanol	516.3	20	1.762	0.211	0.902	1.238	- 0.280	- 0.211	0.5342
		0	1.889	0.468	0.550	1.247	- 0.1124	- 0.382	0.649
Propanol	536.7	20	1.835	0.285	0.932	1.431	- 0.318	- 0.143	0.724
		0	1.889	0.482	0.911	1.442	- 0.433	- 0.145	0.666
Butanol	560.0	20	1.910	0.166	0.924	1.289	- 0.398	- 0.1065	0.645
		0	2.050	0.1522	0.998	1.293	- 0.561	- 0.0782	0.525

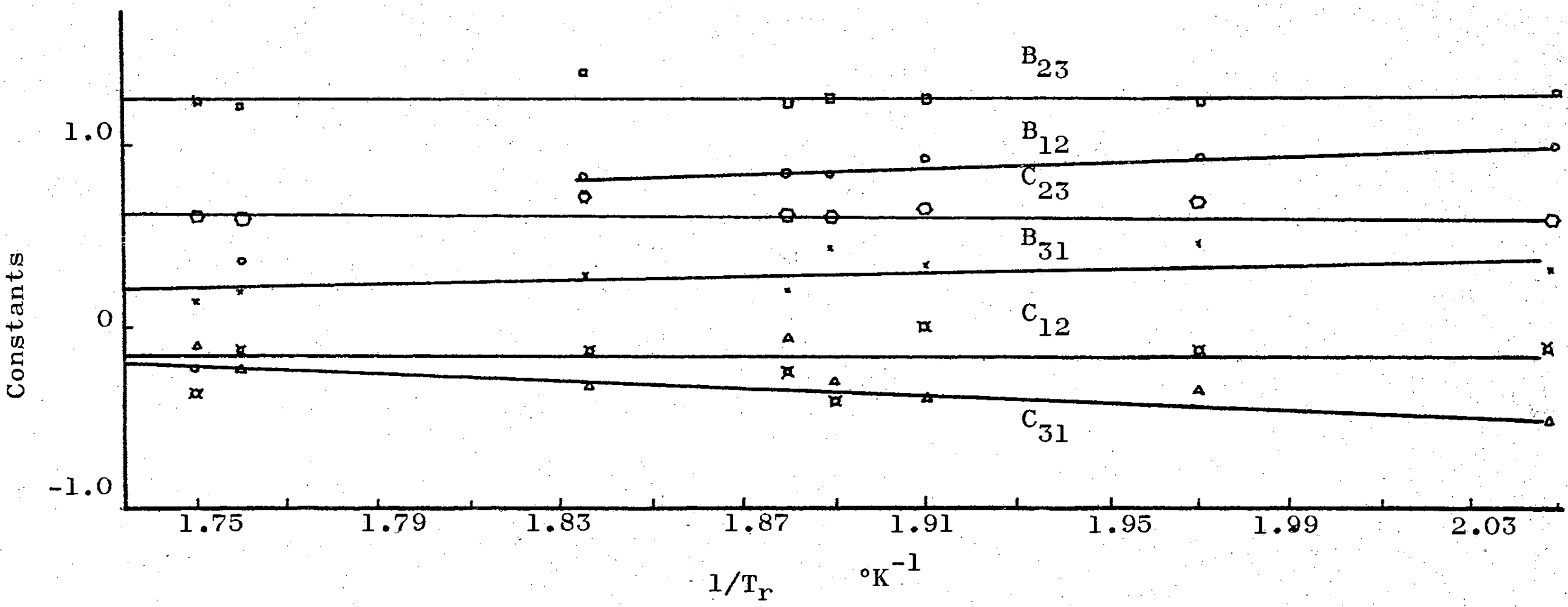


Fig. 12. Temperature Correlation for Alcohol-
H_2O- Ethyl Acetate

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. The Redlich-Kister equations were found to be applicable to the prediction of ternary liquid equilibria for systems of Type I and Type II.
2. The use of the Redlich-Kister equations, combined with a large number of data points and a least squares method for evaluating the Redlich-Kister constants proved more accurate than the use of Margules equations with two pair constants for the system Cyclohaxane-n-Heptane-Furfural.
3. A linear relationship has been found to exist between the Redlich-Kister constants and the reciprocal of the absolute temperature. In general, the Redlich-Kister constants decrease with increasing temperature.
4. The effect of temperature on Redlich-Kister constants is small for those systems whose solubility does not vary much with temperature.
5. A correlation of the Redlich-Kister constants as a function of reduced temperature may hold some promise for predicting equilibrium compositions. However, much additional study is required to establish the validity of this type of correlation.

Recommendations

1. Though the Redlich-Kister equation provides a powerful means for prediction of ternary liquid-liquid equilibria, the accuracy of the predicted values still needs further improvement. A more exact method for the evaluation of the Redlich-Kister constants is desirable. Higher mathematical treatments such as the method of steepest Descent or the Truncated Taylor Series method are recommended.
2. The use of the Redlich-Kister equations should be studied further to establish the relation between the accuracy of the Redlich-Kister constants and the accuracy of the predicted compositions for a variety of solubility curve shapes and tie line slopes.
3. In view of the proposals of Black (4), using a modified van Laar equation, it is recommended that the Black method for the correlation of ternary liquid-liquid equilibrium compositions be developed and compared with the Redlich-Kister equations. Black has developed his equations for binary system. A further derivation for a ternary system is presented in Appendix A. It would be interesting also to develop a correlation of the Black constants with temperature.
4. Further work on the effect of the number of Redlich-Kister constants used on the flexibility and accuracy of the prediction is recommended.
5. Some improvements should be made in the computer programs for this work. It is suggested that one program be written covering all procedures instead of using six separate programs, or that the programs be revised to make output from the one program the input to the next program without repunching data cards.

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NOMENCLATURE

a = activity, empirical constant

A, B = empirical constant

b = empirical constant, coefficient

$$\left.\begin{array}{l} B_{ij} \\ C_{ij} \\ D_{ij} \end{array}\right\} \text{Redlich-Kister constants}$$

d = difference, differential operator

f = fugacity

g = molar free energy

G = total free energy

$\bar{G}$ = dG/dn partial molar free energy

H, h = enthalpy

K = distribution coefficient, empirical constant

ln = logarithm to the base e

log = logarithm to the base 10

MW = molecular weight

n = number of moles

p = pressure

p^o = vapor pressure

q = effective molal volume

Q = $g^E/2.303\ RT$

R = gas constant

S = entropy

S = standard deviation

T = temperature

V = volume

x = composition

z = effective volumetric fraction

Greek Symbols

μ = chemical potential

γ = activity coefficient

Δ = difference

$\sum$ = summation

∂ = partial differential operator

Superscripts

$'$ = raffinate phase

$''$ = extract phase

o = pure component, standard state

E = excess

M = mixing

$*$ = ideal case

Subscripts

i = component i

1 = solute

2 = raffinate solvent

3 = extract solvent

W = weight

M = mole

APPENDIX A

DERIVATION OF EQUATIONS

Wohl's General Equation, van Laar Equations and Margules Equations

Several generally used equations for expressing Gibb's free energy in terms of composition and empirical constants for ternary liquid-liquid system are presented here.

Wohl's General Equation (37)

Wohl expressed the van Laar and Margules equations in a general form. This form represents the total free energy of a homologous system which consists of an arbitrary number of components, r, as:

$$G = \sum_{1}^{r} n_i G_i^o + \sum_{1}^{r} n_i RT \ln x_i + (\sum_{1}^{r} n_i) \Delta G \qquad \text{(A-1)}$$

The partial free energy of the component k is

$$\frac{\partial G}{\partial n_k} = G_k^o + RT \ln n_k + RT \ln \gamma_k \qquad \text{(A-2)}$$

with

$$\ln \gamma_k = \frac{\partial (\sum n_i) \frac{\Delta G}{RT}}{\partial n_k} \qquad \text{(A-3)}$$

van Laar Equations

Wohl expressed the van Laar equations for the free energy change as:

$$\frac{\triangle G}{2.3RT} = \frac{x_1 x_2 q_1 q_2 2a_{12} + x_1 x_3 q_1 q_3 2a_{13} + x_2 x_3 q_2 q_3 2a_{23}}{x_1 q_1 + x_2 q_2 + x_3 q_3} \qquad \text{(A-4)}$$

By application of equation (3) and introducing the abbreviations, $2a_{ij}q_i = A_{ij}$ and $2a_{ij}q_j = A_{ji}$ one obtains the van Laar equation for γ_1:

$$\log \gamma_1 = \left[x_2^2 A_{12} \left(\frac{A_{21}}{A_{12}}\right)^2 + x_3^2 A_{13} \left(\frac{A_{31}}{A_{13}}\right)^2 \right.$$

$$\left. + \; x_2 x_3 \frac{A_{21}}{A_{12}} \frac{A_{31}}{A_{13}} \left(A_{12} + A_{13} - A_{32} \frac{A_{13}}{A_{31}}\right) \right]$$

$$\Big/ \left(x_1 + x_2 \frac{A_{21}}{A_{12}} + x_3 \frac{A_{31}}{A_{13}}\right)^2 \qquad \text{(A-5)}$$

$\log \gamma_2$ and γ_3 can be obtained by rotating the subscripts from 1 to 2, 2 to 3, and 3 to 1.

Margules Equations

Wohl expressed the Margules equations for the free energy change as:

$$\frac{\triangle G}{2.3RT} = x_1 x_2 2a_{12} + x_1 x_3 2a_{13} + x_2 x_3 2a_{23}$$

$$+ \; x_1 x_2 3a_{112} + x_1 x_2 3a_{122} + x_1 x_3 3a_{113}$$

$$+ \; x_1 x_3 3a_{133} + x_2 x_3 3a_{223} + x_2 x_3 3a_{233}$$

$$+ \; x_1 x_2 x_3 6a_{123} \qquad \text{(A-6)}$$

By application of equation (3), introducing the abbreviations $2a_{ij} + 3a_{ijj} = A_{ij}$, $2a_{ij} + 3a_{iij} = A_{ji}$ and $3a_{112} + 3a_{133} + 3a_{223} - 6a_{123} = C$, one obtains the Margules equation for γ_1:

$$\log \gamma_1 = x_2^2 \Big[A_{12} + 2x_1(A_{21} - A_{12})\Big] + x_3^2 \; A_{13} + 2x_1(A_{31} - A_{13})\Big]$$

$$+ \; x_2x_3 \Big| A_{21} - A_{13} - A_{32} - 2x_1 \; (A_{31} - A_{13}) - 2x_3(A_{32} - A_{23})$$

$$- C(1 - 2x_1)\Big] \qquad \text{(A-7)}$$

Derivation of Redlich-Kister Equations (27)

Redlich-Kister expressed the the free energy in terms of compositions and empirical constants as:

$$Q_{12} = x_1x_2 \Big[B_{12} + C_{12}(x_1-x_2) + D_{12}(x_1-x_2)^2 + \dots \Big] \qquad \text{(A-8)}$$

The relation between Q and log γ_i is:

$$Q = x_1 \log \gamma_1 + x_2 \log \gamma_2 + x_3 \log \gamma_3 \qquad \text{(A-9)}$$

where

$$Q = Q_{12} + Q_{23} + Q_{31} \qquad \text{(A-10)}$$

The log γ_1 value can be calculated from the relation:

$$\log \gamma_1 = Q + \frac{\partial Q}{\partial x_1} - x_1 \frac{\partial Q}{\partial x_1} - x_2 \frac{\partial Q}{\partial x_2} - x_3 \frac{\partial Q}{\partial x_3} \qquad \text{(A-11)}$$

Taking partial derivative with respect to x_1, x_2 and x_3, one obtains:

$$\begin{aligned}\frac{\partial Q}{\partial x_1} = {} & x_1x_2\left[C_{12} + 2D_{12}(x_1-x_2)\right] \\ & + x_2\left[B_{12} + C_{12}(x_1-x_2) + D_{12}(x_1-x_2)^2\right] \\ & + x_1x_3\left[-C_{31} - 2D_{31}(x_3-x_1)\right] \\ & + x_3\left[B_{31} + C_{31}(x_3-x_1) + D_{31}(x_3-x_1)^2\right] \\ & + \cdots\cdot \end{aligned} \tag{A-12}$$

$$\begin{aligned}\frac{\partial Q}{\partial x_2} = {} & x_1x_2\left[-C_{12} - 2D_{12}(x_1-x_2)\right] \\ & + x_1\left[B_{12} + C_{12}(x_1-x_2) + D_{12}(x_1-x_2)^2\right] \\ & + x_2x_3\left[C_{23} + 2D_{23}(x_2-x_3)\right] \\ & + x_3\left[B_{23} + C_{23}(x_2-x_3) + D_{23}(x_2-x_3)^2\right] \\ & + \cdots\cdot \end{aligned} \tag{A-13}$$

$$\begin{aligned}\frac{\partial Q}{\partial x_3} = {} & x_2x_3\left[-C_{23} - 2D_{23}(x_2-x_3)\right] \\ & + x_2\left[B_{23} + C_{23}(x_2-x_3) + D_{23}(x_2-x_3)^2\right] \\ & + x_3x_1\left[C_{31} + 2D_{31}(x_3-x_1)\right] \\ & + x_1\left[B_{31} + C_{31}(x_3-x_1) + D_{31}(x_3-x_1)^2\right] \\ & + \cdots\cdot \end{aligned} \tag{A-14}$$

$$
\begin{aligned}
\log \gamma_1 = {} & B_{12}x_2(1-x_1) - B_{23}x_2x_3 + B_{31}x_3(1-x_1) \\
& + C_{31}\left[2x_3(1-x_1)(x_3-x_1) - x_3^2\right] \\
& + D_{31}\left[3x_3(1-x_1)(x_3-x_1)^2 - 2x_3^2(x_3-x_1)\right] \\
& + C_{12}\left[2x_2(1-x_1)(x_1-x_2) + x_2^2\right] \\
& + D_{12}\left[3x_2(1-x_1)(x_1-x_2)^2 + 2x_2^2(x_1-x_2)\right] \\
& + C_{23}\left[-2x_2x_3(x_2-x_3)\right] \\
& + D_{23}\left[-3x_2x_3(x_2-x_3)^2\right]
\end{aligned}
\qquad \text{(A-15)}
$$

Similarly, $\log \gamma_2$ and $\log \gamma_3$ can be expressed by rotating the subscripts from 1 to 2, 2 to 3 and 3 to 1.

Black Equations (4)

Black proposed a correction term for van Laar equations. The general form for the Black equation is:

$$
\log \gamma_i = \left[\sum_j A_{ij}R_{j2}x_j \Big/ \sum_k x_kR_{k2}\right]^2 + E_{si} \qquad \text{(A-16)}
$$

where

$$
R_{ij} = A_{ij}^2 / A_{ji}^2 \qquad i \neq j
$$

$$
R_{j2} = A_{j2}^2 \quad A_{2j}^2 \qquad \text{(A-17)}
$$

For a binary system:

$$
\begin{aligned}
\log \gamma_1 & = \left[A_{12}R_{22}x_2 / (x_1R_{12} + x_2R_{22})\right]^2 + E_1 \\
& = \left[A_{12}x_2 / \left(x_1 \frac{A_{12}^2}{A_{21}^2} + x_2\right)\right]^2 + E_1
\end{aligned}
$$

The above equation can be simplified into the form:

$$\log \gamma_1 = \frac{A_{12}^2 A_{21}^4 x_2^2}{(A_{12}^2 x_1 + A_{21}^2 x_2)^2} + E_1 \qquad \text{(A-18)}$$

Similarly, $$\log \gamma_2 = \left[A_{21} R_{12} x_1 \Big/ (x_1 R_{12} + x_2 R_{22}) \right]^2 + E_2$$

$$= \left[A_{21} x_1 \frac{A_{12}^2}{A_{21}^2} \Big/ \left(x_1 \frac{A_{12}^2}{A_{21}^2} + x_2\right) \right]^2 + E_2$$

$$= \left[\frac{A_{21} A_{12}^2 x_1}{A_{12}^2 x_1 + A_{21}^2 x_2} \right]^2 + E_2$$

$$= \frac{A_{21}^2 A_{12}^4 x_1^2}{(A_{12}^2 x_1 + A_{21}^2 x_2)^2} + E_2 \qquad \text{(A-19)}$$

Subtracting equation (A-18) from equation (A-19) one obtains $\log \gamma_1/\gamma_2$

$$\log (\gamma_1/\gamma_2) = \frac{A_{12}^2 A_{21}^4 x_2^2 - A_{21}^2 A_{12}^4 x_1^2}{(A_{12}^2 x_1 + A_{21}^2 x_2)^2} + E_1 - E_2$$

$$= \frac{A_{12}^2 A_{21}^2 \left[A_{21}^2 x_2^2 - A_{12}^2 x_1^2 \right]}{(A_{12}^2 x_1 + A_{21}^2 x_2)^2} + E_1 - E_2 \qquad \text{(A-20)}$$

The general equation for the correction term is:

$$E_{si} = \sum_j \left[(x_i - x_j)^2 \; (\sum_j C_{ij} x_j) \right] + \sum_j \left\{ (x_i - x_j) \right.$$

$$\left. \left[2 - 3\,(x_i - x_j) \right] \; (\sum_{ij} C_{ij} x_i x_j) \right\} - \frac{3}{2} \sum_{j \neq k} \left[\right.$$

$$\left. (x_j - x_k)^2 (\sum_{jk} C_{jk} x_j x_k) \right] \qquad \text{(A-21)}$$

For a binary system:

$$E_i = (x_i - x_j)^2 (C_{jk} x_j) + \left\{ (x_i - x_j) \left[2 - 3(x_i - x_j) \right] (C_{ij} x_i x_j) \right\}$$

$$= C_{ij} x_j (x_i - x_j) \left[(x_i - x_j) + 2x_i - 3(x_i - x_j) x_i \right]$$

$$= C_{ij} x_j (x_i - x_j) \left[x_i - x_j + 2x_i - 3x_i^2 + 3x_i x_j \right] \qquad \text{(A-22)}$$

To prove the first term in Equation (18) is van Laar's value for $\log \gamma_1$:

$$\left[\frac{A_{12} A_{21}^2 x_2}{A_{12}^2 x_1 + A_{21}^2 x_2} \right]^2 = \frac{A_{12}^2}{\left(\frac{A_{12}^2}{A_{21}^2} \; \frac{x_1}{x_2} + 1 \right)^2} \qquad \text{(A-23)}$$

$$\text{let} \qquad A_{12}^2 = A \qquad\qquad A_{21}^2 = B \qquad \text{(A-24)}$$

$$\therefore \quad \frac{A_{12}^2}{\left(\frac{A_{12}^2}{A_{21}^2} \; \frac{x_1}{x_2} + 1 \right)^2} = \frac{A}{\left(\frac{A}{B} \; \frac{x_1}{x_2} + 1 \right)^2} \qquad \text{(A-25)}$$

To prove the first term in Equation (19) is van Laar's value for log γ_2:

$$\left[\frac{A_{21}A_{12}^{2}x_1}{A_{12}^{2}x_1 + A_{21}^{2}x_2}\right]^2 = \frac{A_{21}^{2}}{\left(1 + \frac{A_{21}^2}{A_{12}^2}\,\frac{x_2}{x_1}\right)^2} \qquad \text{(A-26)}$$

let $A_{12}^{2} = A$ $A_{21}^{2} = B$ (A-27)

$$\therefore \quad \frac{A_{21}^2}{\left(1+ \frac{A_{21}^2}{A_{12}^2}\,\frac{x_2}{x_1}\right)^2} = \frac{B}{\left(1 + \frac{B}{A}\,\frac{x_2}{x_1}\right)^2} \qquad \text{(A-28)}$$

Equation (A-22) can be further derived as:

$$E_i = C_{ij}x_j(x_i-x_j)\left[\,3x_i-x_j-3x_i^2+3x_ix_j\,\right]$$

$$= C_{ij}x_j(x_i-x_j)\left[\,3x_i-3x_j 2x_j-3x_i^2+3x_ix_j\,\right]$$

$$= C_{ij}x_j(x_i-x_j)\left[\,3(x_i-x_j-x_i^2\ x_ix_j)+2x_j\,\right]$$

$$= C_{ij}x_j(x_i-x_j)\left[\,3(x_i-x_j)(1-x_i)+2x_j\,\right] \qquad \text{(A-29)}$$

$$\therefore \quad E_1 = C_{12}x_2(x_1-x_2)\left[\,3(x_1-x_2)(1-x_1)+2x_2\,\right] \qquad \text{(A-30)}$$

$$E_2 = C_{21}x_1(x_2-x_1)\left[\,3(x_2-x_1)(1-x_2)+2x_1\,\right]. \qquad \text{(A-31)}$$

As Black described, the subscripts of C are interchangeable, that is

$$C_{12} = C_{21} \qquad \text{(A-32)}$$

$$\therefore \quad E_2 = C_{12}x_1(x_2-x_1)\left[\,3(x_2-x_1)(1-x_2)+2x_1\,\right] \qquad \text{(A-33)}$$

$$\log \gamma_1 = \frac{A_{12}^2 A_{21}^4 x_2^2}{(A_{12}^2 x_1 + A_{21}^2 x_2)^2} + C_{12} x_2 (x_1 - x_2) \left[3(x_1 - x_2)(1 - x_1)\ 2x_2 \right] \tag{A-34}$$

$$\log \gamma_2 = \frac{A_{21}^2 A_{12}^4 x_1^2}{(A_{12}^2 x_1 + A_{21}^2 x_2)^2} + C_{12} x_1 (x_2 - x_1) \left[3(x_2 - x_1)(1 - x_2)\ 2x_1 \right] \tag{A-35}$$

The Black Equations can be extended for Ternary systems:

$$\begin{aligned} \log \gamma_1 &= \left[\frac{A_{12} R_{22} x_2 + A_{13} R_{32} x_3}{x_1 R_{12} + x_2 + x_3 R_{32}} \right]^2 + E_1 \\ &= \frac{(A_{12} A_{23}^2 A_{21}^2 x_2 + A_{13} A_{32}^2 A_{21}^2 x_3)^2}{(A_{23}^2 A_{12}^2 x_1 + A_{21}^2 A_{23}^2 x_2 + A_{21}^2 A_{32}^2 x_3)^2} + E_1 \end{aligned} \tag{A-36}$$

$$\begin{aligned} \log \gamma_2 &= \left[\frac{A_{21} R_{12} x_1 + A_{23} R_{32} x_3}{x_1 R_{12} + x_2 + x_3 R_{32}} \right]^2 + E_2 \\ &= \frac{(A_{21} A_{23}^2 A_{12}^2 x_1 + A_{23} A_{21}^2 A_{32}^2 x_3)^2}{(A_{23}^2 A_{12}^2 x_1 + A_{21}^2 A_{23}^2 x_2 + A_{21}^2 A_{32}^2 x_3)^2} + E_2 \end{aligned} \tag{A-37}$$

$$\begin{aligned} \log \gamma_3 &= \left[\frac{A_{31} R_{12} x_1 + A_{32} R_{22} x_2}{x_1 R_{12} + x_2 + x_3 R_{32}} \right]^2 + E_3 \\ &= \frac{(A_{31} A_{12}^2 A_{23}^2 x_1 + A_{32} A_{21}^2 A_{23}^2 x_2)^2}{(A_{23}^2 A_{12}^2 x_1 + A_{21}^2 A_{23}^2 x_2 + A_{21}^2 A_{32}^2 x_3)^2} + E_3 \end{aligned} \tag{A-38}$$

Where the correction terms are:

$$\begin{aligned} E_1 = {} & (x_1-x_2)^2(C_{12}x_2+C_{13}x_3)+(x_1-x_3)^2(C_{12}x_2+C_{13}x_3) \\ & + (x_1-x_2)\left\{\left[2-3(x_1-x_2)\right](C_{12}x_1x_2+C_{13}x_1x_3)\right\} \\ & + (x_1-x_3)\left\{\left[2-3(x_1-x_3)\right](C_{12}x_1x_2+C_{13}x_1x_3)\right\} \\ & - 6\left[(x_2-x_3)^2C_{23}x_2x_3\right] \end{aligned} \tag{A-39}$$

$$\begin{aligned} E_2 = {} & (x_2-x_3)^2(C_{23}x_3+C_{21}x_1)+(x_2-x_1)^2(C_{23}x_3+C_{21}x_1) \\ & + (x_2-x_3)\left\{\left[2-3(x_2-x_3)\right](C_{23}x_2x_3+C_{21}x_2x_1)\right\} \\ & + (x_2-x_1)\left\{\left[2-3(x_2-x_1)\right](C_{23}x_2x_3\ C_{21}x_2x_1)\right\} \\ & - 6\left[(x_3-x_1)^2C_{31}x_3x_1\right] \end{aligned} \tag{A-40}$$

$$\begin{aligned} E_3 = {} & (x_3-x_1)^2(C_{31}x_1+C_{32}x_2)+(x_3-x_2)^2(C_{31}x_1+C_{32}x_2) \\ & + (x_3-x_1)\left\{\left[2-3(x_3-x_1)\right](C_{31}x_3x_1\ C_{32}x_3x_2)\right\} \\ & + (x_3-x_2)\left\{\left[2-3(x_3-x_2)\right](C_{31}x_3x_1\ C_{32}x_3x_2)\right\} \\ & - 6\left[(x_1-x_2)^2C_{12}x_1x_2\right] \end{aligned} \tag{A-41}$$

APPENDIX B

TERNARY LIQUID PHASE DIAGRAMS

Ternary Liquid Phase Equilibria Diagram

A typical diagram representing ternary liquid-liquid equilibrium at constant temperature and pressure is shown in Figure 28. Component 1 is the solute which is distributed between the immiscible solvents 2 and 3. The area under the solubility curve APB is a two-phase region. Phases in equilibrium with each other are termed conjugated phases. Compositions at equilibrium are joined by tie-lines. P is designated as the plait point, the point representing the composition where the two conjugated phases become mutually soluble. The phase rich in pure solvent is called extract phase, and the conjugated phase is called raffinate phase. The notation 1, 2 and 3 is arbitrary. In this work the component 1 is generally designated as solute, and the components 2 and 3 denote extract and raffinate solvents respectively.

Two types of ternary systems are of the most interest in liquid extraction (36). Type I, formation of one pair of partially miscible liquids, is shown in Figure 29. Type II, formation of two pairs of partially miscible liquids, is shown in Figure 30. Temperature will affect the solubility curve and the slopes of tie-lines. The solubility curve may change from one type to another type with changing temperature.

Figure 31 shows one example of the effect of temperature on liquid-liquid solubility. Systems belonging to these two types have been studied in this work.

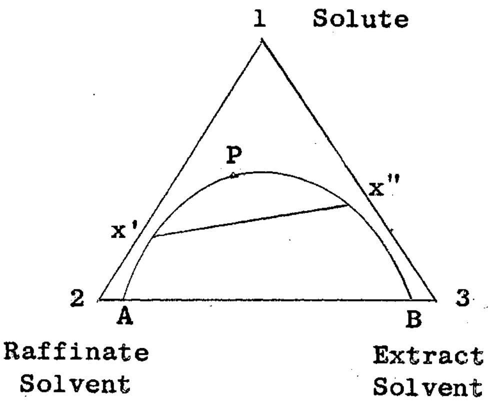

Fig. 13. A Typical Ternary Liquid Phase Diagram

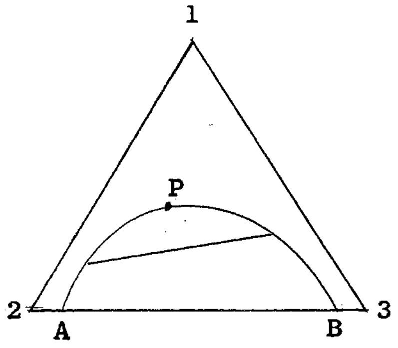

Fig. 14. Type I Ternary Liquid Equilibria

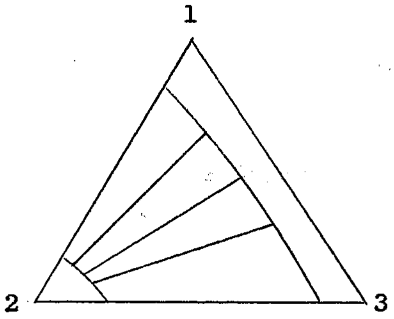

Fig. 15. Type II Ternary Liquid Equilibria

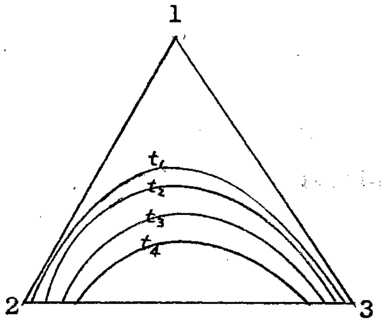

Fig. 16. Temperature Effect on Solubility Curve

TABLE XV

THE SYSTEM ACETONE-H_2O-BENZENE AT 30°C. (6)

Raffinate Phase Composition Weight Fraction			Extract Phase Composition Weight Fraction					
Experimental			Experimental			Calculated		
Acetone	H_2O	Benzene	Acetone	H_2O	Benzene	Acetone	H_2O	Benzene
0.50	0.949	0.001	0.058	0.002	0.940	0.060	0.001	0.939
0.10	0.898	0.002	0.131	0.002	0.867	0.135	0.002	0.863
0.15	0.846	0.004	---	---	---	0.231	0.010	0.759
0.20	0.796	0.004	0.304	0.009	0.687	0.310	0.017	0.673
0.25	0.744	0.006	---	---	---	0.396	0.280	0.574
0.30	0.691	0.009	0.472	0.030	0.498	0.479	0.040	0.481
0.35	0.637	0.013	---	---	---	0.532	0.058	0.410
0.40	0.582	0.018	0.589	0.066	0.345	0.590	0.080	0.330
0.50	0.459	0.041	0.641	0.120	0.235	0.637	0.150	0.213
					$\bar{d}$	0.016	0.010	0.01267
					$S_{\bar{d}}$	0.00163	0.0044	0.0063

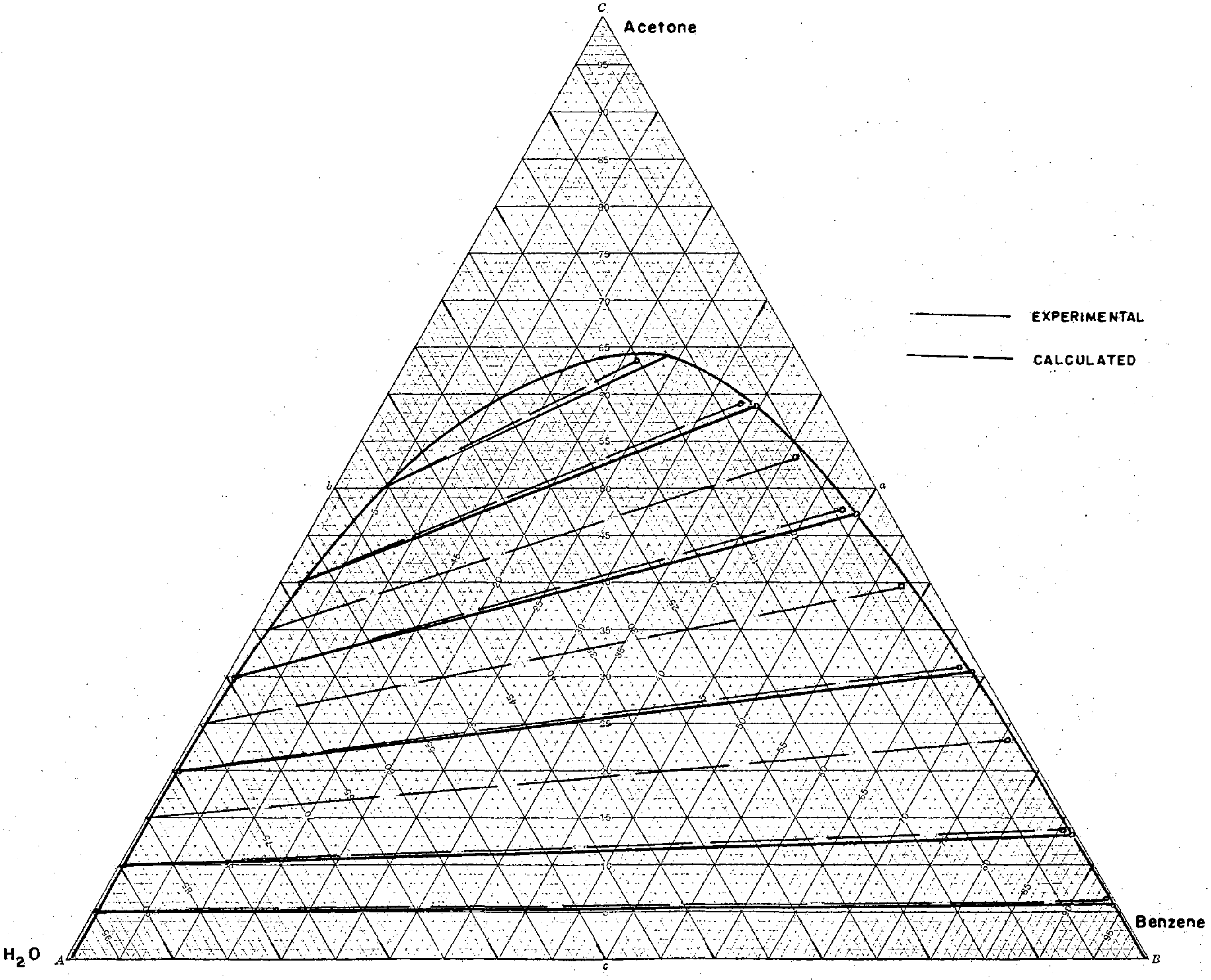

Fig. 17. The System Acetone-H_2O-Benzene at 30°C

TABLE XVI

THE SYSTEM ACETONE-H_2O BENZENE AT 15°C. (6)

Raffinate Phase Composition Weight Fraction			Extract Phase Composition Weight Fraction					
Experimental			Experimental			Calculated		
Acetone	H_2O	Benzene	Acetone	H_2O	Benzene	Acetone	H_2O	Benzene
0.05	0.949	0.001	0.047	0.001	0.952	0.050	0.001	0.949
0.10	0.899	0.001	0.108	0.002	0.890	0.110	0.002	0.888
0.15	0.845	0.005	---	---	---	0.203	0.003	0.794
0.20	0.797	0.003	0.261	0.005	0.734	0.271	0.011	0.718
0.25	0.744	0.006	---	---	---	0.355	0.016	0.629
0.30	0.693	0.007	0.430	0.018	0.552	0.438	0.019	0.543
0.35	0.640	0.010	---	---	---	0.501	0.039	0.460
0.40	0.586	0.014	0.565	0.044	0.391	0.571	0.052	0.377
0.45	0.528	0.022	---	---	---	0.601	0.070	0.329
0.50	0.468	0.032	0.639	0.085	0.276	0.638	0.103	0.259
					$\bar{d}$	0.00182	0.0055	0.00916
					$S_{\bar{d}}$	0.00254	0.00392	0.00266

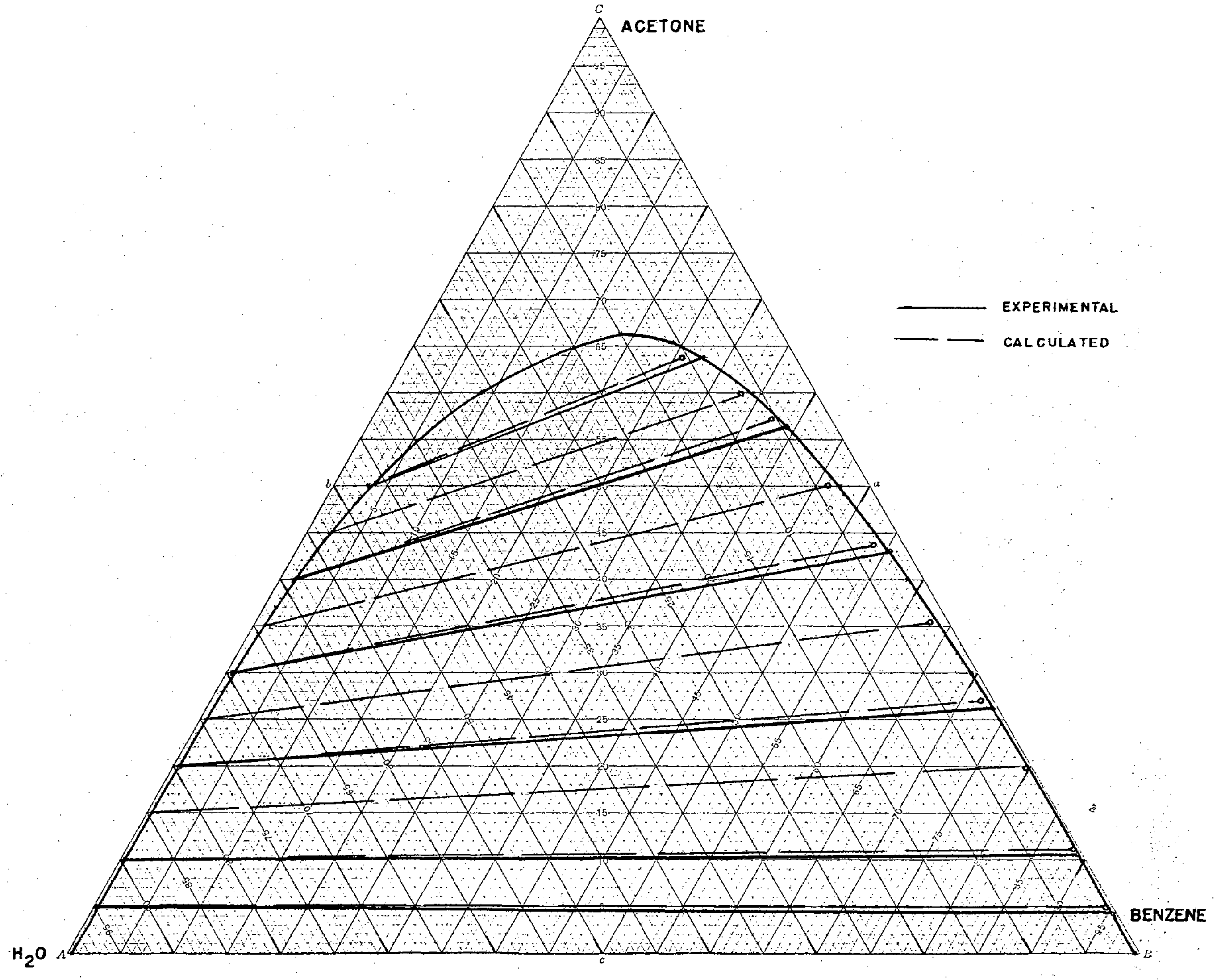

Fig. 18. The System Acetone-H_2O-Benzene at 15°C.

TABLE XVII

THE SYSTEM ACETONE-H_2O-BENZENE AT 45°C. (6)

Raffinate Phase Composition Weight Fraction			Extract Phase Composition Weight Fraction					
Experimental			Experimental			Calculated		
Acetone	H_2O	Benzene	Acetone	H_2O	Benzene	Acetone	H_2O	Benzene
0.05	0.948	0.002	0.069	0.002	0.929	0.071	0.008	0.921
0.10	0.898	0.002	0.156	0.004	0.840	0.169	0.009	0.831
0.15	0.845	0.005	---	---	---	0.260	0.019	0.721
0.20	0.795	0.005	0.346	0.018	0.636	0.354	0.024	0.632
0.25	0.740	0.010	---	---	---	0.441	0.040	0.519
0.30	0.689	0.011	0.512	0.048	0.440	0.519	0.051	0.430
0.35	0.640	0.019	---	---	---	0.573	0.073	0.354
0.40	0.577	0.023	0.606	0.097	0.297	0.609	0.109	0.282
					$\bar{d}$	0.0067	0.0064	0.0092
					$S_{\bar{d}}$	0.0038	0.00376	0.00486

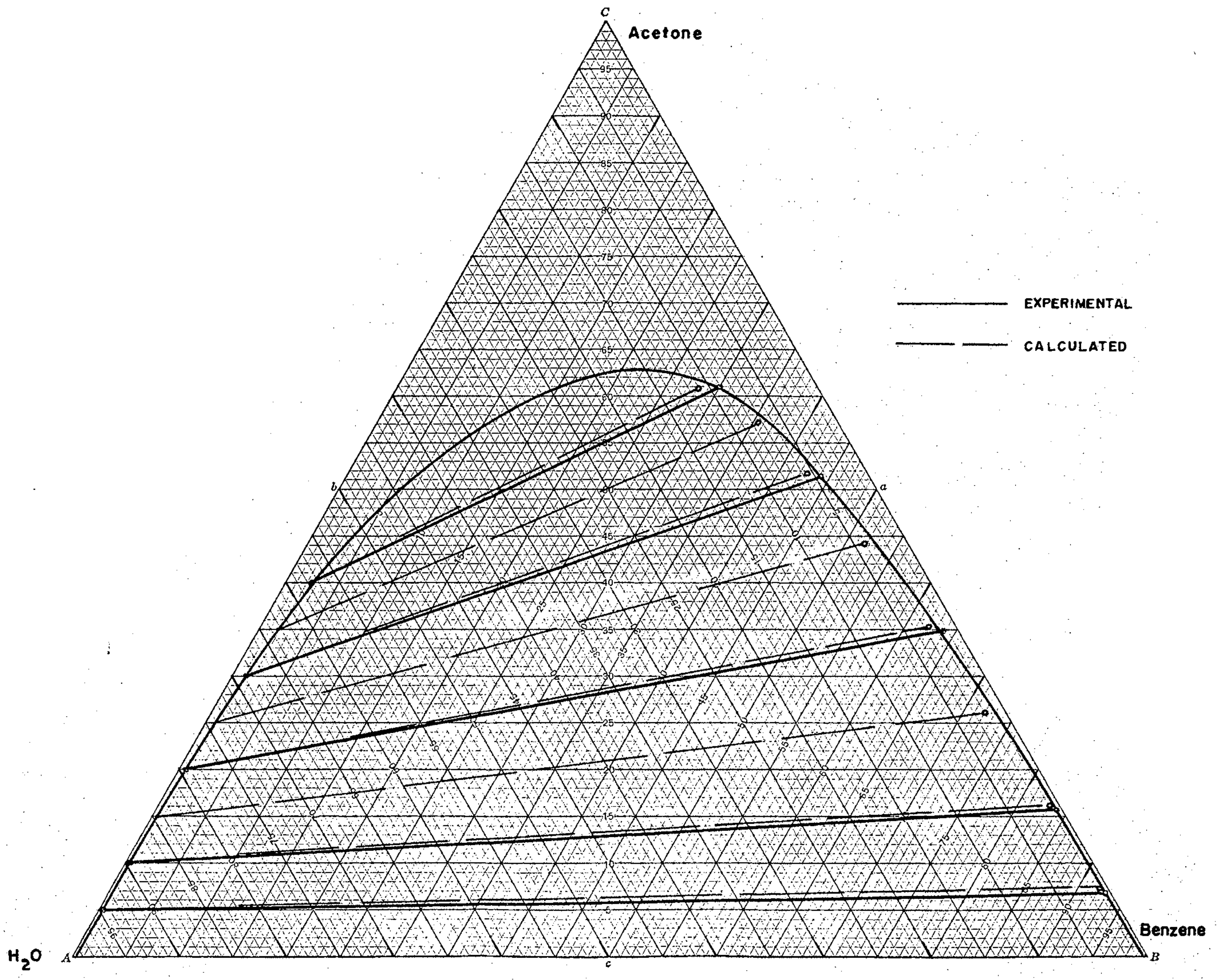

Fig. 19. The System Acetone-H_2O-Benzene at 45°C

TABLE XVIII

THE SYSTEM METHANOL-H_2O-N-BUTANOL AT 0°C. (19)

Raffinate Phase Composition Weight Fraction			Extract Phase Composition Weight Fraction					
Experimental			Experimental			Calculated		
x'_1	x'_2	x'_3	x''_1	x''_2	x''_3	x''_1	x''_2	x''_3
0.070	0.837	0.093	0.042	0.223	0.735	0.049	0.231	0.720
0.100	0.800	0.100	---	---	---	0.068	0.255	0.677
0.155	0.7166	0.1284	0.1225	0.3238	0.5537	0.130	0.340	0.530
0.175	0.650	0.155	---	---	---	0.140	0.361	0.499
0.189	0.6447	0.1663	0.145	0.3783	0.4767	0.150	0.380	0.470
0.194	0.600	0.214	0.165	0.143	0.405	0.172	0.448	0.380
					$\bar{d}$	0.0067	0.00897	0.0176
					$S_{\bar{d}}$	0.0038	0.0076	0.0107

TABLE XIX

THE SYSTEM METHANOL-H_2O-N-BUTANOL AT 15°C. (19)

Raffinate Phase Composition Weight Fraction			Extract Phase Composition Weight Fraction					
Experimental			Experimental			Calculated		
x'_1	x'_2	x'_3	x''_1	x''_2	x''_3	x''_1	x''_2	x''_3
0.025	0.895	0.080	---	---	---	0.012	0.199	0.789
0.048	0.872	0.080	0.023	0.212	0.765	0.030	0.220	0.750
0.068	0.850	0.082	---	---	---	0.036	0.236	0.738
0.084	0.907	0.093	0.043	0.2297	0.7273	0.049	0.240	0.711
0.107	0.801	0.092	0.067	0.2566	0.6764	0.071	0.262	0.667
0.132	0.7638	0.1042	0.093	0.2939	0.6131	0.100	0.302	0.598
0.156	0.7081	0.1359	0.127	0.3536	0.5194	0.130	0.370	0.500
0.163	0.6696	0.1674	0.144	0.4468	0.4092	0.151	0.428	0.421
					$\bar{d}$	0.0055	0.0049	0.01455
					$s_{\bar{d}}$	0.0081	0.0054	0.00661

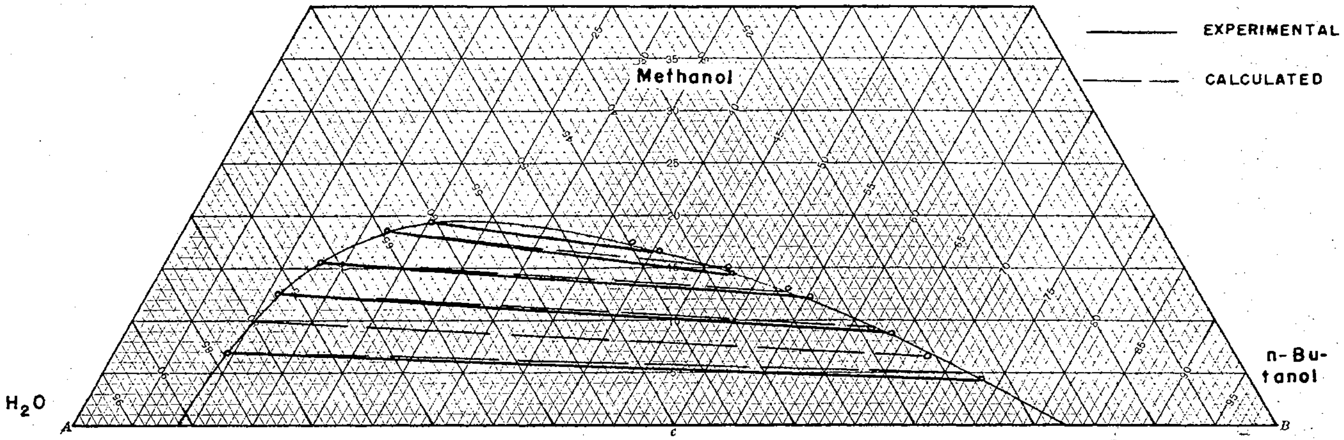

Fig. 20. The System Methanol-H_2O-n-Butanol at 0°C

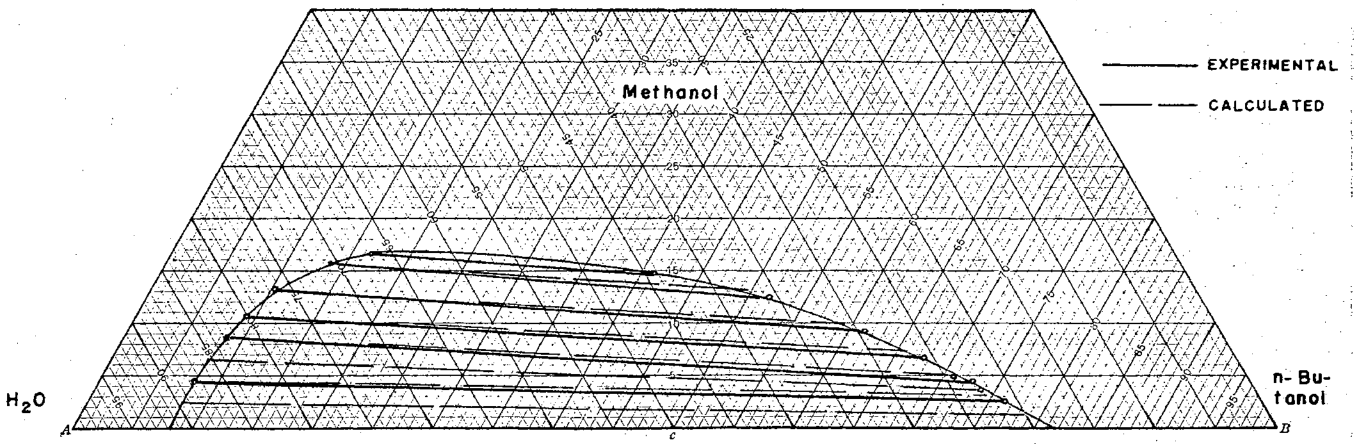

Fig. 21. The System Methanol-H_2O-n-Butanol at 15°C

TABLE XX

THE SYSTEM METHANOL-H_2O-N-BUTANOL AT 30°C. (19)

Raffinate Phase Composition Weight Fraction			Extract Phase Composition Weight Fraction					
Experimental			Experimental			Calculated		
x'_1	x'_2	x'_3	x''_1	x''_2	x''_3	x''_1	x''_2	x''_3
0.067	0.8806	0.0724	0.024	0.2323	0.7437	0.029	0.239	0.268
0.070	0.851	0.0790	---	---	---	0.041	0.253	0.707
0.091	0.8245	0.0845	0.053	0.2689	0.6781	0.061	0.271	0.668
0.112	0.7885	0.0995	0.075	0.3052	0.6198	0.079	0.302	0.619
0.125	0.7586	0.1164	0.085	0.3284	0.5866	0.092	0.331	0.577
0.135	0.7249	0.1401	0.100	0.3735	0.5265	0.104	0.359	0.537
0.142	0.6624	0.1956	0.123	0.4578	0.4192	0.120	0.400	0.480
					$\bar{d}$	0.00416	0.0086	0.0065
					$S_{\bar{d}}$	0.0133	0.011	0.0118

TABLE XXI

THE SYSTEM METHANOL-H_2O-N-BUTANOL AT 60°C. (19)

Raffinate Phase Composition Weight Fraction			Extract Phase Composition Weight Fraction					
Experimental			Experimental			Calculated		
x_1'	x_2'	x_3'	x_1''	x_2''	x_3''	x_1''	x_2''	x_3''
0.022	0.9076	0.0704	0.1015	0.259	0.726	0.019	0.267	0.714
0.045	0.875	0.080	---	---	---	0.031	0.280	0.689
0.062	0.867	0.091	0.041	0.300	0.659	0.044	0.309	0.647
0.080	0.8068	0.092	0.065	0.358	0.577	0.068	0.362	0.570
0.088	0.777	0.135	0.077	0.400	0.523	0.081	0.401	0.518
					$\bar{d}$	0.0181	0.0055	0.009
					$S_{\bar{d}}$	0.0234	0.0036	0.0053

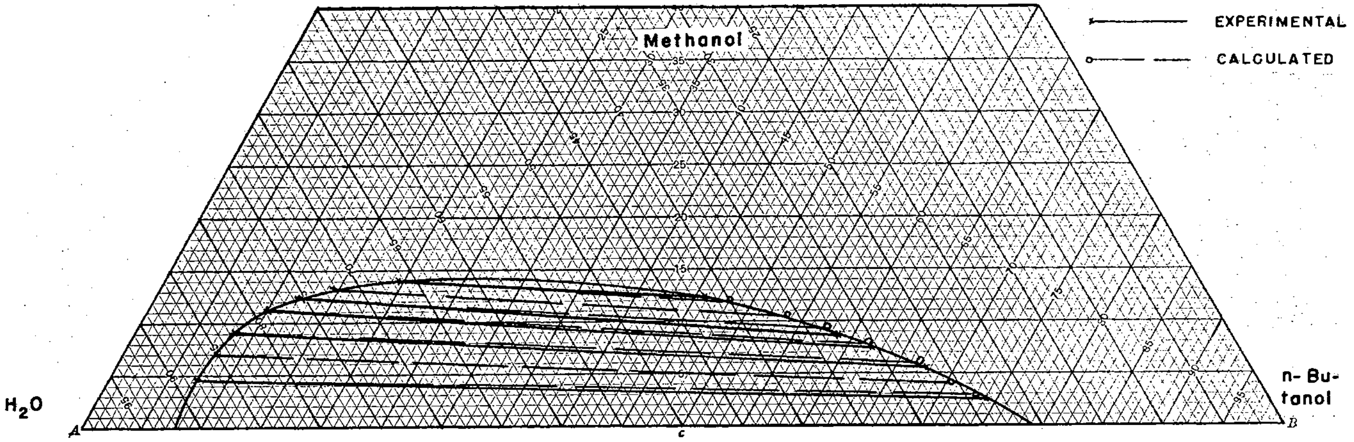

Fig. 22. The System Methanol-H_2O-n-Butanol at 30°C

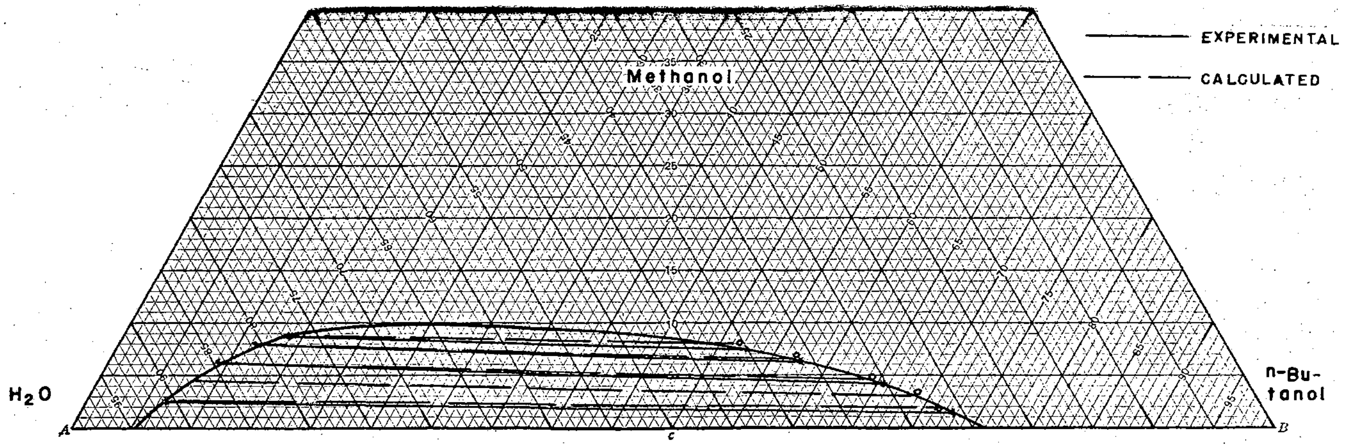

Fig. 23. The System Methanol-H_2O-n-Butanol at 60°C

TABLE XXII

THE SYSTEM METHANOL-H_2O-N-BUTANOL AT 45°C. (19)

Raffinate Phase Composition Weight Fraction			Extract Phase Composition Weight Fraction					
Experimental			Experimental			Predicted		
x'_1	x'_2	x'_3	x''_1	x''_2	x''_3	x''_1	x''_2	x''_3
0.027	0.9078	0.0652	0.034	0.2502	0.7158	0.0288	0.251	0.720
0.045	0.885	0.070	---	---	---	0.0422	0.272	0.686
0.063	0.8602	0.0768	0.059	0.2908	0.6502	0.0621	0.292	0.646
0.085	0.8189	0.0961	0.078	0.3328	0.5892	0.0803	0.337	0.583
0.105	0.7608	0.1342	0.093	0.390	0.517	0.103	0.407	0.491
0.115	0.6991	0.1859	0.107	0.4706	0.4224	0.121	0.488	0.391
					$\bar{d}$	0.00084	0.00518	0.01904
					$S_{\bar{d}}$	0.00466	0.0040	0.0121

TABLE XXIII

THE SYSTEM METHANOL-H_2O-ETHYL ACETATE AT 0°C. (2)

Raffinate Phase Composition Mole Fraction			Extract Phase Composition Mole Fraction					
Experimental			Experimental			Calculated		
x'_1	x'_2	x'_3	x''_1	x''_2	x''_3	x''_1	x''_2	x''_3
0.0318	0.947	0.0216	0.0075	0.115	0.876	0.01221	0.1150	0.8728
0.0614	0.916	0.0240	0.0312	0.137	0.833	0.02704	0.1370	0.8360
0.0618	0.916	0.022	0.0312	0.1364	0.832	0.0274	0.1364	0.8367
0.1128	0.8598	0.0274	0.0856	0.187	0.727	0.0744	0.1870	0.7386
0.171	0.786	0.043	0.1468	0.2679	0.585	0.1380	0.261	0.600
					$\bar{d}$	0.00466	0.00138	0.00593
					$S_{\bar{d}}$	0.00277	0.00138	0.00318

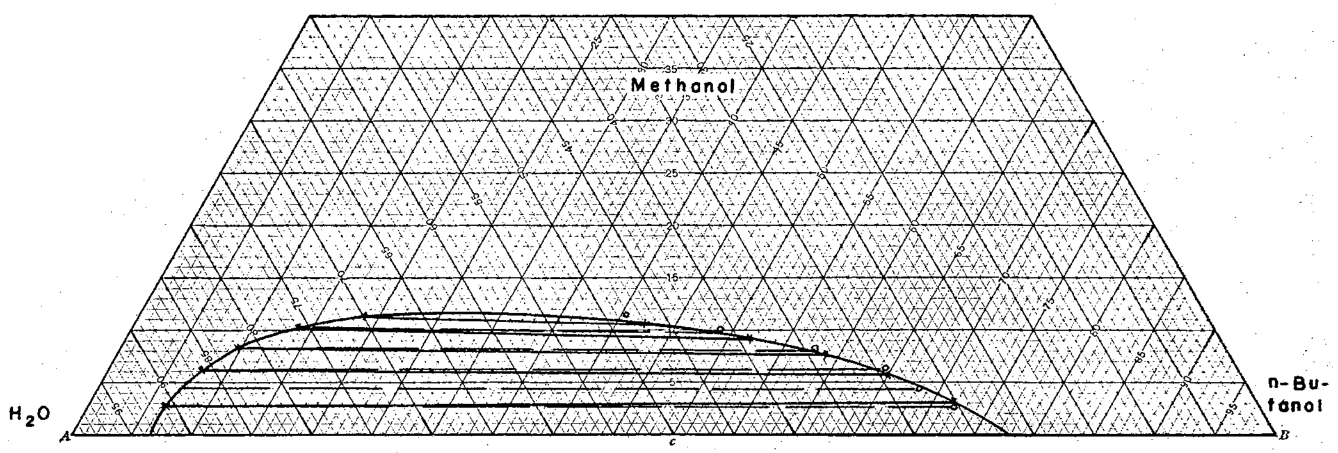

Fig. 24. The System Methanol-H_2O-n-Butanol at 45°C.

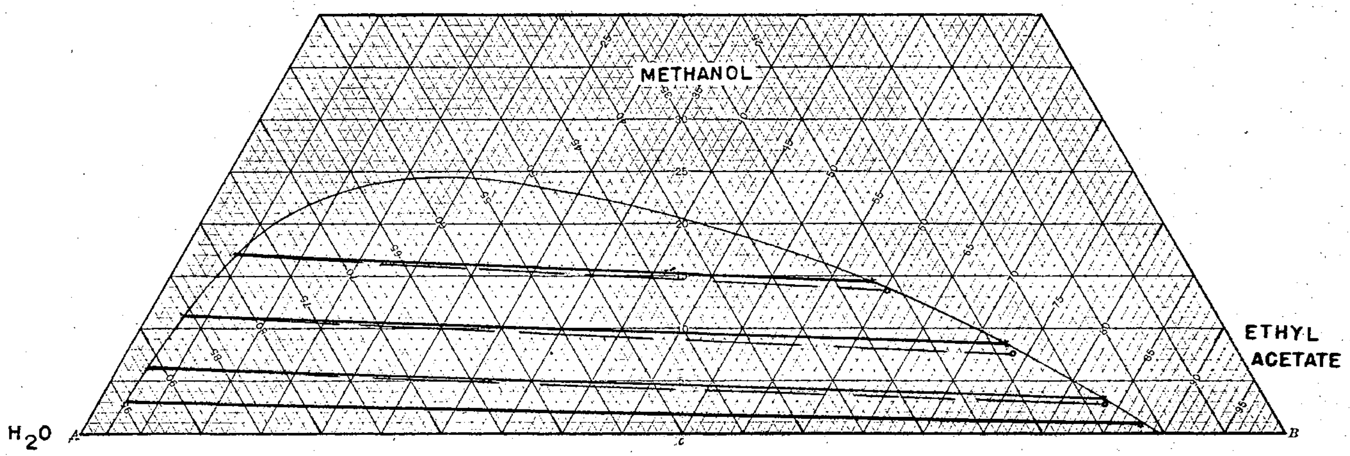

Fig. 25. The System Methanol-H_2O-Ethyl Acetate at 0°C

TABLE XXIV

THE SYSTEM ETHANOL-H_2O-ETHYL ACETATE AT 20°C. (2)

Raffinate Phase Composition Mole Fraction			Extract Phase Composition Mole Fraction					
Experimental			Experimental			Calculated		
x_1'	x_2'	x_3'	x_1''	x_2''	x_3''	x_1''	x_2''	x_3''
0.0171	0.964	0.0189	0.0331	0.1521	0.814	0.042	0.159	0.799
0.0335	0.947	0.0194	0.0837	0.2063	0.710	0.0862	0.2158	0.698
0.0472	0.932	0.0208	0.111	0.254	0.635	0.120	0.258	0.622
0.0644	0.909	0.263	0.1366	0.2945	0.569	0.1401	0.3089	0.551
0.0806	0.885	0.0335	0.168	0.396	0.436	0.1750	0.416	0.409
0.103	0.847	0.049	0.1753	0.522	0.3027	0.191	0.520	0.289
					$\bar{d}$	0.00777	0.0088	0.0161
					$S_{\bar{d}}$	0.00193	0.00327	0.00203

TABLE XXV

THE SYSTEM ETHANOL-H_2O-ETHYL ACETATE AT 0°C. (2)

Raffinate Phase Composition Mole Fraction			Extract Phase Composition Mole Fraction					
Experimental			Experimental			Calculated		
x_1'	x_2'	x_3'	x_1''	x_2''	x_3''	x_1''	x_2''	x_3''
0.01646	0.9625	0.0211	0.00175	0.1073	0.891	0.0031	0.1179	0.879
0.0295	0.950	0.0210	0.0255	0.126	0.844	0.0236	0.1184	0.858
0.049	0.930	0.0214	0.0539	0.1504	0.7956	0.0501	0.1379	0.812
0.0657	0.915	0.0223	0.091	0.182	0.726	0.0803	0.1687	0.751
0.0785	0.897	0.0241	0.1308	0.244	0.6255	0.1261	0.2149	0.659
0.0982	0.873	0.290	0.1665	0.3405	0.493	0.1646	0.3044	0.531
					$\bar{d}$	0.00345	0.0145	0.0192
					$S_{\bar{d}}$	0.00172	0.00208	0.00731

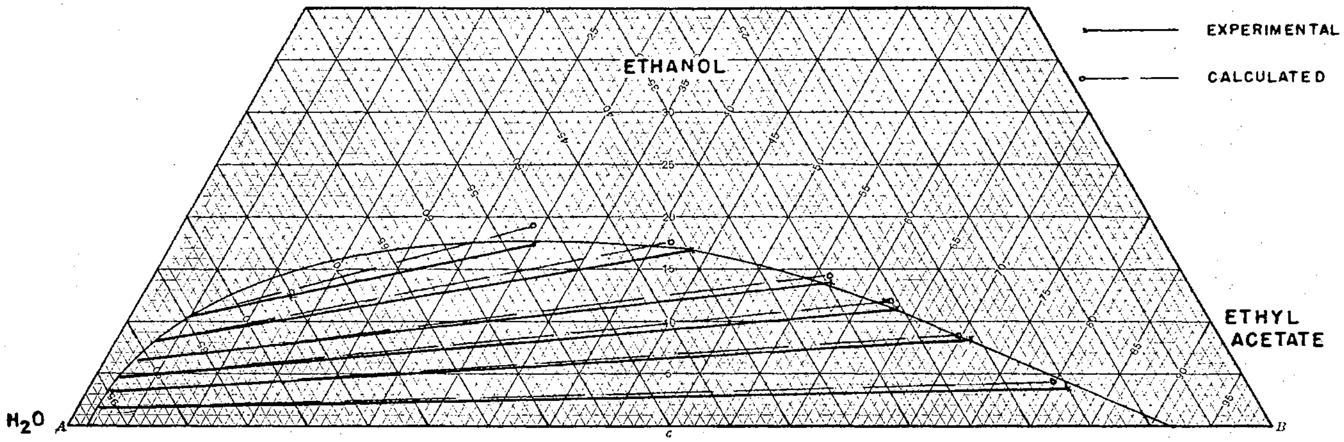

Fig. 26. The System Ethanol-H_2O-Ethyl Acetate at 20°C.

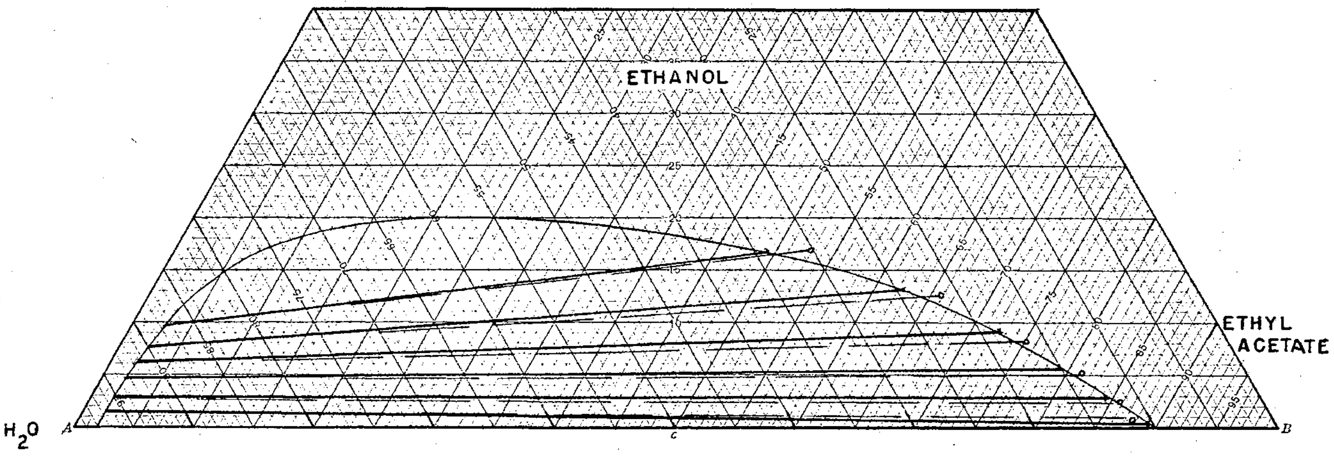

Fig. 27. The System Ethanol-H_2O-Ethyl Acetate at 0°C

TABLE XXVI

THE SYSTEM PROPANOL-H_2O-ETHYL ACETATE AT 20°C. (2)

Raffinate Phase Composition Mole Fraction			Extract Phase Composition Mole Fraction					
Experimental			Experimental			Calculated		
x'_1	x'_2	x'_3	x''_1	x''_2	x''_3	x''_1	x''_2	x''_3
0.01145	0.971	0.0174	0.0662	0.172	0.757	0.0599	0.1609	0.7792
0.0206	0.963	0.0103	0.130	0.274	0.595	0.1248	0.2563	0.6189
0.0262	0.955	0.0192	0.166	0.363	0.471	0.1688	0.341	0.4902
0.0402	0.936	0.0235	0.191	0.566	0.242	0.1981	0.4506	0.3513
0.0338	0.945	0.0214	0.1925	0.484	0.323	0.2005	0.5284	0.2711
0.0574	0.914	0.0315	0.170	0.683	0.147	0.1899	0.6389	0.1712
					$\bar{d}$	0.0044	0.011	0.0245
					$S_{\bar{d}}$	0.00396	0.012	0.0066

TABLE XXVII

THE SYSTEM PROPANOL-H_2O-ETHYL ACETATE AT 0°C. (2)

Raffinate Phase Composition Mole Fraction			Extract Phase Composition Mole Fraction					
Experimental			Experimental			Calculated		
x_1'	x_2'	x_3'	x_1''	x_2''	x_3''	x_1''	x_2''	x_3''
0.021	0.958	0.021	0.0879	0.206	0.705	0.0801	0.1979	0.722
0.0292	0.950	0.0209	0.1495	0.325	0.525	0.1403	0.2987	0.561
0.0424	0.936	0.0234	0.190	0.454	0.355	0.1911	0.3897	0.4192
0.0103	0.969	0.0209	0.1836	0.5554	0.0261	0.2034	0.4864	0.3102
0.0584	0.920	0.0258	0.176	0.630	0.194	0.1962	0.5627	0.2411
					$\bar{d}$	0.00924	0.047	0.0227
					$S_{\bar{d}}$	0.0147	0.0124	0.0197

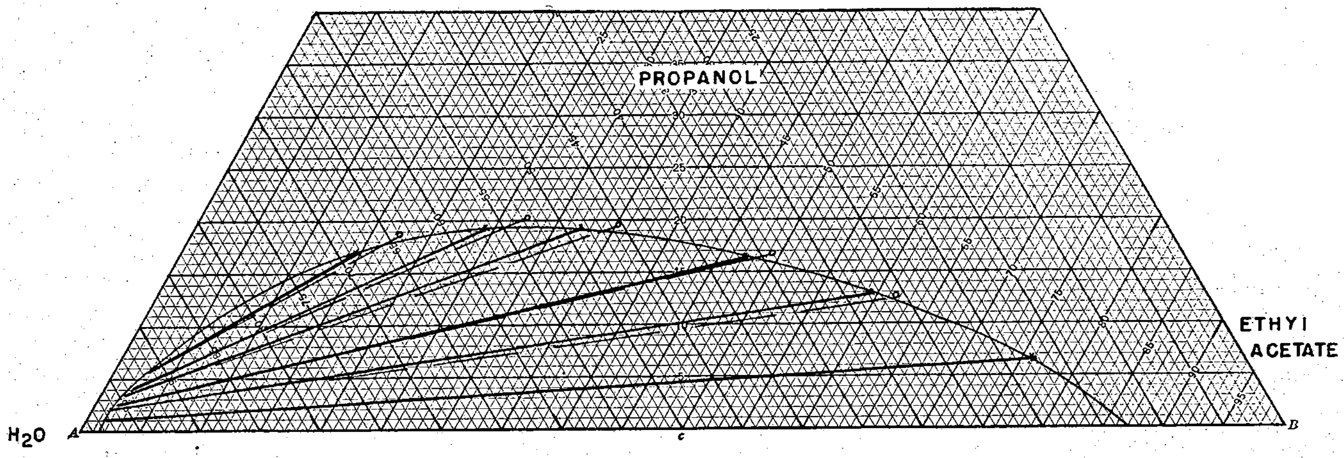

Fig. 28. The System Propanol-H_2O-Ethyl Acetate at 20°C

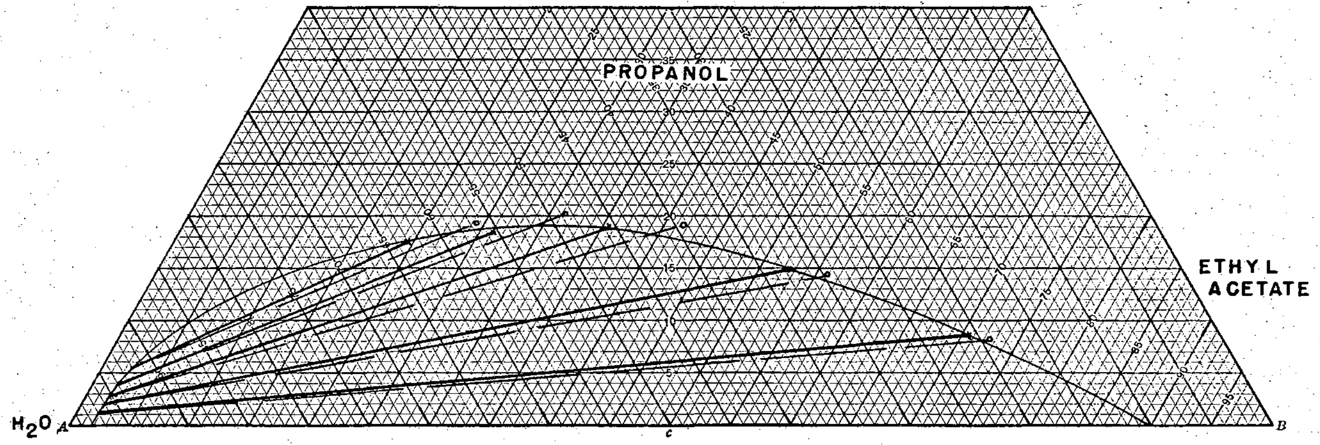

Fig. 29. The System Propanol-H_2O-Ethyl Acetate at 0°C.

TABLE XXVIII

THE SYSTEM N-BUTANOL-H_2O-ETHYL ACETATE AT 20°C. (2)

Raffinate Phase Composition Mole Fraction			Extract Phase Composition Mole Fraction					
Experimental			Experimental			Calculated		
x_1'	x_2'	x_3'	x_1''	x_2''	x_3''	x_1''	x_2''	x_3''
0.0044	0.982	0.0137	0.1315	0.2623	0.6062	0.121	0.250	0.629
0.0057	0.9816	0.0127	0.210	0.3571	0.4330	0.219	0.358	0.423
0.0093	0.9815	0.0091	0.294	0.463	0.243	0.285	0.463	0.252
0.0108	0.982	0.0074	0.349	0.494	0.158	0.349	0.495	0.157
0.01336	0.9828	0.0039	0.416	0.508	0.0758	0.386	0.5251	0.0889
					$\bar{d}$	0.00451	0.00134	0.00678
					$s_{\bar{d}}$	0.00734	0.00466	0.00569

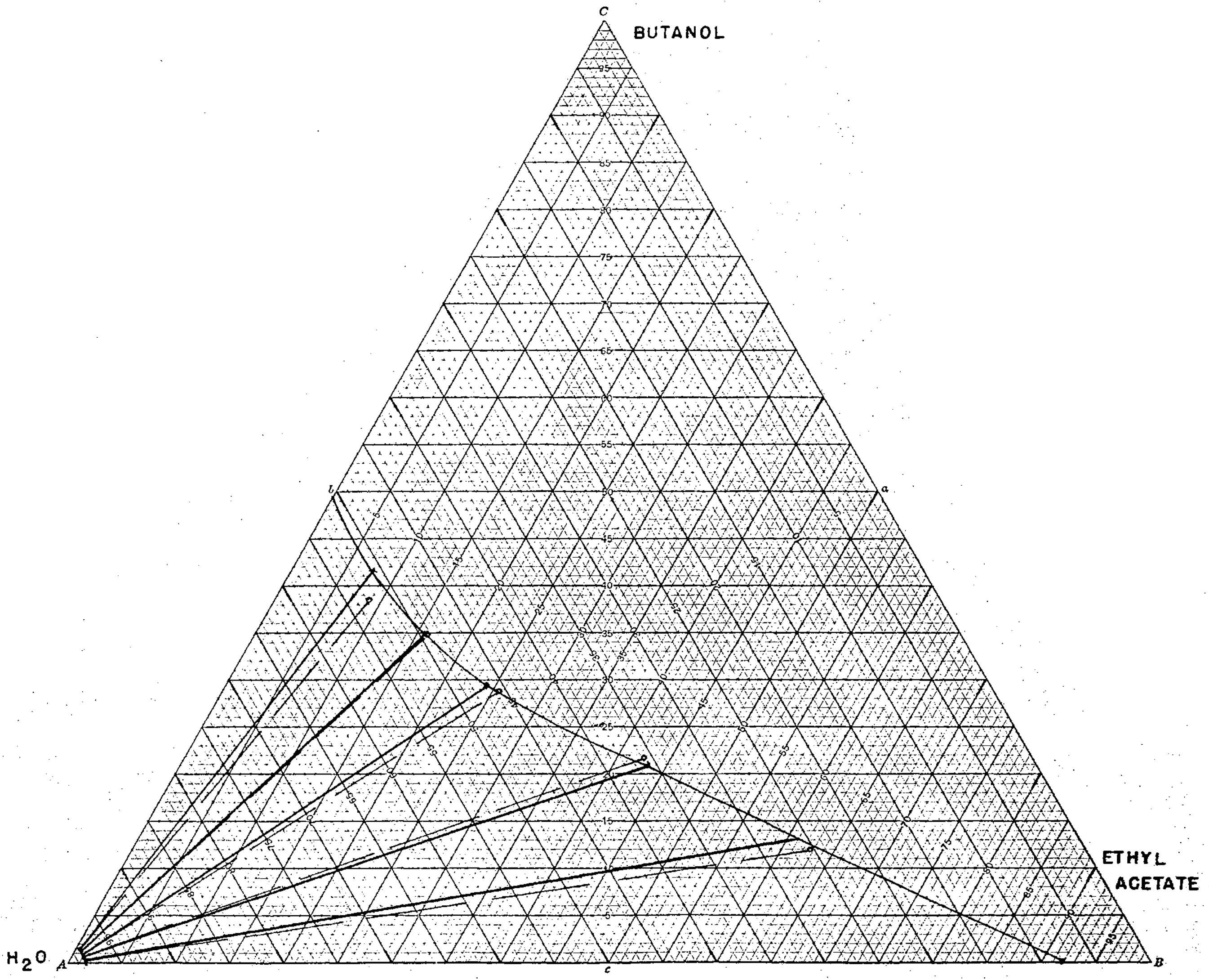

Fig. 30. The System n-Butanol-H_2O-Ethyl Acetate at 20°C

TABLE XXIX

THE SYSTEM N-BUTANOL-H_2O-ETHYL ACETATE AT 0°C. (20)

Raffinate Phase Composition Mole Fraction			Extract Phase Composition Mole Fraction					
Experimental			Experimental			Calculated		
x_1'	x_2'	x_3'	x_1''	x_2''	x_3''	x_1''	x_2''	x_3''
0.00608	0.975	0.01782	0.141	0.245	0.619	0.124	0.241	0.635
0.009	0.976	0.0163	0.205	0.341	0.454	0.199	0.329	0.472
0.0122	0.973	0.01406	0.290	0.460	0.250	0.290	0.450	0.260
0.0164	0.975	0.0176	0.345	0.495	0.1625	0.345	0.485	0.170
0.0202	0.972	0.00819	0.416	0.507	0.076	0.411	0.502	0.087
					$\bar{d}$	0.0056	0.0062	0.0123
					$S_{\bar{d}}$	0.0098	0.00163	0.010

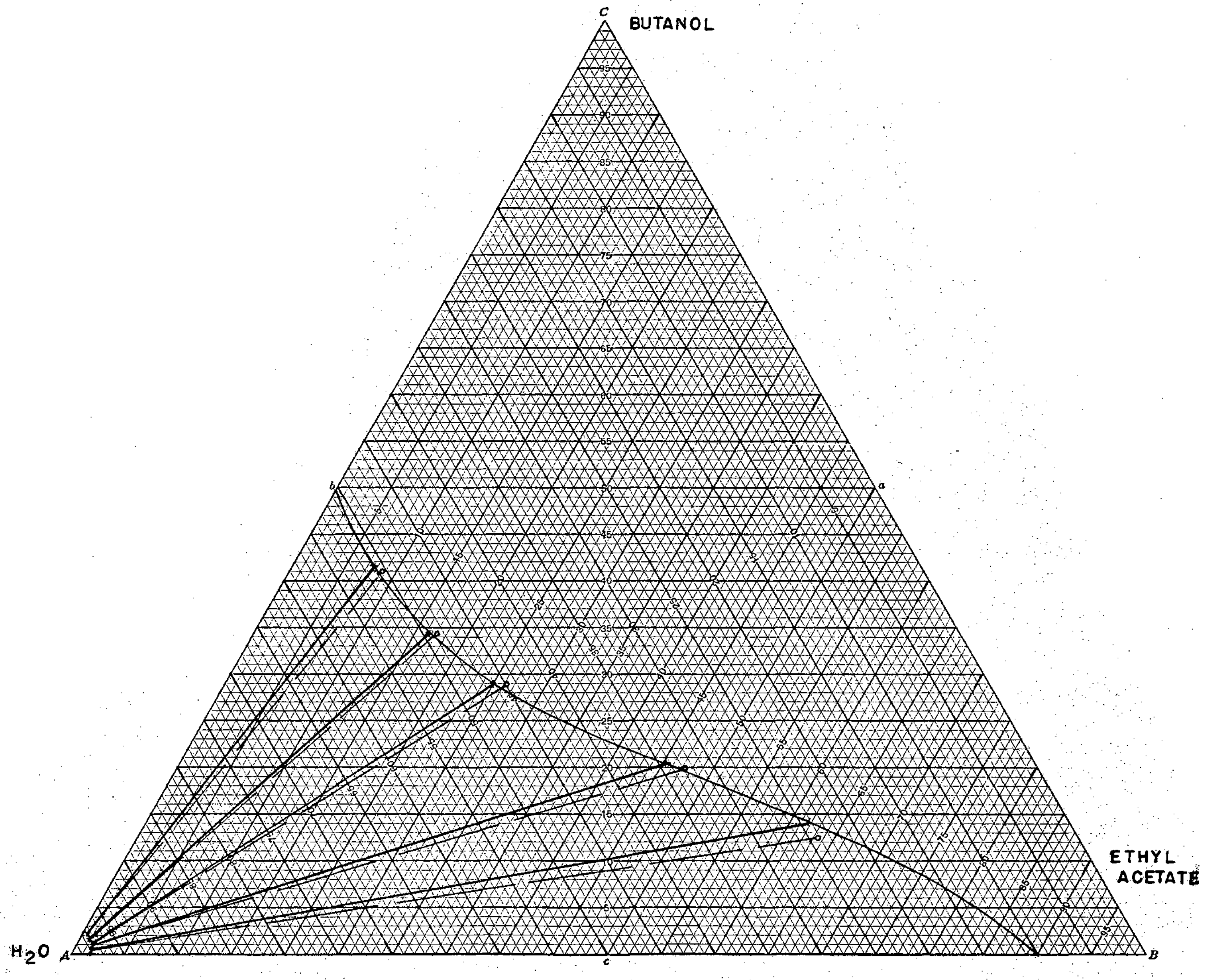

Fig. 31. The System n-Butanol-H_2O-Ethyl Acetate at 0^oC

APPENDIX C

COMPUTER PROGRAMS

Eight individual IBM 650 computer programs have been used for the correlation of the ternary liquid-liquid equilibria. They are listed in Table XXXI.

TABLE XXX

PROGRAMS FOR THE CORRELATION OF TERNARY LIQUID-LIQUID EQUILIBRIA

Number		Title
1.	0021	Conversion of Weight Fraction to Mole Fraction
2.	0022	Calculation of Coefficients in Redlich-Kister Equation
3.	----	Beaton Correlation Routine
4.	----	Granet Multiple Regression
5.	----	Core IV
6.	----	Core IV^{-1}
7.	0040	Calculation of Equilibrium Compositions From Redlich-Kister Equation
8.	0045	Conversion of Mole Fraction To Weight Fraction

The Beaton Correlation and Multiple Regression programs are used for the purpose of solving Redlich-Kister Constants by least squares method. Core 4 and Core 4^{-1} programs are alternative programs which have the same functions as Beaton and Regression programs. Program 0040 was written for the purpose of the calculation of equilibrium compositions from Redlich-Kister constants by using Redlich-Kister equations. The details of each program will be described in this Appendix.

Program 0021

Conversion of Weight Fraction to Mole Fraction

Purpose of Program:

This program was developed for the purpose of conversion of weight fraction to mole fraction. Compositions in Redlich-Kister equation are expressed as mole fractions, while most of the experimental data are expressed in weight fraction. Thus, it is necessary to convert the data from weight fraction to mole fraction before applying Redlich-Kister equations.

Flow Diagram: Table XXXI

Program Language: IBM 650 Fortran

Program: Table XXXII

Input and Output Data:

Data are in floating point system. The detailed format for input data is shown in Table XXXIII and the format for output data is shown in Table XXXIV.

Punch Instruction:

1. High punch column 73
2. No high punch column 1
3. Leave last word blank

TABLE XXXI

FLOW DIAGRAM OF PROGRAM 0021-CONVERSION OF WEIGHT FRACTION TO MOLE FRACTION

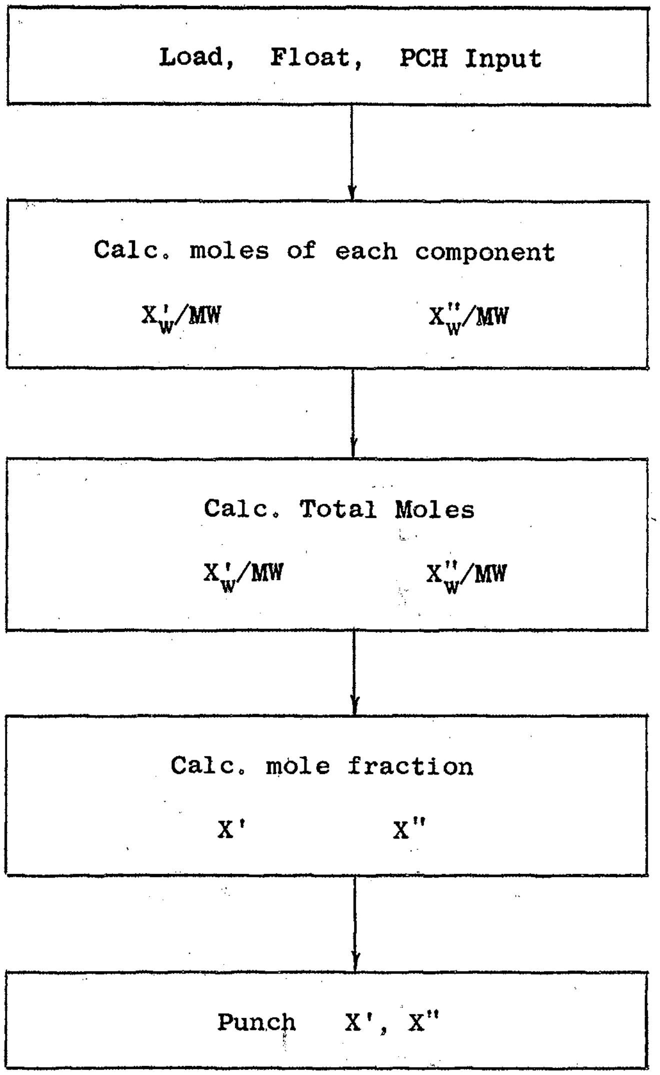

TABLE XXXII

PROGRAM 0021

```
C 0000 0 CONVERSION OF WEIGHT FRACTION
C 0000 0 TO MOLE FRACTION
     1 0 READ,XWAA,XWAB,XWAC,XWBA,XWBB,
     1 1 XWBC,XWCA,XWCB,XWCC,AMW,BMW,
     1 2 CMW
     2 0 A=XWAA/AMW
     3 0 B=(XWAA/AMW)+(XWBA/BMW)+
     3 1 (XWCA/CMW)
     4 0 AAX=A/B
     5 0 PUNCH,AAX
     6 0 C=XWAB/AMW
     7 0 D=(XWAB/AMW)+(XWBB/BMW)+
     7 1 (XWCB/CMW)
     8 0 BAX=C/D
     9 0 PUNCH,BAX
    10 0 E=XWAC/AMW
    11 0 G=E+(XWBC/BMW)+(XWCC/CMW)
    12 0 CAX=E/G
    13 0 PUNCH,CAX
    14 0 P=XWBA/BMW
    15 0 R=(XWAA/AMW)+P+(XWCA/CMW)
    16 0 ABX=P/R
    17 0 PUNCH,ABX
    18 0 S=XWBB/BMW
    19 0 T=(XWAB/AMW)+S+(XWCB/CMW)
    20 0 BBX=S/T
    21 0 PUNCH,BBX
    22 0 V=XWBC/BMW
    23 0 W=(XWAC/AMW)+V+(XWCC/CMW)
    24 0 CBX=V/W
    25 0 PUNCH,CBX
    26 0 X=XWCA/CMW
    27 0 Y=(XWAA/AMW)+(XWBA/BMW)+X
    28 0 ACX=X/Y
    29 0 PUNCH,ACX
    30 0 AA=XWCB/CMW
    31 0 BB=(XWAB/AMW)+(XWBB/BMW)+AA
    32 0 BCX=AA/BB
    33 0 PUNCH,BCX
    34 0 CC=XWCC/CMW
    35 0 DD=(XWAC/AMW)+(XWBC/BMW)+CC
    36 0 CCX=CC/DD
    37 0 PUNCH,CCX
    40 0 READ,XWAA,XWAB,XWAC,XWBA,XWBB,
    40 1 XWBC,XWCA,XWCB,XWCC,AMW,BMW,
    40 2 CMW
    41 0 IF(AMW)42,42,2
    42 0 END
```

TABLE XXXIII

INPUT DATA FORMAT

Card No.	Word No.	Fortran Code	Actual Value
1	1	XWAA	X'_{w1a}
	2	XWAB	X'_{w1b}
	3	XWAC	X'_{w1c}
	4	XWBA	X'_{w2a}
	5	XWBB	X'_{w2b}
	6	XWBC	X'_{w2c}
	7	XWCA	X'_{w3a}
	8	----	----
2	1	XWCB	X'_{w3b}
	2	XWCC	X'_{w3c}
	3	AMW	MW_1
	4	BMW	MW_2
	5	CMW	MW_3
	6	----	----
	7	----	----
	8	----	----
3	1	YWAA	X''_{w1a}
	2	YWAB	X''_{w1b}
	3	YWAC	X''_{w1c}
	4	YWBA	X''_{w2a}
	5	YWBB	X''_{w2b}

TABLE XXXIII (Continued)

Card No.	Word No.	Fortran Code	Actual Value
	6	YWBC	X''_{w2c}
	7	YWCA	X''_{w3a}
	8	----	----
4	1	YWCB	X''_{w3b}
	2	YWCC	X''_{w3c}
	3	AMW	MW_1
	4	BMW	MW_2
	5	CMW	MW_3
	6	----	----
	7	----	----
	8	----	----

TABLE XXXIV

OUTPUT DATA FORMAT

Card No.	Actual Code	Actual Value
1	AAX	X'_{1a}
2	BAX	X'_{1b}
3	CAX	X'_{1c}
4	ABX	X'_{2a}
5	BBX	X'_{2b}
6	CBX	X'_{2c}
7	ACX	X'_{3a}
8	BCX	X'_{3b}
9	CCX	X'_{3c}

TABLE XXXIV (Continued)

Card No.	Actual Code	Actual Value
10	AAY	X''_{1a}
11	BAY	X''_{1b}
12	CAY	X''_{1c}
13	ABY	X''_{2a}
14	BBY	X''_{2b}
15	CBY	X''_{2c}
16	ACY	X''_{3a}
17	BCY	X''_{3b}
18	CCY	X''_{3c}

Machine Operation:

Console Settings:

Storage entry	70 1952 9999
Programmed	RUN
Half Cycle	RUN
Control	RUN
Display	UPPER
Overflow	SENSE
Error	STOP

Operation:

1. Ready machine with proper settings, 650 FORTRAN 533 control panel and blank cards in the punch hopper.
2. Ready read hopper with 650 FORTRAN system deck.
3. Push computer reset and program start key, and when read hopper empties, push end of file key.

Running time: about 3 minutes per each run.

Program 0022

Calculation of Coefficients in Redlich-Kister Equations

Purpose of Program:

This program was developed for the purpose of calculation of the coefficients of each term in Redlich-Kister equations. The Redlich-Kister equation is written in the general form:

$$\log\,(x_i'/x_i'') = \sum\left[\, f_l(x_i'',\ x_j'',\ x_k'') - f_m(x_i',\ x_j',\ x_k')\,\right] B_{ij}$$

$$+ \sum\left[\, f_p(x_i'',\ x_j'',\ x_k'') - f_q(x_i',\ x_j',\ x_k')\,\right] C_{ij}$$

$$+ \qquad \cdots\cdots \qquad \text{(C-1)}$$

The purpose of this program is to calculate each summation value in the brackets and log x_i'/x_i'' in each equation, in order to simplify each equation into the form of

$$Y = b_1X_1 + b_2X_2 + b_3X_3 + \cdots\cdot \qquad \text{(C-2)}$$

which is used to calculate the Redlich-Kister constants for the Beaton or Core 4 programs.

Flow Diagram: Table XXXV

Program Language: IBM 650 Fortran

Program: Table XXXVI

Input and Output Data:

Data are in the floating point system. The detailed format for the input data is shown in Table XXXVII and for output data is shown in Table XXXVIII.

TABLE XXXV

FLOW DIAGRAM OF PROGRAM 0022 - CALCULATION OF COEFFICIENTS IN REDLICH-KISTER EQUATIONS

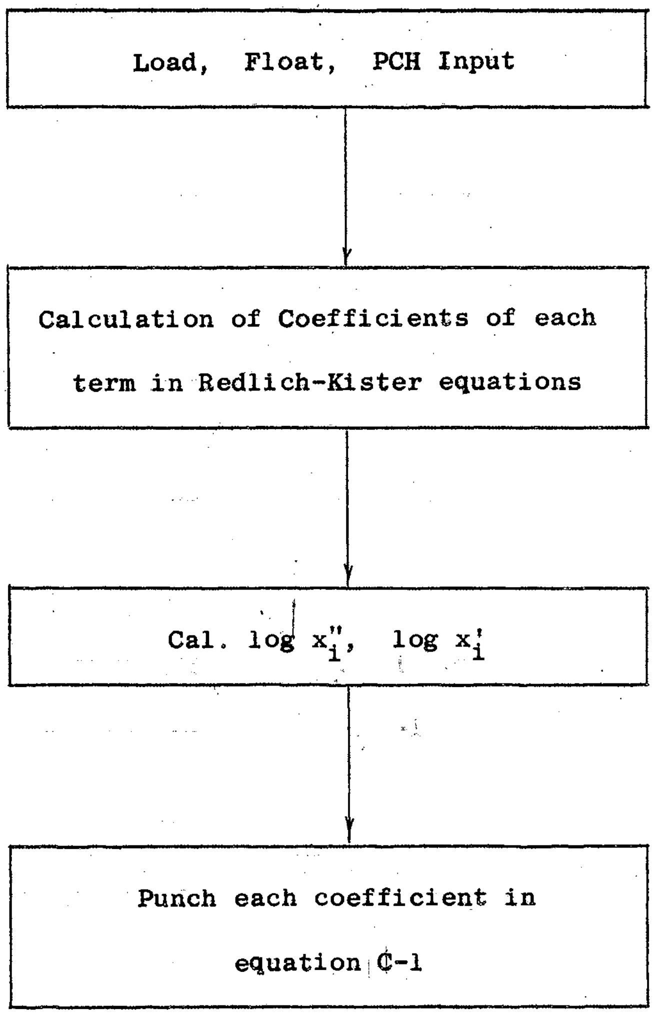

TABLE XXXVI

PROGRAM 0022

```
C 0000 0 CALCULATION OF THE COEFFICIE-
C 0000 0 NTS OF EACH TERM IN REDLICH
C 0000 0 KISTER EQUATIONS
     2 0 READ,XAA,XBB,XCA,
     1 1 YAA,YBA,YCA,PNB
   138 0 BCA=(XCA*(1.0-XAA))-(YCA*
   138 1 (1.0-YAA))
   139 0 BAB=(XBA*(1.0-XAA))-(YBA*
   139 1 (1.0-YAA))
   140 0 BBC=(YBA*YCA)-(XBA*XCA)
   141 0 ACB=BCA
  1411 0 BDB=BAB
  1412 0 CBB=BBC
  1413 0 PUNCH,ACB,BDB,CBB,PNB
   142 0 CCA=
   142 1 ((2.0*XCA)*(1.0-XAA)*(XCA-XAA)
   142 2 -(XCA**2))-((2.0*YCA)*(1.0-
   142 3 YAA)*(YCA-YAA)-(YCA**2))
   143 0 CAB=((2.0*XBA)*(1.0-XAA)*
   143 1 (XAA-XBA)+(XBA**I))-((2.0*YBA)
   143 2 *(1.0-YAA)*(YAA-YBA)+(YBA**2.0
   143 3 ))
   144 0 CBC=((-2.0*XBA)*XCA*(XBA-XCA))
   144 1 -((-2.0*YBA)*YCA*(YBA-YCA))
   145 0 ACC=CCA
   146 0 BAC=CAB
   147 0 CDC=CBC
   245 0 PUNCH,ACC,BAC,CDC,PNB
   170 0 R=(3.0*XCA)*(1.0-XAA)
   171 0 S=R*((XCA-XAA)**2.0)
   172 0 T=2.0*(XCA**2.0)
   173 0 U=T*(XCA-XAA)
   174 0 V=S-U
   175 0 W=(3.0*YCA)*(1.0-YAA)
   176 0 RA=W*((YCA-YAA)**2.0)
   177 0 RB=2.0*(YCA**2.0)
   178 0 RC=RB*(YCA-YAA)
   179 0 RD=RA-RC
   180 0 DCA=V-RD
   181 0 SA=3.0*XBA*(1.0-XAA)
   182 0 SB=SA*((XAA-XBA)**2.0)
   183 0 SC=2.0(XBA**2.0)
   184 0 SD=SC*(XAA-XBA)
   185 0 SE=SB+SD
   186 0 TA=3.0*YBA*(1.0-YAA)
   187 0 TB=TA*((YAA-YBA)**2.0)
   188 0 TC=2.0*YYBA**2.0)
   189 0 TD=TC*(YAA-YBA)
   190 0 TE=TB+TD
   191 0 DAB=SE-TE
   152 0 DBC=((-3.0*XBA)*XCA*((XBA-XCA)
   152 1 **2))-((-3.0*YBA)*YCA*((YBA-
   152 2 YCA)**2))
   153 0 ACD=DCA
   154 0 BAD=DAB
   155 0 CBD=DBC
   156 0 PUNCH,ACD,BAD,CBD,PNB
   157 0 RR=LOGF(YAA)
   158 0 SS=LOGF(XAA)
   159 0 Y=RR-SS
   160 0 PUNCH,Y,PNB
   161 0 READ,XXA,XBA,XCA,
   161 1 YAA,YBA,YCA,PNB
   162 0 IF(PNB-9.0)138,138,165
   165 0 END
```

TABLE XXXVII

INPUT DATA FORMAT

Card No.	Word No.	Fortran Code	Actual Value
1	1	XAA	X'_{1a}
	2	XBA	X'_{2a}
	3	XCA	X'_{3a}
	4	YAA	X''_{1a}
	5	YBA	X''_{2a}
	6	YCA	X''_{3a}
	7	10 0000 0051	
	8	----	
2	1	XAB	X'_{1b}
	2	XBB	X'_{2b}
	3	XCB	X'_{3b}
	4	YAB	X''_{1b}
	5	YBB	X''_{2b}
	6	YCB	X''_{3b}
	7	20 0000 0051	
	8	---	
3	1	XAC	X'_{1c}
	2	XBC	X'_{2c}
	3	XCC	X'_{3c}
	4	YAC	X''_{1c}
	5	YBC	X''_{2c}
	6	YCC	X''_{3c}

TABLE XXXVII (Continued)

Card No.	Word No.	Fortran Code	Actual Value
	7	30 0000 0051	
	8	----	
4	1	XBA	X'_{2a}
	2	XCA	X'_{3a}
	3	XAA	X'_{1a}
	4	YBA	X''_{2a}
	5	YCA	X''_{3a}
	6	YAA	X''_{1a}
	7	40 0000 0051	
	8	----	
5	1	XBB	X'_{2b}
	2	XCB	X'_{3b}
	3	XAB	X'_{1b}
	4	YBB	X''_{2b}
	5	YCB	X''_{3b}
	6	YAB	X''_{1b}
	7	50 0000 0051	
	8	----	
6	1	XBC	X'_{2c}
	2	XCC	X'_{3c}
	3	XAC	X'_{1c}
	4	YBC	X''_{2c}
	5	YCC	X''_{3c}

TABLE XXXVII (Continued)

Card No.	Word No.	Fortran Code	Actual Value
	6	YAC	X''_{1c}
	7	60 0000 0051	
	8	----	
7	1	XCA	X'_{3a}
	2	XAA	X'_{1a}
	3	XBA	X'_{2a}
	4	YCA	X''_{3a}
	5	YAA	X''_{1a}
	6	YBA	X''_{2a}
	7	70 0000 0051	
	8	----	
8	1	XCB	X'_{3b}
	2	XAB	X'_{1b}
	3	XBB	X'_{2b}
	4	YCB	X''_{3b}
	5	YAB	X''_{1b}
	6	YBB	X''_{2b}
	7	80 0000 0051	
	8	----	
9	1	XCC	X'_{3c}
	2	XAC	X'_{1c}
	3	XBC	X'_{2c}
	4	YCC	X''_{3c}

TABLE XXXVII (Continued)

Card No.	Word No.	Fortran Code	Actual Value
	5	YAC	X''_{1c}
	6	YBC	X''_{2c}
	7	90 0000 0051	X"
	8	----	

TABLE XXXVIII

OUTPUT DATA FORMAT

Card No.	Word 1	Word 2	Word 3	Word 4	Word 5 - 8
1	ACB	BDB	CBB	PNB 1	
2	ACC	BAC	CDC	PNB 1	
3	ACD	BAD	CBD	PNB 1	
4	Y_1	PNB 1			
5	ACB	BDB	CBB	PNB 2	
6	ACC	BAC	CDC	PNB 2	
7	ACD	BAD	CBD	PNB 2	
8	Y_2	PNB 2			
9	ACB	BDB	CBB	PNB 3	
10	ACC	BAC	CDC	PNB 3	
11	ACD	BAD	CBD	PNB 3	
12	Y_3	PNB 3			
13	BDB	CBB	ACB	PNB 4	
14	BAC	CDC	ACC	PNB 4	
15	BAD	CBD	ACD	PNB 4	
16	Y_4	PNB 4			
17	BDB	CBB	ACB	PNB 5	

TABLE XXXVIII (Continued)

Card No.	Word 1	Word 2	Word 3	Word 4	Word 5 - 8
18	BAC	CDC	ACC	PNB 5	
19	BAD	CBD	ACD	PNB 5	
20	Y_5	PNB 5			
21	BDB	CBB	ACB	PNB 6	
22	BAC	CDC	ACC	PNB 6	
23	BAD	CBD	ACD	PNB 6	
24	Y_6	PNB 6			
25	CBB	ACB	BDB	PNB 7	
26	CDC	ACC	BAC	PNB 7	
27	CBD	ACD	BAD	PNB 7	
28	Y_7	PNB 7			
29	CBB	ACB	BDB	PNB 8	
30	CDC	ACC	BAC	PNB 8	
31	CBD	ACD	BAD	PNB 8	
32	Y_8	PNB 8			
33	CBB	ACD	BDB	PNB 9	
34	CDC	ACC	BAC	PNB 9	
35	CBD	ACD	BAD	PNB 9	
36	Y_9	PNB 9			

TABLE XXXIX

DESCRIPTION OF FORTRAN CODE OUTPUT OF PROGRAM 0022

Fortran Code	
ACB	Coefficient of B_{31}
BDB	Coefficient of B_{12}
CBB	Coefficient of B_{23}
ACC	Coefficient of C_{31}
BAC	Coefficient of C_{12}
CDC	Coefficient of C_{23}
ACD	Coefficient of D_{31}
BAD	Coefficient of D_{12}
CBD	Coefficient of D_{23}
PNB	No. of equation of the calculated coefficient

Machine Operation: Same as program 0021

Program

Beaton Correlation Routine

<u>Purpose of Program:</u>

This program is used to calculate the regression matrix of normal equations from the least squares method described in Chapter III.

The variables b_1, b_2 .... are obtained from the inverse of the regression matrix by multiplying XY matrix. This procedure is computed by Multiple Regression program.

<u>Program Language:</u> 650 Machine Language

<u>Program:</u> Table XL

<u>Order of Program for Loading:</u>

1. Two drum clear cards
2. Beaton Correlation Deck
3. One read card
4. One header card
5. Data cards
6. One trailer card

<u>Preparation of Data:</u>

Read Card: $\overset{+}{7}0$ 1950 $300\overset{-}{0}$

Header Card:

This is a load card with high punches in columns 1, 10, 20 ....

Column	Description
1 - 2	Number of variables
3	0
4	0
5	0

TABLE XL

PROGRAM: BEATON CORRELATION

```
8000501954+ 4019531956+ 5100018003+ 6119551952+ 2092101952+ 7090029900+ 1519589004+  813008000+
6090031957- 2920009005+ 2790108003+ 5119509006+ 4090079009+ 5090089004+       2000+ 2790008002+
6919521958+ 7019950000+ 2419961957+ 6919541953+ 2419971954+ 6919561955+ 7019510000+ 2419991956+
6919521953+ 6919521951+ 2419951958+                                     2419981999+ 6919581957+
2419071996+ 6919271962+ 2419221997+          7+ 2419391998+      10000+ 2419681999+ 2219631971+
2419081996+ 6919281962+ 2419231997+ 1080018002+ 2419401998+ 6519521911+ 2419691999+ 1080011976+
2419091996+ 6919291962+ 2419241997+ 1080011934+ 2419411998+ 1119151920+ 2419701999+ 2219631967+
2419101996+ 6919631968+ 2419251997+ 2219778002+ 2419421998+ 1619151937+ 2419711999+ 2019918001+
2419111996+ 1019141919+ 2419261997+ 7119771911+ 2419431998+ 1519531941+ 2419721999+ 1019911948+
2419121996+ 1019391944+ 2419271997+ 6019521963+ 2419441998+ 1619531913+ 2419741999+ 2219791991+
2419131996+ 1180031921+ 2419281997+ 1019521963+ 2419461998+ 1019491961+ 2419751999+ 2219911965+
2419141996+ 2419781912+ 2419291997+ 1119521963+ 2419481998+ 6919631970+ 2419761999+ 1119791932+
2419151996+ 2419851912+ 2419301997+ 1519331989+ 2419611998+ 1519641969+ 2419871999+ 7019943000+
2419161996+ 1519771917+ 2419321997+ 4419351987+ 2419621998+ 2419331987+ 2419881999+ 6519911946+
2419171996+ 2019771918+ 2419331997+ 6019521963+ 2419631998+ 2100001988+ 2419891999+ 2419491974+
2419181996+ 7119771987+ 2419341997+ 1519391943+ 2419641998+      10000+ 2419911999+ 6000001949+
2419191996+ 6919221925+ 2419351997+ 1080011993+ 2419651998+ 3500041930+ 2419931999+ 2119491910+
2419201996+ 4419231926+ 2419361997+ 6580011942+ 2419661998+ 4680011972+ 2419941999+ 6519511966+
2419211996+ 4519241936+ 2419371997+ 3000041916+ 2419671987+ 6980031975+ 24    1999+
  11270007+  111273333+ 2411311134+ 2419551208+ 6512191173+             1119541309+ 1512191156+
  11340007+ 6519771181+ 1719541259+  111363333+ 1511401145+ 6080021147+ 1012031157+          1+
  11410007+ 1011361206+ 6911961299+ 1119641419+ 1680021453+ 3500021151+ 6911991352+ 3600001469+
  11480007+          5+ 2313531356+ 2411531156+ 2019771130+ 2119851338+  111533333+  111543333+
  11550007+  100001459+ 2011611164+ 2112121265+ 1580011165+ 1519641369+ 4512641465+  111613333+
  11620007+ 1512231269+ 6980031170+ 1019641169+ 2012191172+ 1112741279+ 2411311484+ 1580011173+
  11690007+ 2111741177+ 9812731325+ 1180021129+ 6911751128+ 1619641269+  111743333+ 6512231227+
  11760007+   25420000+ 2419551158+ 2412811184+ 1116161221+ 9811831265+ 3000021137+         49+
  11830007+ 6580021141+ 2011891136+ 1912231144+ 2012741264+ 2012201189+  111883333+  111893333+
  11900007+ 1612931197+ 1511941197+ 2111531456+ 1712741379+ 3508901417+ 1911481451+       1417+
  11970007+ 2019541358+ 1511528002+ 6913251202+ 2412031206+ 3500021457+ 2412741428+  112033333+
  12040007+ 4512581281+ 1916171391+ 1112091163+ 2119541257+ 4612111162+   25410000+ 4613631314+
  12110007+ 6912141167+ 6516171201+ 6980031270+ 6011741179+ 4511681319+ 6500001300+ 1511891143+
  12180007+ 2000001250+  112193333+  112203333+ 4412751153+ 6519551159+  112233333+  112243333+
  12250007+ 2411318001+ 2112241477+ 1611611215+ 6780031285+ 4611321233+ 3000011337+ 2111361139+
  12320007+ 2019781331+ 1019541309+ 4511381375+ 1711881193+ 2112201374+ 4611901191+  112383333+
  12390007+ 1514171471+ 1513938002+ 2119841338+ 6913001603+ 1613201276+ 6580031451+ 2019771280+
  12460007+ 6016041291+ 1012521360+ 6514781336+ 1514521410+ 6012121217+ 3500021308+ 6500001301+
  12530007+  112533333+ 3500021311+ 1014611354+ 6913591312+ 6080021365+ 6080021317+ 1712621267+
  12600007+ 3000021467+ 6512741954+         50+ 4611661367+ 6512881343+ 6912181271+ 2012091316+
  12670007+ 1812201425+   26180000+ 2012238001+ 9813731475+ 2213751178+ 2112381341+ 1011761231+
  12740007+  112743333+ 1080011133+ 3500041237+ 2112121315+ 6080031335+ 1013531357+ 7119771378+
  12810007+  112813333+ 6012861291+ 2014171131+ 1112091213+ 1512381243+ 6519521310+ 6480011601+
  12880007+ 5000000000+ 2399900000- 6500001417+ 1519771332+ 6912461399+ 3108901417+ 2012531256+
  12950007+ 4511981326+ 2419561411+ 6512981255+ 6013051462+ 2413751192+ 3500021207+ 4512541155+
  13020007+ 6516171372+ 6913061423+ 1013461354+ 6516171474+         69+ 6512741229+ 2012741228+
  13090007+ 3000021375+ 4513641907+ 2012741278+ 2411311284+ 1680021417+ 1580011421+ 1112681323+
  13160007+ 6913661416+ 6913201423+  113183333+ 6912221225+         59+ 6412241234+ 4513761380+
  13230007+ 6980031180+ 1513281283+ 6014781333+ 6519771481+ 6880021135+ 2019851331+ 1113531357+
  13300007+ 2319778003+ 6613341239+ 1519641370+ 1019641669+ 2019841331+ 1912881458+ 1512898002+
  13370007+ 6080021195+ 1612411295+ 1080021247+ 2112741440+ 2019521478+ 6512461454+ 1080011351+
  13440007+ 4412971298+ 4612481325+ 6516171600+ 6913251150+ 6512681448+ 6912511299+ 2412531256+
  13510007+ 1912741244+ 2412811600+  113533333+ 6912511449+ 6919601414+ 6580031263+ 3000021281+
  13580007+ 9712611313+ 6011541284+ 1519641420+         25+ 4110000000+ 1580011371+ 3500011272+
  13650007+ 3000011321+ 6913801483+ 1012741329+  113683333+ 1016161171+ 1680021330+ 1580011230+
```

TABLE XL (Continued)

```
13720007+ 6914261480+ 1011761450+ 2012241274+  113753333+ 1580011339+ 3600001149+ 6512321283+
13790007+ 1811821187+ 6019561291+ 6014391443+ 6512901395- 6013251142+ 6013941349- 6013251142+
13860007+ 6013251349+ 6913421296+ 6513981304- 6512901347+ 6513971347+ 1112741441+ 6014451249+
13930007+ 2119781338+ 6516171472+ 6913921150+ 2111881446+ 6500001251+ 6519591413+ 2419561325+
14100007+ 6914631200+ 6513251442+ 1516651470+ 1616161322+ 2216161447+ 1180031473+ 2414781466+
14170007+ 2019781331+  114183333+ 1580011277+ 2219591412+ 1019551260+ 1980011146+ 2412741377+
14240006+ 6914441200+ 2019541307+ 6914821167+ 6080021185+ 3500021236+ 3000011186+ 2412741377+
14370007+ 4512401131+ 1080011345+ 6516171417+ 2019541189+ 1619541600+ 1013461602+ 6913251350+
14440007+        273- 6016171212+ 2012231212+ 6919531464+ 1516161455+ 2413751294+ 2111548001+
14510007+ 1012741479+ 6000001205+ 3600001226+ 1014611602+ 2011761605+ 6514601156+ 2112741427+
14580007+ 1013611415+ 6513621467+ 6500001300+ 6516171300+ 1512161424+ 4099999872- 2419771348+
14650007+ 6512741429+ 6012521666+  114673333+  114683333+ 2112741327+ 2214671670+ 4513241326+
14720007+ 6914761352+ 2419551160+ 3500021396+ 6912531167+ 6912421202+ 6880021235+ 6913801483+
14790007+ 1680021287+ 2411311417+ 1511401245+ 6016171422+ 4480011438+ 6514171671+ 2118441497+
14860007+ 1499991898+ 6919991502+ 6019511888+ 6914921495+ 6519511506+ 2018241527+ 2130041820+
14930007+ 2018881543+ 6017011690+ 2418461749+ 4415011738+ 1515001606+ 2418901493+ 1019021510+
15000007+ 3600019684+ 6919381693+ 2219998003+ 6516071773+ 6080031512+ 3000011511+ 3500021514+
15070007+ 3500011516+ 6518661672+ 6916751729+ 6918741728+ 3500011517+ 2416161519+ 3500041523+
15140007+ 2019511504+ 6915181521+ 2019511704+ 1580011525+ 6916741727+ 1580011678+ 1017241529+
15210007+ 2419871972+ 3500041533+ 1517371491+ 6516161522+ 6915281531+ 6519511730+ 6519601515+
15280007+   16070000+ 1515321487+ 6518321842+ 2319601513+ 1915521823+ 1080021691+ 3500011692+
15350007+ 6914881728+ 6519991736+ 2019511754+ 3500011496+ 1180031697+ 4414941694+ 1980021714+
15420003+ 6918951495+ 6519511538+  115443333+ 3500011496+ 1180031697+ 4414941694+ 1980021714+
15390007+ 1180031697+ 4414941694+ 1980021714+ 6918951495+ 6519511538+  115443333+  115453333+
15460007+  115463333+  115473333+  115483333+ 1915521823+  115503333+  115513333+  115523333+
15530007+  115533333+  115543333+  115553333+  115563333+  115573333+  115583333+  115593333+
15600007+  115603333+  115613333+  115623333+  115633333+  115643333+  115653333+  115663333+
15670007+  115673333+  115683333+  115693333+  115703333+  115713333+  115723333+  115733333+
15740007+  115743333+  115753333+  115763333+  115773333+  115783333+  115793333+  115803333+
15810007+  115813333+  115823333+  115833333+  115843333+  115853333+  115863333+  115873333+
15880007+  115883333+  115893333+  115903333+  115913333+  115923333+  115933333+  115943333+
15950007+  115953333+  115963333+  115973333+  115983333+  115993333+ 4413031204+ 1680011210+
16020007+ 6911961449+ 2412811292+ 6012381344+ 1619641266+ 2018211524+  116073333+  116083333+
16090007+  116093333+  116103333+  116113333+  116123333+  116133333+ 2419871940+  116153333+
16060007+ 2018211524+  116073333+  116083333+  116093333+  116103333+  116113333+  116123333+
16130002+  116133333+ 2419871940+  116083333+  116093333+  116103333+  116113333+  116123333+
16630007+  116633333+  116643333+ 2016171398+ 2212521302+  116673333+  116683333+ 2114781282+
16700002+ 2112528001+ 1612321437+ 2016171398+ 2212521302+  116673333+  116683333+ 2114781282+
16720007+ 2419961499+ 1516761681+ 7019943000+ 6518141773+ 6916178003+ 2419871940+ 1019311485+
16790007+  100011716+ 2018161526+ 2419521707+ 6519851489+ 1016861541+ 6516871992+ 2117771680+
16860007+       5000+ 2117421795+ 1580031695+ 2117601789+ 1517061740+ 2416161520+ 2019511904+
16930007+ 2417721539+ 6018971744+ 1519521713+ 6917461990+ 3500021689+ 2018481998+ 6015031725+
17000007+ 6516161673+ 1041031853+ 6519511507+ 1517561761+ 4415081509+ 2418591712+ 6516171788+
17070007+ 2019531708+ 6917111614+ 2418481788+ 6516161973+ 6019531858+ 6916151718+ 2019531766+
17140007+ 1980021688+ 6517701775+ 7019951995+ 2417261739+ 2417501903+ 1618241881+ 4617231774+
17210007+ 1580011679+     790000+ 6517261731+ 2015491702+ 1515301535+ 6514311741+ 2419871490+
17280007+ 2418321685+ 2419961699+ 3500011537+ 1519391796+ 6514861542+ 6519511534+ 6517371892+
17350007+ 1519511815+ 6917391498+ 6516071767+ 6917431693+ 6917501812+ 6916151990+ 1017521761+
17420007+  117423333+ 7019961996+ 1519471696+ 1517481803+ 4699991803+ 3500011540+ 5000000000+
17490007+ 2016151733+  117503333+ 2017561762+     100000+             4416821732+ 2016171900+
17560007+  117563333+ 1517601716+ 6917631717+ 3500041822+  117603333+ 1119641720+ 1017658003+
17630007+ 6514291741+ 4517211996+ 6017421400+ 6916741677+ 4618701880+ 1517221878+ 6917761781+
17700007+ 2415431865+ 1680021882+ 7019961996+ 6917761779+ 1180031783+ 2418791782+ 6019521888+
17770007+ 2118851889+ 2018311787+ 2418321786+ 2018851896+ 3500041790+ 6517351890+ 3500011794+
```

TABLE XL (Continued)

```
17840007+ 1018371891+ 1580031793+ 3500011894+ 6918401893+ 1517911755+ 1180031747+ 1080011797+
17910007+          1+ 1018471851+ 6980021799+ 2417981751+ 6017981703+ 2017268001+ 2117531818+
17980007+  117983333+ 9618021804+ 6516071767+ 1680021759+ 1018081873+ 2030041820+ 1618071811+
18050007+ 1519641719+ 1118091813+     890000+ 3500001771+ 6015450000+ 2218151768+ 1180021819+
18120007+ 2418231777+ 4618161817+  118143333+ 3540021771+ 6518321842+ 2018231826+ 6518211876+
18190007+ 1018721877+ 6518231827+ 3600019684+ 2418251828+ 1530031898+ 6516071767+  118253333+
18260007+ 1018291833+ 1518301835+ 1518311785+ 6015440000+      10000+     890000+ 6518851839+
18330007+ 2118388001+ 2118391818+ 1018381843+ 2418391792+      10000+ 6015441549+ 3540011847+
18400007+ 1519511815+ 1618441899+ 1518451850+ 6918461849+ 3899269729+      10000+ 2031041820+
18470007+ 1519521815+ 6017011705+ 2218031806+ 1617531857+ 6918551810+ 6918071864+ 2140041820+
18540007+ 2418141769+ 3500001771+ 6918591862+ 4518601861+ 2219521710+ 1041031853+ 1580011867+
18610007+ 6518141869+ 2218651868+ 2118251778+ 2418311734+ 1040031853+ 6518251880+ 2018321818+
18680007+ 1518711875+ 4517721848+ 6180021780+  299260045+ 3500001847+ 2018311834+ 6518851839+
18750007+ 2018791832+ 1518791883+ 1180031836+ 2218311784+ 2415441865+ 4518871886+ 4518841848+
18820007+ 2418851888+ 2018381841+ 1580011892+             6518001805+ 3500011801+ 2117421795+
18890007+ 2018471852+ 2117981758+ 2118471818+ 2018008001+ 2418471772+ 1680021854+ 2030041820+
18960007+ 1518071863+       1853+ 4419011803+ 2018531856+ 7019971715+  100011905+ 2118851889+
19030004+ 6917061709+ 4416841536+ 6080031803+ 4680011715+ 7019971715+  100011905+ 2118851889+
19310001+ 3899269729+ 4416841536+ 6080031803+ 4680011715+ 7019971715+  100011905+ 2118851889+
19380001+ 6519511757+ 4416841536+ 6080031803+ 4680011715+ 7019971715+  100011905+ 2118851889+
19450001+ 2117981758+ 4416841536+ 6080031803+ 4680011715+ 7019971715+  100011905+ 2118851889+
19470001+ 6017011705+ 4416841536+ 6080031803+ 4680011715+ 7019971715+  100011905+ 2118851889+
19500001+ 6619511505+ 4416841536+ 6080031803+ 4680011715+ 7019971715+  100011905+ 2118851889+
19730001+ 3000041683+ 4416841536+ 6080031803+ 4680011715+ 7019971715+  100011905+ 2118851889+
19900001+ 2417501698+ 4416841536+ 6080031803+ 4680011715+ 7019971715+  100011905+ 2118851889+
19920001+ 6919451498+ 4416841536+ 6080031803+ 4680011715+ 7019971715+  100011905+ 2118851889+
19950005+ 1619511764+ 6518141773+ 6519511906+ 2118591900+ 2115521879+  100011905+ 2118851889+
```

Column	Description
6	0
7	0
8	0
9	0
10	1
11 - 13	In each column indicate the No. of variables per card
14 - 20	0

Data Cards:

Word 1 is reserved for identification.

Words 2 - 8 are for data. Five digits are used for each variable in fixed decimal point. For example 00 0000 645$\bar{8}$ means - 0.6458.

Punch Instruction:

1. No High punch column 1
2. No High punch column 73

Trailer Card:

This is a load card with high punch columns 1, 20 and 30; a low punch in column 10.

Columns 1 - 10: 00 00xx 135$\bar{5}$

xx total No. variables

Columns 11 - 30 are zeros except column 17 and column 19 are 1.

Output:

Output data cards are ready for Regression Deck. Be sure to high punch column 1 before input to Regression deck.

Machine Operation:

Console Settings:

Storage entry	70 1951 3000
Programmed	STOP
Half Cycle	RUN
Control	RUN
Display	UPPER
Overflow	SENSE
Error	STOP

Punch Feed:

80-80 Board

Switch	1	up
	2	middle
	3-5	down

Starting Procedure:

1. Clear punch feed hopper and load with blank cards.
2. Load read feed.
3. Punch computer reset and program start.
4. Push read feed start, wait for end of file.
5. Push end of file.
6. End of display: 70 1999 1000
7. Clear punch hopper.

Running time: About 3 minutes for each run.

Program

Granet Multiple Regression

Purpose of Program:

This program will calculate the regression coefficients from the regression matrix by the least squares method. Other calculations in this program are: standard deviation of betas, multiple regression, and the inverse of matrices.

Program Language: 650 Machine language

Program: Table XLI

Preparation of Data:

The input consists of three parameter cards and one control card plus the following from the Beaton Correlation Routine:

1. the correlation matrix
2. the standard deviations
3. the means

The First Parameter Card:

Columns 1 - 6	0
Columns 7 - 8	Number of variables
Columns 9 - 10	Total number of variables
Columns 11 - 30	For 7 variables: $0102030\overset{+}{305}\ 060700000\overset{+}{0}$

The Second Parameter Card: (designated as card no. 38A)

Same as the first parameter card except columns 2 - 6 are 10704.

The Third Parameter Card: (designated as card no. 40A)

Same as the first parameter card except columns 2 - 6 are 10729.

TABLE XLI

PROGRAM: MULTIPLE REGRESSION

```
8000501954+ 4019531956+ 5100018003+ 6119551952+ 2092101952+ 7090029900+ 1519589004+  813008000+
6090031957- 2920009005+ 2790108003+ 5119509006+ 4090079009+ 5090089004+       2000+ 2790008002+
6919521953+ 6919521951+ 2419951954+ 6919551956+ 6919541953+ 2419961957+ 6919588000+ 6919561955+
2419971952+ 6919531954+ 6919581957+ 2419981955+ 6919561957+ 7019958000+ 2419998001+ 3500041895+
2418611996+ 2218581911+ 2419111997+ 3500021867+ 2418671998+ 4418711872+ 2418721999+ 6918751878+
2418711996+ 6918741878+ 2418781997+ 2418811884+ 2418841998+ 3500041895+ 2418951999+ 1180031853+
2418531996+ 3500021859+ 2418591997+ 1180031917+ 2419171998+ 2418701873+ 2418731999+ 3500021879+
2418791996+ 6680031887+ 2418871997+ 6918901893+ 2418931998+ 2318901943+ 2419431999+ 3500041903+
2419031996+ 1518561862+ 2418621997+ 6918651868+ 2418681998+ 2219211924+ 2419241999+ 2418771880+
2418801996+ 6918831886+ 2418861997+ 2218831936+ 2419361998+ 1618891993+ 2419931999+ 2018971900+
2419001996+ 6918541857+ 2418571997+ 2418601967+ 2418561998+ 6018491904+ 2419211999+ 1000001982+
2418581996+ 2400001964+ 2418751997+ 2018978001+ 2419501998+ 7019613000+ 2419611999+ 6518971851+
2418511996+ 1619051909+ 2419091997+ 4519128000+ 2419121998+ 1519151881+ 2418811999+ 2018978001+
2419041996+ 1918701940+ 2419401997+ 3500011947+ 2419471998+ 4419011852+ 2418521999+ 3000011910+
2419101996+ 1518581863+ 2418631997+ 2018581913+ 2419131998+ 6080011971+ 2419711999+ 1519218001+
2418741996+ 2018971902+ 2419021997+ 6019061864+ 2418641998+ 2418811910+ 2419061999+ 2018971907+
2419071996+ 6518701925+ 2419251997+ 3500041910+ 2419821998+ 6919528003+ 2419831999+ 6919538003+
2419841996+ 6919548003+ 2419851997+ 6919558003+ 2419861998+ 6919568003+ 2419871999+ 6919578003+
2419881996+ 6919588003+ 2419891997+ 7019908000+ 2419901998+ 1618941982+ 2419651999+ 1019181964+
2419641996+ 1518698002+ 2419661997+ 6918771930+ 2419301998+ 2319211961+ 2418691999+      10001+
2419011996+ 6519211876+ 2418761997+ 6980031882+ 2418821998+ 2318851888+ 2418881999+ 6580011945+
2419451996+ 1518981908+ 2419081997+ 1018908002+ 2419631998+ 1518548002+ 2418541999+          1+
2418981996+ 1118540000+ 2418901997+ 4419633000+ 2419621998+ 6919211974+ 2419741999+ 2319271961+
2418661996+ 6018831937+ 2419371997+ 1518911896+ 2418961998+ 1018891944+ 2419441999+ 1518541916+
2419161996+ 1119191923+ 2419231997+ 4419281950+ 2419281998+ 1080011935+ 2419351999+ 2118821938+
2419381996+ 2018911994+ 2419941997+ 6519481891+ 2418911998+ 3500021975+ 2419751999+ 2019481969+
2419761996+ 2019481969+ 2419771997+ 2019481969+ 2419781998+ 2019481969+ 2419791999+ 2019481969+
2419801996+ 6519331939+ 2419691997+ 4419731926+ 2419731998+ 2119291932+ 2419321999+ 6618601920+
2419201996+ 1519291934+ 2419341997+ 3500041946+ 2419461998+ 2418601883+ 2418831999+ 2018481866+
2419261996+ 6619181883+ 2419181997+ 2400009999+ 2419801998+ 6519331939+ 2419391999+ 1518891899+
2418991996+ 1619701931+ 2419311997+ 4519411991+ 2419411998+ 1580011949+ 2419491999+ 2019338001+
2419221996+ 2419481972+ 2419721997+ 6919811892+ 2418921998+ 2418911994+ 2419911999+ 7019673000+
2419671996+ 6519421949+ 2419421997+ 6919521922+ 2419811998+ 3500021975+ 2418891999+      10000+
2419191996+ 2018491866+ 2419051997+ 6018481904+ 2419151998+ 6018491904+ 2418651999+ 2400001964+
2418651996+ 1000001982+ 2418941997+          7+ 2419701998+ 6919591922+ 2418491999+ 2400009998-
2419181999+ 2399999999+
2418501996+ 7019683000+ 2419681997+ 6519511855+ 2418551998+ 6918581861+ 2419118000+ 3500021867+
      1850+

6919521953+ 6919521951+ 2419951954+ 6919551956+ 6919541953+ 2419961957+ 6919588000+ 6919561955+
2419971952+ 6919531954+ 6919581957+ 2419981955+ 6919571956+ 2419991999+ 7019950000+
2419881996+ 7019941951+ 2419941997+ 6519511979+ 2419791998+ 6919821986+ 2419861999+ 2219821989+
2419891996+ 3500041981+ 2419811997+ 1580011990+ 2419901998+ 2219781984+ 2419841999+ 6519911992+
2419921996+ 1019828002+ 2419771999+ 1019801985+
2419851996+ 1580011993+ 2419931997+ 1119781983+ 2419831998+ 4419871988+ 2419871999+ 1080018002+
2419821996+ 2400001977+ 2419911997+ 6919528003+ 2419801998+      10000+ 2419781999+
      1988+                                              *
    7540007+ 6507571080+                         6607600765+  308000955+ 2006760779+ 5010000000+
    7610007+ 6511081063+ 6516091763+ 1607660771+ 2419280831+ 6400000950+      10000+ 2410790882+
    7680007+ 6516061512+ 2409841037+ 2119341038+ 4507740775+ 2016051758+ 2017591062+ 2015080761+
    7750007+ 6907780781+ 2015081811+ 6906761079+     200000+  308001105+ 6907830786+ 2407840787+
    7820007+ 6515111115+                         6507300985+ 2415081511+ 2419270780+ 6509851539+
    7890007+ 1607661571+             6500001505+           * 2417081712+ 2415141518+
    7960007+                                     1680021807+        922+  100000922+ 2006761629+
```

TABLE XLI (Continued)

```
 8030007+ 6580021061+ 6009041109+  100958000+  100968000+  100978000+  100988000+  100998000+
 8100007+ 6580010923+ 6680010923+ 6508021507+ 2009680971+ 6580010856+ 6580010923+ 6680010923+
 8170007+ 6780010923+ 6880010923+ 6580010829+ 3000020877+ 3000020877+ 3000020877+ 3000020877+
 8240007+ 3000020877+ 3000020837+             3500020838+ 1708400848+ 3500020885+ 6680020897+
 8310007+ 6509840789+ 6580030839+ 3500010990+ 2009190922+ 6580020897+ 3008060854+ 2000000922+
 8380007+ 2009041058+ 3500010996+             1906761131+ 2111470952+ 6080020851+ 6009041009+
 8450007+ 6009041012+ 6009041013+ 6009041014+ 2009190922+ 2409040957+ 2109040857+ 1909040878+
 8520007+ 1509060912+ 2208590918+ 1580010963+ 2209228001+ 3500020813+ 6880020966+ 6909110914+
 8590007+ 3100000880+ 6580010827+ 6680010827+ 4409150917+ 1109190825+ 6580010856+ 6580010827+
 8660007+ 6680010827+ 6780010827+ 6880010827+ 6580010827+ 6908740977+ 6909740977+
 8730007+ 1808260834+ 7000000922+ 3000021032+ 2015080762+ 6909800983+ 4508320899+ 4609320883+
 8800007+ 1509330887+         50+ 6911160769+ 1080010939+ 6910871040+ 2108400843+ 6511430898+
 8870007+ 4508900899+ 6518301085+ 1511471104+ 4408930896+                         3100010999+
 8940007+ 2009041007+ 6509041010+ 6080020910+ 6909190836+ 6909020855+ 2009040907+ 2009040958+
 9010007+ 1509040909+ 6500001080+ 6909561111+             2009110916+      90000+ 6780030965+
 9080007+ 6709110920+ 4508620899+ 3600000947+ 2009010900+ 4609220924+ 6880020934+ 2409190922+
 9150007+ 6909190972+ 1809190973+ 6080020928+ 1609210925+             1509440965+     100000+
 9220007+ 6500001080+ 3500020929+ 6509330949+ 4609310930+ 3500040937+ 6509330901+ 3600000850+
 9290007+ 2009330948+ 6509330942+ 6509040859+ 1180010938+ 2409550973+ 1709110965+        800+
 9360007+ 2415081661+ 4609400941+ 1109440899+ 1009440899+ 6909430946+ 6909450853+ 2009040858+
 9430007+ 3199990901+          1+ 3199990880+ 2209490852+ 2109040913+ 6780030905+ 3100000901+
 9500007+ 2007550758+ 2017141667+ 6509040969+ 6507561911+  308001655+ 6511081080+
 9570007+ 6609601016+ 6609611016+ 3000011015+         49+         50+ 6500001080+ 2009190922+
 9640007+ 1009190825+ 2009190922+ 1709190965+ 2119341137+             6910721150+ 2107561560+
 9710007+ 2108260979+ 3100010879+ 4509260927+ 7100000922+ 6515081563+ 2015081112+ 3000021033+
 9780007+ 2015081751+ 6009040959+ 2000000922+ 4410861088+ 6911161019+ 2208370895+
 9850007+ 1906761131+ 2415081761+ 6510791133+ 6519271831+ 1507661622+ 4409930894+
 9920007+             3000011049+ 2409851588+             4408490900+
 9990007+ 2009040908+  100938000+ 2017141817+             6507041659+             1907550759+
10060007+ 2007551908+ 6509601066+ 6509611066+ 4408860922+ 4608630964+ 6507591513+ 4508860922+
10130007+ 4608860922+ 4708860922+ 6409681078+ 1709190828+ 2209220875+ 2415031707+ 2409841537+
10200007+ 1515751882+ 2011081011+ 4507761127+ 2007841687+ 2009840987+ 4509781129+ 1108811036+
10270007+ 2009041076+  120002000+  100928000+ 7119271785+ 2109041121+ 1009351143+ 2210928001+
10340007+ 6918651068+ 1507661773+ 4510900842+ 6515111515+ 6507551909+ 1507661822+ 2211431146+
10410007+                         2417081812+
10480007+             2009041008+ 2007551558+             1011611170+ 6910561111+ 6509041069+
10550007+ 3600001031+          1+ 6909621017+ 6780031065+ 1507661821+ 6511281883+ 3000028002+
10620007+ 6517151080+ 1507661021+ 2409678001+ 2009190922+ 1709190873+ 6009191073+ 2415031757+
10690007+ 3100010969+ 1410741124+ 2011471054+ 3500010981+ 4510261027+ 2000000000+ 6907830986+
10760007+ 2009190922+ 2015141661+ 4508330922+ 2419280831+ 4611350884+ 1510840889+ 1511171071+
10830007+ 2011470952+         49+ 1507661873+ 3000011094+ 6900008003+ 6080021055+ 1507661023+
10900007+ 3000011148+                         1107661525+ 2009041120+
10970007+                                     1011611166+ 1680021159+             1980011190+
11040007+ 2009190922+ 6515080763+ 6907831536+ 2006761579+ 6500011005+ 4611131067+ 6680021969+
11110007+ 2411171070+ 6517151619+  100048000+ 6907641517+ 1507661671+      70000+
11180007+ 2407591764+ 1508721077+ 6508810889+ 6880021081+ 2015641567+ 4511261627+ 4410821083+
11250007+ 1516241879+ 2015081612+ 6507840989+ 2119341038+ 6519271504+ 2415111114+ 1519291683+
11320007+ 6507851080+ 1507661621+ 6915781534+  100918000+ 2410190780+ 6507551059+ 6907910794+
11390007+ 1507661523+                                   * 6900008003+
11460007+ 3500041057+             4609031053+           * 2411531156+ 1980011152+ 3000011158+
11530007+             1980011198+ 1011611168+ 2011611164+ 1011601165+ 1011611167+ 1980011196+
11600007+  100000000+             1580011182+ 1580011174+ 4511691153+ 1680021173+ 1680021176+
11670007+ 1680021177+ 1680021178+ 3000011175+ 1680021180+ 1580011181+ 1580011192+ 3000011179+
11740007+ 1011891195+ 1080021183+ 3000011184+ 3000011185+ 3000011186+ 6480011100+ 3000011188+
```

TABLE XLI (Continued)

```
11810007+ 1011891194+ 1011891193+ 1511871191+ 6480011162+ 6480011171+ 6480011163+  400000000+
11880007+ 6480011172+          5+ 3000011052+ 1080031199+ 1011971101+ 1680021151+ 1680021154+
11950007+ 1680021103+ 3000011153+          5+ 3000011155+ 1080031157+ 2412381206+
12020007+                                                 6912091212+ 2213031415+ 6599991312+
12090007+ 2000001324+ 1512431255+ 2212081300+ 2212091264+ 3500021219+
12160007+             2214781234+ 6512591289+ 1180031327+ 2099991386+ 1580011371+ 6599991437+
12230007+          2+ 2212201278+ 2112351245+
12300007+             2414591262+ 2014881442+ 2414901446+ 6980031240+
12370007+                         3000021253+ 2212431305+ 2414991408+ 6999998002+
12440007+             3000021213+                       +
12510007+ 2214451252+ 6914111217+ 1580011261+ 2012591263+ 2012601218+             2099991386+
12580007+ 6599991362+                         3500041272+ 1512431254+ 1914771210+ 6914451251+
12650007+ 6912201224+ 2214071269+ 6912711273+      10000+ 6912221276+ 1514591304+          1+
12720007+ 1080021231+ 2414851417+ 2214971294+ 2212571287+ 2214921297+ 2414801267+ 2414891292+
12790007+ 1514831288+ 2412351239+ 1614591290+ 2499991308+ 6913411277+ 2214081296+ 2414831286+
12860007+ 2414941301+ 6912221293+ 6912421274+ 6914071266+ 6912821291+ 2214541270+ 6912581448+
12930007+ 2214961299+ 1514591400+ 2212581279+ 6913031207+ 6914081284+             2412221302+
13000007+ 6512601281+ 6912081211+ 6912581295+ 2199991422+ 6912571275+ 1680011213+ 6912421416+
13070007+ 2014641325+ 1112421317+ 4413221320+ 4513181366+ 3500051323+ 3500021319+ 4513161326+
13140007+ 1012231321+ 2014771408+ 3500041377+ 4414211423+ 1580011329+ 2014731434+ 6514731378+
13210007+ 3000021427+ 6514811343+ 4413821328+ 6014271331+ 2114911426+ 6514811435+ 2414771280+
13280007+ 6514811335+ 1514831337+ 6780031338+ 1512451441+ 1614851340+ 2213411344+
13350007+ 6914881341+         49+ 2013928001+ 1714911346+ 4413931394+ 4513151238+ 3099991363+
13420007+ 6780031349+ 3100021351+ 4613471348+ 3500021307+ 1614991403+ 3500051309+ 6914521405+
13490007+ 2014521355+ 4613531404+ 4513541427+ 3000011360+ 1014581314+ 6080021413+ 1614581313+
13560007+ 1014591221+ 1514111365+ 2114661420+ 6512081368+ 6914641432+ 6014641369+ 3500021419+
13630007+ 1580011343+ 1112231321+ 4413701359+ 6112221373+ 1612711375+ 6912091374+ 1914731376+
13700007+ 1012201429+ 2114261379+ 2114271380+ 1014261431+ 2414271381+ 2014791433+ 2114811245+
13770007+ 6914801333+ 6914811341+ 2013341387+ 2012451439+ 2012451389+ 6514881343+ 3100011390+
13840007+ 1580031391+ 1180011443+ 6114891396+ 6614901345+ 1580018003+ 6014921447+ 3500021398+
13910007+ 1180021350+             1014961356+ 6014971401+ 2114501406+ 1014501357+ 1614531310+
13980007+ 4413521424+ 2014551358+ 1614831265+ 1514548003+ 6414551383+ 2014581361+ 1114581364+
14050007+ 2484581311+ 2014118001+ 2499991445+ 6999991233+ 2014641367+ 1814661425+ 6599991418+
14120007+ 1012571429+ 3600001384+ 1580011372+ 1512681285+ 2212421283+ 6913361241+ 3500021232+
14190007+ 2014731330+ 6514781412+ 1080011430+ 6512581329+ 6514771332+ 6914791432+ 1514281409+
14260007+                                 50+ 1014831438+ 1014831388+ 1513341339+ 4613851436+
14330007+ 6014881444+ 2414881342+ 1514881343+ 1080011443+ 2414901334+ 1580011395+ 6513921397+
14400007+ 3500021399+ 1014941414+ 6780031410+ 3000021450+ 3000011402+ 6500001440+ 6914491407+
14470007+ 1513031356+ 2214531306+ 5010000000+           *
15030007+ 2419281631+ 1516241529+  408001555+ 6515081713+ 1507661772+             1507660772+
15100007+ 3000021717+ 6906761079+ 1507661972+ 1507661521+ 6500001505+ 1507661771+ 6600011606+
15170007+ 2410790982+ 6916751678+ 1507661122+ 2116141917+ 2007590955+ 2017551808+ 2007850788+
15240007+ 2007551558+ 2107831736+ 2009841937+ 6507841039+ 2007551060+ 2019271030+ 6915331136+
15310007+  308001906+  308001756+ 2409841550+ 2408721625+ 1607661923+ 2415081961+ 6907830936+
15380007+ 6908410994+ 1507661573+                                     2417081912+
15450007+                                                             6509531080+ 2119341137+
15520007+             6917661820+             2007551658+ 6907831636+             6915511064+
15590007+ 1507661522+ 6019531907+ 6907640767+ 2119291132+ 1611161721+ 6600011705+ 6407551605+
15660007+ 6916701875+ 6517551559+ 2415641618+ 1607601615+ 2409841138+ 4510240975+ 2011071761+
15730007+ 2009851132+ 2007551608+         55+ 2007551859+ 6507841089+              308001805+
15800007+ 6915831586+ 1516241729+ 6500001806+ 2409841600+ 2411081962+ 1507661973+ 2410190780+
15870007+ 2419271530+ 6916111666+ 1507661623+           *
15940007+                                                                         6510031080+
16010007+ 7119271561+                                   * 2006510954+ 6407051656+ 1507661723+
```

TABLE XLI (Continued)

16080007+	6509671871+	6406520802+	2107551660+	6900001503+	6507851139+	1607661971+	
16150007+	1900001855+	6917201925+	6907701724+	6917251728+	1507661922+	2417151818+	2010790782+
16220007+	2007841587+	2007841787+	1+	6916281584+	2017811034+	6516801080+	6500011005+
16290007+	308001506+	6916331686+	6509841639+	300000+	2409841700+	2415111814+	1517141919+
16360007+	2415081062+	2419271580+		1607661673+			
16500007+	2007551709+	2019271601+				6517081613+	1907551759+
16570007+	6518301035+	6507601565+	6400001650+	6680021020+	6515141080+	2119311950+	1607661022+
16640007+	6507551609+	6407551905+	2418301734+	6007551510+	2411071860+	2409841837+	2006761679+
16710007+	2015118001+	4508761527+	4515261727+	2017081711+	2006510954+		6911161669+
16780007+	2416051760+	308001706+	6507291733+	7119271877+	6518301635+	2019291532+	6911161570+
16850007+	2016761735+	2410190780+	2419271630+	*			
16990007+		6507831737+	1516241651+	*			1906511755+
17060007+	6515081813+	6911161769+		308001556+	3000021867+	6516051509+	6018151719+
17130007+	1607661672+		6600011606+	6917701975+	1017140970+	2416091965+	1016241779+
17200007+	6507300985+	4615241025+	2016090812+	2015031657+	2411288001+	1906521107+	4516850754+
17270007+	6517081963+	2417551810+	2019271780+	6519271581+	1516241829+	2107551110+	1619291783+
17340007+	6918651868+	6510501816+	3600001610+	2415081562+			
17480007+			408001856+	6519271701+			
17550007+	1906521107+	6515081913+	6907901043+	6515141119+	2006761679+	6918641568+	6515641080+
17620007+	6918651018+	1507661722+	6907771634+	6400001750+	250000+	1007661924+	2006761629+
17690007+	2409840888+	2106761834+	2015118001+	2008021961+	2018308001+	4515281682+	2408021910+
17760007+	2010508001+	4518801681+	2416061566+	1016321887+	2119301662+		3500080951+
17830007+	2019291582+	6180031050+	6907771130+	2415081862+	2419271730+		
18040007+		6515081663+	1607601765+	3000081125+	6511071861+	6517591863+	6919141668+
18110007+	6515641519+	6911161819+	1607661872+	6907641967+	100+	1507661776+	6007551710+
18180007+	6918251778+	2409840988+	2416761784+	4515741129+	2007841637+	4615761777+	2011288001+
18250007+	6407051656+		6519271731+		2019271830+	6900001503+	3500080799+
18320007+	1107661974+	7119271827+	6516761884+			6907900793+	
18460007+					6019521857+	7119271677+	
18530007+			2007551858+	2019281531+	3600001732+	6507601665+	2017141617+
18600007+	6919641718+	1507661572+	6907901543+	1507660773+	6600011705+	2419281631+	
18670007+	1017141520+	2415031716+	2019271881+	-	1607661921+	4509761577+	2018301833+
18740007+	59+	2417591616+		6517811535+		1518151869+	2017081762+
18810007+	6518301585+	3500081001+	1607661824+	1607661726+			2119271830+
18950007+						2119331901+	2119341851+
19020007+				408001006+	6507841589+	3500041767+	308001106+
19090007+	1507661774+	6915161620+	1616141569+	2417811134+	1607661123+	2006761579+	2006760779+
19160007+	1519271917+	6907831786+	7119271900+	2018301681+	4419231926+	2009678001+	2017150768+
19230007+	4516261028+	2115781832+	2407851538+	7119271911+			
19300007+						1519391943+	6580011942+
19370007+	6515031607+		10000+	6519011911+	1119151920+	1619151937+	1519021941+
19440007+	1619021913+						2119321900+
19610007+	6516641080+	6919151118+	1611161823+	6406520802+	6917681775+		2410791684+
19680007+		1518741782+		4516741075+	2016061809+	2018308001+	2107901093+
19750002+	2410501553+			4516741075+	2016061809+	2018308001+	2107901093+

Control Card: (card no. 210)

This is the last card read into the machine.

Column	Description	
1 - 10	Machine constant	65 1954 1955
11 - 20	No. of equations	00 0000 00XX
21 - 30	Order of matrix	00 0000 00XX
31 - 40	XX is same above	XX 0000 0000
41 - 50	Machine constant	69 1956 1200
51 - 60	Machine constant	00 0000 1850
61 - 80	Blank	

Order of Program for Loading:

1. Two drum clear cards
2. First 35 cards of Granet Multiple Regression deck
3. 1 - card no. 36 Transfer card $\overset{+}{0}0\ 0000\ 185\overset{+}{0}$
4. 1 - card no. 36-A 1st parameter card
5. Correlation matrix as punched out by the Beaton Correlation routine. Identification no. 11 in Columns 5 - 6. This is in floating point arithmetic. The characteristic in this floating point arithmetic is in the 9th and 10th digit of the word; i.e. the two left digits. Note: There must be a 1 in Column 19 of the trailer card of the Beaton routine.
6. 1 - card no. 37 Blank card
7. 1 - card no. 38 Transfer card $\overset{+}{0}0\ 0000\ 185\overset{+}{0}$
8. 1 - card no. 38-A 2nd parameter card
9. Standard deviations as punched out by the Beaton Correlation routine. Identification no. 09 in Columns 5 - 6. This is in floating point arithmetic. Note: There must be a 1 in Column

17 of the trailer card of the Beaton routine.

10.	1 - card no. 39	Blank card	
11.	1 - card no. 40	Transfer card	00 0000 1850
12.	1 - card no. 40-A	3rd parameter card	

13. Means as punched out by the Beaton Correlation routine. Identification no. 07 in Columns 5 - 6. This is in floating point arithmetic. Note: There must be a 1 in Column 17 of the trailer card of the Beaton routine.

14. 1 - card no. 41 Blank card

15. 169 cards - cards no. 42 to 209
Granet Multiple Regression Program

16. 1 - card no 210 Control card

Punch Instruction: Same as Beaton Program

Output:

1.	20 in Col. 5-6	Betas (std. partial regression coeff.)
2.	21 in Col. 5-6	r_{ij} (partials)
3.	22 in Col. 5-6	s_{bi} (std. deviation of betas)
4.	23 in Col. 5-6	b_i (regression coeff.)
5.	24 in Col. 5-6	R, b_o or a (multiple R and regression constant)
6.	30 in Col. 5-6	Inverse matrix

Machine Operation:

Console Settings:

Storage entry	70 1951 3000
Programmed	STOP
Half Cycle	RUN
Control	RUN
Display	PROGRAM REGISTER

Overflow	STOP
Error	STOP

Punch Feed:

533 Read-Punch unit with the 80-80 board

Switch	1	up
	2-4	down

Operation: Same as Beaton Program

End of display: 01 0000 0000

Running time: About 4 minutes for each run

Program

Core IV

Purpose of Program:

This program will compute the uncorrected and corrected sums of squares and cross products, the correlation coefficients and standard deviation.

Program Language: 650 machine language

Program: Table XLII

Input Card:

1. Program:
   - 2 core-drum clear
   - 2 4-Card loader
   - 5 7-card loader
   - 41 program deck
2. Control card
3. Data

Output Sequence:

A. Uncorrected sum of squares and cross products

B. Corrected sum of squares and cross products

C. Correlation coefficients

D. Standard deviations

E. Means

F. Sums

Control Card Format:

Word 1	00000000NN	No. of variables
Word 2	00000MMMMM	No. of observations
Word 3	Floated M	No. of observations in floating point

Word 4	KKKK000000	Identification
Word 5	ABCDEF0000	Control word. A non-zero digit in any of the first 6 digits will cause output corresponding to it in output sequence.

Input Format:

Variables in words 1 - 5 in floating point

Zero in 6 - 7

Word 8	xxxiiiijj	where iiii is the observation number and jj is the card number under the particular observation

If the number of variables is not divisible by five the odd number of variables must be placed in the first card starting with variable 1.

Output Format:

Word 1	KKKKPPPPPQ	KKKK is taken from word four of control card. Q is the digit corresponding to the numerical digit in word five of control card. PPPPP is the card no. under Q.
Word 2	No. of words in card	
Word 3	No. of variables	
Word 4 - 8	Answers	

Machine Operation:

Console Settings:

Storage entry	70 1951 9999
Programmed	STOP
Half Cycle	RUN
Control	RUN
Display	DISTRIBUTOR

Overflow	STOP
Error	STOP

Running Time: About 3 minutes per each run.

To process more than one problem without reloading program place input data sets directly in back of each other, each set preceded by a proper control card.

TABLE XLII

PROGRAM: CORE IV

```
8000501954+ 4019531956+ 5100018003+ 6119551952+ 2092101952+ 7090029900+ 1519589004+  813008000+
6090031957- 2920009005+ 2790108003+ 5119509006+ 4090079009+ 5090089004+       2000+ 2790008002+
8000501954+ 4019531956+ 5100018003+ 6119551952+ 2092101952+ 7090029900+ 1519589004+  813008000+
6090031957- 2920009005+ 2790108003+ 5119509006+ 4090079009+ 5090089004+       2000+ 2790008002+
6919521953+ 7019953000+ 2419991954+ 6919551956+ 6919521951+ 2419951999+                    411
2419961996+ 6919541953+ 2419971997+ 6919561955+ 2419981999+ 6919581957+                    412
2419881996+ 7019940100+ 2419941997+ 6519511979+ 2419791998+ 6919821986+ 2419861999+ 2219821989+
2419891996+ 3500041981+ 2419811997+ 1580011990+ 2419901998+ 2219781984+ 2419841999+ 6519911992+
2419921996+ 1019828002+ 2419771997+ 1019801985+ 2419851998+ 1580011993+ 2419931999+ 1119781983+
2419831996+ 4419871988+ 2419871997+ 1080018002+ 2419821998+ 2400001977+ 2419911999+ 6919528003+
2419801988+      10000+
         7+ 6580030007+ 4500042000+ 2100060026+ 1000060011+ 2100100013+ 6500100021+
     70007+ 1000100015+                                     4100160032+ 1580010002+ 3000020019+
    140007+ 6580030022+ 1680020023+ 3280030024+                         1180030028+ 1180030031+
    210007+ 3500010030+ 1000250029+ 3480010027+ 3280010032+ 5000000050+ 1180010033+ 3280010014+
    280007+ 3500020036+ 1680020038+ 8280030035+ 3780010001+ 8200030000+ 4500370005+ 5300010040+
    350007+ 6040400003+ 1900390012+ 8120000005+ 3980010034+ 5000000000+ 4200008005+ 1223000025+
    420007+ 1650000025+ 1960000025+ 2230000025+ 2460000025+ 2680000025+ 2880000025+ 3070000025+
    490007+ 3240000025+
    560007+                                                             2790500066+ 6990020118+
    630007+ 5080010069+          5+ 1000510107+  802800092+  100670116+ 5000010124+ 6002500206+
    700007+ 8280030228+ 6079990264+ 4502030177+ 2490020079+ 4400770078+ 2179990152+ 5000010082+
    770007+ 6980030084+ 6900640084+ 6092600165+ 6900510204+ 4202660085+ 6980050088+ 8280010079+
    840007+ 7002510151+ 6990020091+ 6100890143+ 2790500142+ 8280010178+ 1000000051+ 6900510232+
    910007+ 8980010147+ 8917100098+ 6400960157+  802750137+ 6990020263+          2+ 3400530208+
    980007+ 2790500103+ 2002360243+ 7000510101+ 6900520105+ 4801550106+ 2879900102+ 4000780108+
   1050007+ 2490010061+ 6910000153+ 8180010163+ 6001610065+ 5800010216+ 3279990075+ 1400640074+
   1120007+ 8080030070+ 4601160067+ 4200790068+ 8980020073+ 2402500104+ 3994600162+ 8180010174+
   1190007+ 1980010093+ 3490010173+ 5800010170+ 8980010178+ 2123470150+ 4001270128+ 2179990202+
   1260007+ 1601610171+ 6980050083+ 6900510154+ 2090020086+ 2179990276+ 3500010187+ 6023470226+
   1330007+ 2401860239+ 6080050141+ 4002210139+ 5800010193+ 6500550131+ 4001320242+ 6901920133+
   1400007+ 8180030148+ 4000700095+  802510221+ 3200530179+        10+ 6500510277+ 5000010191+
   1470007+ 6100510112+ 2190530237+ 7190520199+ 5000010207+ 2792600156+ 5800010158+ 2402500203+
   1540007+ 8180010160+ 5800100098+  802510063+ 1601610115+ 5200010114+ 6900620133+ 6092600215+
   1610007+          1+ 2190010269+ 8380010119+ 8002140020+ 3994600110+ 6990020122+ 6180030217+
   1680007+ 5200010224+ 1601610265+ 6079990164+ 8380020129+ 4201780076+ 2179990262+ 6900510209+
   1750007+ 5200010081+ 2490000132+ 6900800133+ 6123470201+ 2190000087+ 8980020189+ 4401850186+
   1820007+ 5800010138+ 6900530176+ 1501610234+ 1000540231+             2000550181+ 6590020195+
   1890007+ 6923470200+ 6000640140+ 4002370245+ 6500510273+ 4001890197+             8980010184+
   1960007+             6901000133+             4901900186+ 2479990230+ 3943470097+ 4901090159+
   2030007+ 6500510205+ 8180010210+ 8180010111+ 1102580113+ 4001600211+ 3279990125+ 8380010266+
   2100007+ 8380010166+ 6590010169+ 4601670217+ 6980060219+ 2190010071+ 3223470123+ 5200010172+
   2170007+ 3980010120+ 6090010225+ 5180010175+ 6902230133+ 6092600271+ 2790500227+ 6500510270+
   2240007+ 4202280278+ 2179990268+ 3490000130+ 2802510220+ 6092600117+ 5000010135+ 5000010136+
   2310007+ 2102360090+ 2490540188+ 1601610180+ 1400640235+ 4401400190+             6979990238+
   2380007+ 2492600240+ 2790500094+ 5800010146+ 1501440099+ 6901450133+ 2490520149+
   2450007+ 6502360241+
   2520007+
   2590007+                         2494600213+ 5800010168+ 8980010170+ 4602670218+ 2090010072+
   2660007+ 6939990261+ 6190010225+ 4901210222+ 6079990212+ 8180010126+ 3490000274+ 5200010229+
   2730007+ 8180010279+ 2159990272+ 8980020183+ 5000010182+ 8180010233+ 5000010134+ 1601610275+
```

Program

Core IV^{-1}

Purpose of Program:

This program will compute regression coefficients for the equation

$$Y = b_1X_1 + b_2X_2 + b_3X_3 + \ldots . \qquad \text{(C-5)}$$

Other calculations are inverse of the regression matrix, inverse of the inverse regression matrix and XY matrix.

Program Language: 650 machine language

Program: Table XLIII

Input Sequences:

1. Program
2. Output data from Core 4
3. Trailer card

Output Sequences:

1. Inverse of regression matrix
2. $b_1, b_2, b_3 \ldots .$
3. Inverse of inverse regression matrix
4. XY matrix

Trailer Card: $00\ 0000\ 015\overset{+}{0}$ $\quad 00\ 000N\ 000\overset{+}{1}$ $\quad$ N No. of b_i

Console Setting:

Same as Core 4 program except storage entry is "-".

TABLE XLIII

PROGRAM: CORE IV^{-1}

```
      8000+  CORE 4      INVERSE
8000501954+ 4019531956+ 5100018003+ 6119551952+ 2092101952+ 7090029900+ 1519589004+  813008000+
6090031957- 2920009005+ 2790108003+ 5119509006+ 4090079009+ 5090089004+       2000+ 2790008002+
7090109010+
7090029002+             6939511988+ 5220001987+ 5100011991+ 3000041986+ 6519511985+ 7019981998+
2119841999+ 4680021989+ 8280021995+ 5300011994+ 2440001990+ 8080021997+ 5300011996+ 4019941999+
         7+ 2400030006+ 2100560009+ 6900050008+        107+   40000000+ 8800680043+ 2000110014+
     70007+ 4200100101+ 2200050058+ 6500110015+ 6100520079+  100000000+ 8200680070+ 6900180071+
    140007+ 3000040025+ 3500040075+ 6900190022+   20000000+ 3900680069+ 8200680029+ 2100680088+
    210007+ 6900240027+ 2200190072+ 2200690073+ 2100680102+ 2100300033+ 6900290032+ 2200240077+
    280007+ 3400680020+ 6900680037+  100000000+ 2200280081+ 2200290082+ 1180010041+      10000+
    350007+ 6900380091+ 1500110066+ 2400680054+ 6000680028+ 2000110064+ 6900430096+ 3500040001+
    420007+ 6500560061+ 6100680099+ 2000490002+ 2000560059+ 1500800036+ 6900500053+
    490007+  100000000+ 3200680024+ 5000010007+  100000000+ 2200500103+ 5300010060+ 1600340105+
    560007+  100000000+ 4800430019+ 6000560062+ 6900120065+ 4200290104+ 1500300085+ 1900300100+
    630007+ 1680010078+ 1500170021+ 2200120016+ 6900690023+ 6900200074+             2100680092+
    700007+ 6000870028+ 2200180076+ 1600340089+ 1500340040+ 2200200026+ 6900280031+ 6900790083+
    770007+ 1500800035+ 6900370093+ 3900680050+   20010000+ 1600340039+ 1500560013+ 2200790084+
    840007+ 1600560063+ 3500040045+ 3500040097+ 1000000051+ 5300010094+ 6900920095+ 4500440048+
    910007+ 2200380042+ 8300680051+ 2200370012+ 4200380098+ 2200920046+ 2200430047+ 1600340090+
    980007+ 8000000005+ 2400520018+ 1500040109+ 5900010057+ 5200010051+ 6500300086+ 6500490055+
   1050007+ 4600030106+ 2000490012+                         1500110067+ 3000040210+
   1160007+ 6503090263+ 3500040277+ 2403210174+ 1001610227+ 2192020177+ 2001250178+
   1230007+ 2201700173+ 1602500206+             2402230226+
   1350007+ 2001890142+ 2801270139+ 1990020160+ 6790020195+ 2390010146+ 1590010147+ 3000040201+
   1420007+ 6501550159+ 5090010186+ 5900010200+ 5090000211+ 3000040257+ 3500040158+ 5100010204+
   1490007+ 1690020307+ 6590020157+ 1501559027+ 1501559035+ 6890020261+ 6790020311+    3250000+
   1560007+ 2003090312+ 3000060121+ 6902110264+ 3000040119+ 1501630117+             6902650118+
   1630007+       2325+ 8000070120+ 2002110215+ 4503200241+ 6901700123+ 6703090313+ 6901720175+
   1700007+ 6902230280+ 2090020228+ 2402230276+ 6901260179+ 2003090266+ 2201720225+ 4002790211+
   1770007+ 4001800181+ 6719520207+ 2201260229+ 5100010120+ 2790020136+ 5190000190+ 2202800233+
   1840007+ 2001260234+ 2001720283+ 6902230172+ 3000040197+                         4001450186+
   1910007+ 5100010170+ 4690100142+ 6702220285+ 2490000300+ 3500040205+ 5200010252+ 8280020256+
   1980007+ 2790020254+ 6701550110+ 4801530154+ 1690010209+          7+ 1701880294+ 4802600299+
   2050007+ 1780010213+ 2090000166+ 2001610164+ 1880050268+ 3500040169+ 1702900245+ 6902230126+
   2120007+ 4501160267+ 2002170220+ 1590010171+ 6802750282+ 1702170271+             6980030324+
   2190007+ 2402220235+ 6701550259+ 2002750278+                         1890010237+ 8890000283+
   2260007+ 5000010182+ 6902300000+ 6580000135+ 3000040140+ 6090000137+ 2001700273+ 5190010240+
   2330007+ 6901860239+ 6802750284+ 2002900193+ 1590000243+ 1702500306+ 3000040249+ 2201860289+
   2400007+ 4001430144+ 6902900194+ 3000040203+ 1602500255+ 2001890192+ 6980020251+ 5800010318+
   2470007+ 4603010302+ 4003160321+ 1702020308+          1+ 3500040262+ 4003100299+ 2461340288+
   2540007+ 2801270248+ 2003090162+ 5180020316+ 2390000214+ 1001250238+ 3000040269+ 5800010318+
   2610007+ 3500040221+ 1780010319+ 1502170162+ 2202110314+ 6590000323+ 8080020187+ 6902900293+
   2680007+ 1702870292+ 1580010236+ 2003150168+ 2003090313+ 4802460299+ 6802750281+ 2002870291+
   2760007+ 5000010232+ 6902800183+ 1701700231+ 5100010170+ 2402230176+ 1702110165+ 1701260184+
   2830007+ 8090010191+ 1701720185+ 4501380241+ 1602500156+             5200010295+ 3000040149+
   2910007+ 6803090218+ 3500060258+ 2490000199+ 1702500208+ 4001480299+ 6503210247+ 2001270302+
   2990007+ 1580070322+ 6601890244+ 6801270297+ 7101270198+ 2461340196+             2090000212+
   3060007+ 1890000317+ 3500040167+ 8900060318+             5100010272+ 1890010219+ 6803150270+
   3130007+ 6903150118+ 6501860141+ 6590000124+ 6790020224+ 3500020274+ 6940000303+ 1702220286+
   3200007+ 6703090216+             2001270296+ 1602500305+ 2301880242+
   4000007+ 7090029011+ 6090049012+ 2190009045+ 8200019014+ 8800019016+ 7090029016+ 8190039017+
   4070007+ 6690019018+ 1590029019+ 4590209059+ 4690599021+ 2490019050+ 1190529023+ 1990009024+
   4140007+ 1580079025+ 1690529026+ 3500040151+ 6990539028+ 2290539029+ 6080079030+ 1190529031+

   4210007+ 1990009032+ 1580069033+ 1690529034+ 3500040152+ 6990549036+ 2290549037+ 5000099038+
   4280007+ 6992019053+ 5980019040+ 4890579056+ 5800019058+ 4290498000+ 5200019044+ 8840009058+
   4350007+ 2090019013+                                     5280019043+ 4090519015+ 6080069022+
   4420007+          1+ 2499999054+ 2499999055+ 6990009039+ 5380019042+ 5880019041+ 5100089050+
   4490007+  100009050+
      1952- 2790101953+  904009010+
```

Program 0040

Calculation of Equilibrium Compositions From Redlich-Kister Constants

Purpose of Program:

This program was written for the purpose of the calculating the equilibrium compositions from Redlich-Kister constants by using Redlich-Kister equations. The three unknown compositions x_1'', x_2'' and x_3'' in Redlich-Kister equations are fourth order. To solve these values an iterative trial and error method is involved. This program does not converge very rapidly. Before applying this program, be sure the input Redlich-Kister constants are the best possible values.

Flow Diagram: Table XLIV

Program Language: 650 Fortran

Program: Table XLV

Input and Output Data:

Data are in floating point system. The detailed formats for input and output data are as shown in Table XLVI and Table XLVII respectively.

Punch Instruction:

1. High punch column 73
2. No high punch column 1
3. Leave last word blank

TABLE XLIV

FLOW DIAGRAM OF PROGRAM 0040 - CALCULATION OF TERNARY LIQUID - LIQUID EQUILIBRIUM COMPOSITIONS FROM REDLICH-KISTER EQUATIONS

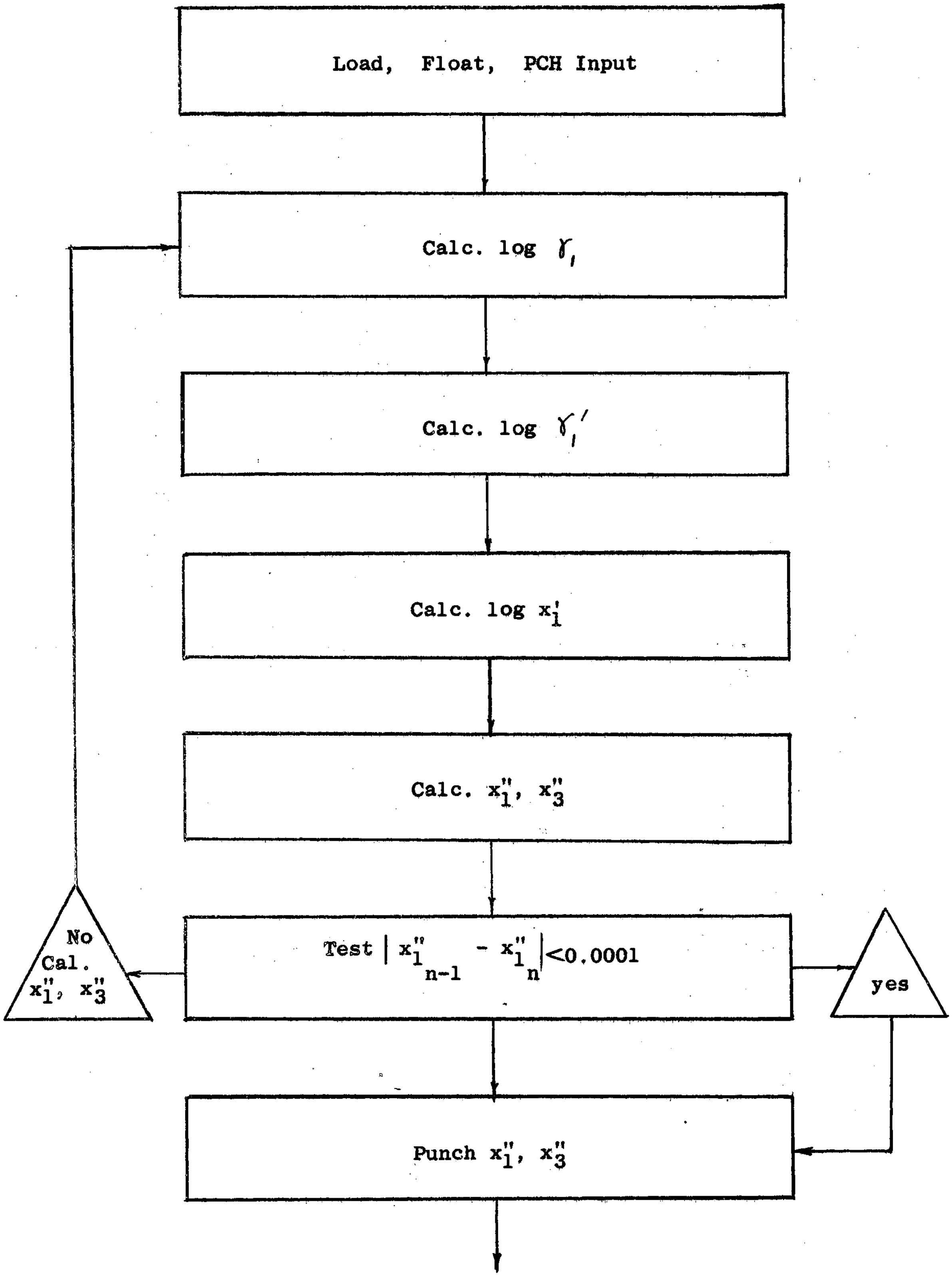

TABLE XLIV (Continued)

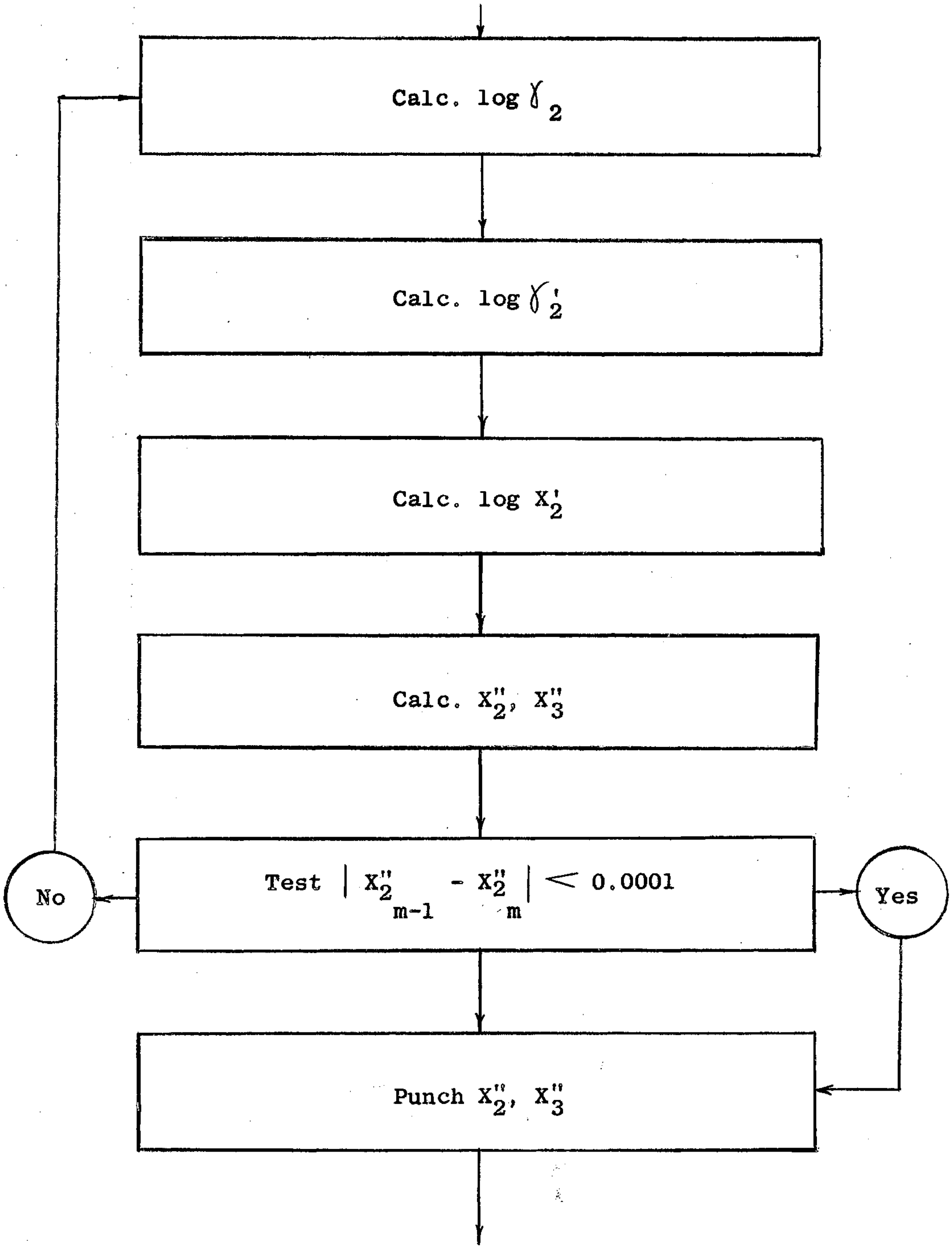

TABLE XLIV (Continued)

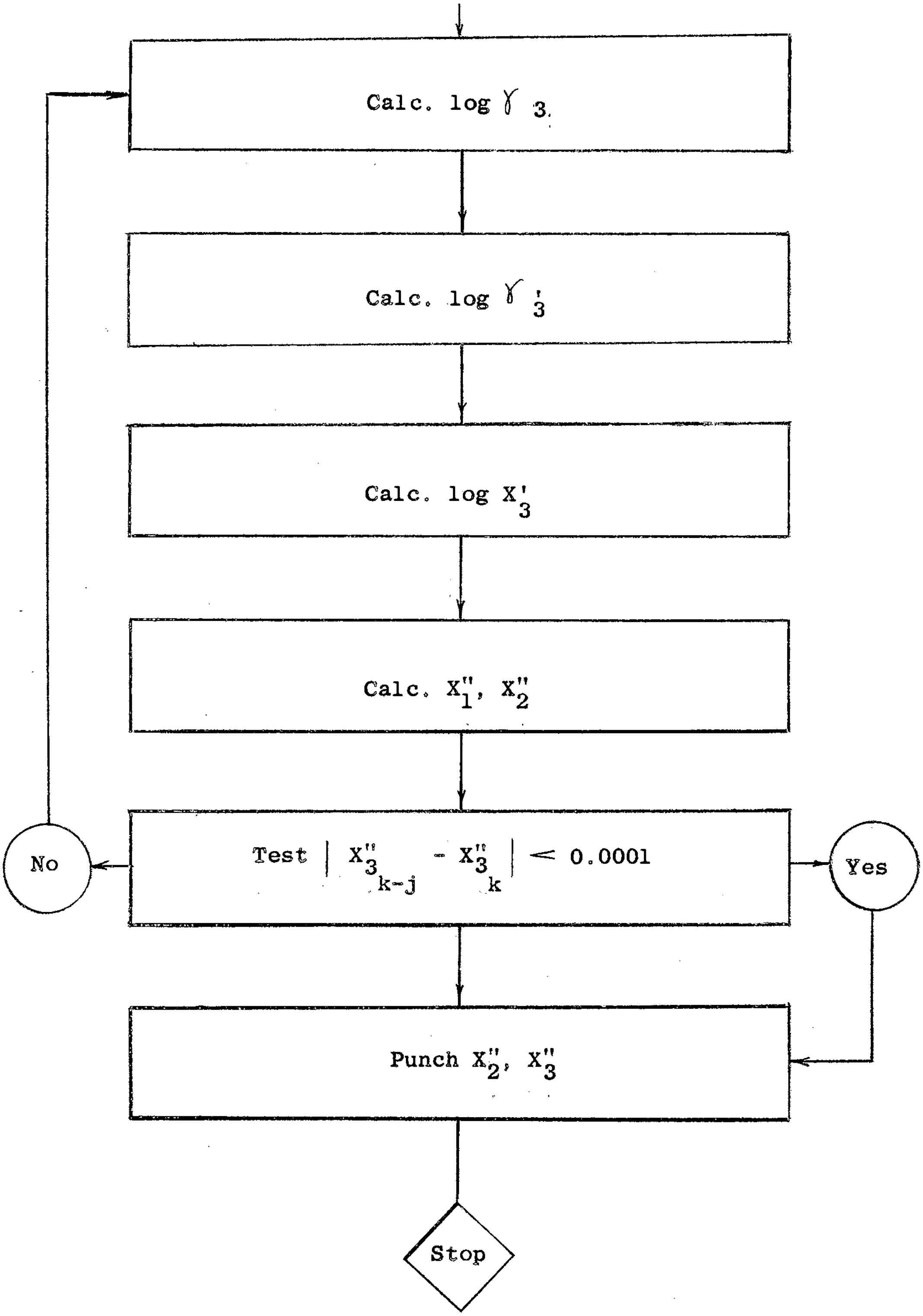

TABLE XLV

PROGRAM 0040

```
C 0000 0 CALCULATION OF LIQUID COMPOSITION FROM
C 0000 0 REDLICH-KISTER CONSTANTS
         READ,DAVE
     1 0 READ,XAA,XBA,XCA,YAA,YBA,
     1 1 YCA,AAAA
     2 0 READ,BCA,BAB,BBC,CCA,CAB,
     2 1 CBC,DCA,DAB,DBC,PROB
     3 0 CHUNG=123456789
     4 0 UTS=12345
     5 0 WW=0
   101 0 RRR=XAA
   102 0 SA=BCA*XCA*(1.0-XAA)
   103 0 SB=SA+(BAB*XBA*(1.0-XAA))
   104 0 SC=SB-(BBC*XBA*XCA)
   105 0 SD=CCA*((2.0*XCA*(1.0-XAA)*
   105 1 (XCA-XAA))-(XCA**2.0))
   106 0 SE=DCA*(3.0*XCA*(1.0-XAA)
   106 1 *((XCA-XAA)**2.0)-(2.0*(
   106 2 XCA**2.0)*(XCA-XAA)))
   107 0 SFA=CAB*((2.0*XBA)*((1.0-XAA)
   107 1 *(XAA-XBA))+(XBA**2.0))
   108 0 SG=DAB*(3.0*XBA*(1.0-XAA)
   108 1 *((XAA-XBA)**2.0)+(2.0*
   108 2 (XBA**2.0)*(XAA-XBA)))
   109 0 SH=CBC*(-2.0*XBA*XCA*(XBA
   109 1 -XCA))
   110 0 SJA=DBC*(-3.0*XBA*XCA*((XBA
   110 1 -XCA)**2.0))
   111 0 S=SC+SD+SE+SFA+SG+SH+SJA
   202 0 UA=BCA*YCA*(1.0-YAA)
   203 0 UAA=UA+(BAB*YBA*(1.0-YAA))
   204 0 UAB=UAA-(BBC*YBA*YCA)
   205 0 UAC=CCA*((2.0*YCA*(1.0-YAA)
   205 1 *(YCA-YAA))-(YCA**2.0))
   206 0 UAD=DCA*(3.0*YCA*(1.0-YAA)
   206 1 *((YCA-YAA)**2.0)-(2.0*(
   206 2 YCA**2.0)*(YCA-YAA)))
   207 0 UBA=CAB*((2.0*YBA)*((1.0-YAA)
   207 1 *(YAA-YBA))+(YBA**2.0))
   208 0 UBB=DAB*(3.0*YBA*(1.0-YAA)
   208 1 *((YAA-YBA)**2.0)+(2.0*
   208 2 (YBA**2.0)*(YAA-YBA)))
   209 0 UBC=CBC*(-2.0*YBA*YCA*(YBA
   209 1 -YCA))
   210 0 UBD=DBC*(-3.0*YBA*YCA*((YBA-
   210 1 YCA)**2.0))
   211 0 U=UAB+UAC+UAD+UBA+UBB+UBC
   211 1 +UBD
   300 0 A=LOGF(YAA)
   301 0 H=-S+U+A
   302 0 XAA=EXPF(H)
   303 0 XCA=1.0-XBA-XAA
   304 0 W=RRR-XAA
   305 0 CHUA=ABSF(W)
```

TABLE XLV (Continued)

```
 315 0 IF(CONSF(1.0))1502,1502,316
1502 0 PUNCH,CHUA,XAA,RRR
1503 0 GOTO306
 316 0 CONTINUE
 306 0 IF(CHUA-DAVE)400,400,101
 400 0 PUNCH,XAA,XCA
 499 0 ATS=12345
 500 0 VV=0
 501 0 SSS=XBA
 502 0 TA=BAB*XAA*(1.0-XBA)
 503 0 TAA=TA+(BBC*XCA*(1.0-XBA))
 504 0 TAB=TAA-(BCA*XCA*XAA)
 505 0 TAC=CAB*((2.0*XAA*(1.0-XBA)
 505 1 *(XAA-XBA))-(XAA**2.0))
 506 0 TAD=DAB*(3.0*XAA*(1.0-XBA)
 506 1 *((XAA-XBA)**2.0)-(2.0*(
 506 2 XAA**2.0)*(XAA-XBA)))
 507 0 TBA=CBC*((2.0*XCA)*((1.0-XBA)
 507 1 *(XBA-XCA))+(XCA**2.0))
 508 0 TBB=DBC*(3.0*XCA*(1.0-XBA)
 508 1 *((XBA-XCA)**2.0)+(2.0*
 508 2 (XCA**2.0)*(XBA-XCA)))
 509 0 TBC=CCA*(-2.0*XCA*XAA*(XCA
 509 1 -XAA))
 510 0 TBD=DCA*(-3.0*XCA*XAA*((XCA
 510 1 -XAA)**2.0))
 511 0 T=TAB+TAC+TAD+TBA+TBB+TBC
 511 1 +TBD
 602 0 WA=BAB*YAA*(1.0-YBA)
 603 0 WAA=WA+(BBC*YCA*(1.0-YBA))
 604 0 WAB=WAA-(BCA*YCA*YAA)
 605 0 WAC=CAB*((2.0*YAA*(1.0-YBA)
 605 1 *(YAA-YBA))-(YAA**2.0))
 606 0 WAD=DAB*(3.0*YAA*(1.0-YBA)
 606 1 *((YAA-YBA)**2.0)-(2.0*(
 606 2 YAA**2.0)*(YAA-YBA)))
 607 0 WBA=CBC*((2.0*YCA)*((1.0-YBA)
 607 1 *(YBA-YCA))+(YCA**2.0))
 608 0 WBB=DBC*(3.0*YCA*(1.0-YBA)
 608 1 *((YBA-YCA)**2.0)+(2.0*
 608 2 (YCA**2.0)*(YBA-YCA)))
 609 0 WBC=CCA*(-2.0*YCA*YAA*(YCA
 609 1 -YAA))
 610 0 WBD=DCA*(-3.0*YCA*YAA*((YCA
 610 1 -YAA)**2.0))
 611 0 W=WAB+WAC+WAD+WBA+WBB+WBC
 611 1 +WBD
 700 0 B=LOGF(YBA)
 701 0 G=-T+W+B
 702 0 XBA=EXPF(G)
 703 0 XCA=1.0-XAA-XBA
 704 0 V=SSS-XBA
 705 0 CHNA=ABSF(V)
 715 0 IF(CONSF(1.0))1504,1504,716
```

TABLE XLV (Continued)

```
1504 0 PUNCH,CHNA,XBA,SSS
1505 0 GOTO706
 716 0 CONTINUE
 706 0 IF(CHNA-DAVE)800,800,501
 800 0 PUNCH,XBA,XCA
 899 0 BTS=12345
 900 0 VVA=0
 901 0 TTT=XCA
 902 0 EA=BBC*XBA*(1.0-XCA)
 903 0 EAA=EA+(BCA*XAA*(1.0-XCA))
 904 0 EAB=EAA-(BAB*XAA*XBA)
 905 0 EAC=CBC*((2.0*XBA*(1.0-XCA)
 905 1 *(XBA-XCA))-(XBA**2.0))
 906 0 EAD=DBC*(3.0*XBA*(1.0-XCA)
 906 1 *((XBA-XCA)**2.0)-(2.0*(
 906 2 XBA**2.0)*(XBA-XCA)))
 907 0 EBA=CCA*((2.0*XAA)*((1.0-XCA)
 907 1 *(XCA-XAA))+(XAA**2.0))
 908 0 EBB=DCA*(3.0*XAA*(1.0-XCA)
 908 1 *((XCA-XAA)**2.0)+(2.0*
 908 2 (XAA**2.0)*(XCA-XAA)))
 909 0 EBC=CAB*(-2.0*XAA*XBA*(XAA
 909 1 -XBA))
 910 0 EBD=DAB*(-3.0*XAA*XBA*((XAA
 910 1 -XBA)**2.0))
 911 0 E=EAB+EAC+EAD+EBA+EBB+EBC
 911 1 +EBD
1002 0 RA=BBC*YBA*(1.0-YCA)
1003 0 RAA=RA+(BCA*YAA*(1.0-YCA))
1004 0 RAB=EAA-BAB*YAA*YBA
1005 0 RAC=CBC*((2.0*YBA*(1.0-YCA)
1005 1 *(YBA-YCA))-(YBA**2.0))
1006 0 RAD=DBC*(3.0*YBA*(1.0-YCA)
1006 1 *((YBA-YCA)**2.0)-(2.0*(
1006 2 YBA**2.0)*(YBA-YCA)))
1007 0 RBA=CCA*((2.0*YAA)*((1.0-YCA)
1007 1 *(YCA-YAA))+(YAA**2.0))
1008 0 RBB=DCA*(3.0*YAA*(1.0-YCA)
1008 1 *((YCA-YAA)**2.0)+(2.0*
1008 2 (YAA**2.0)*(YCA-YAA)))
1009 0 RBC=CAB*(-2.0*YAA*YBA*(YAA
1009 1 -YBA))
1010 0 RBD=DAB*(-3.0*YAA*YBA*((YAA
1010 1 -YBA)**2.0))
1011 0 R=RAB+RAC+RAD+RBA+RBB+RBC
1011 1 +RBD
1020 0 C=LOGF(YCA)
1021 0 D=-E+R+C
1022 0 XCA=EXPF(D)
1023 0 XAA=1.0-XBA-XCA
1024 0 VA=TTT-XCA
1305 0 CHG=ABSF(VA)
1315 0 IF(CONSF(1.0))1500,1500,1316
1500 0 PUNCH,CHG,XCA,TTT
1501 0 GOTO1306
1316 0 CONTINUE
1306 0 IF(CHG-DAVE)1400,1400,901
1400 0 PUNCH,XCA,XAA
1401 0 PUNCH,E,R,C,D
1402 0 READ,XAA,XBA,XCA,YAA,YBA,
1402 1 YCA,AAAA
1403 0 IF(AAAA)1405,101,2
1405 0 END
```

TABLE XLVI

INPUT DATA FORMAT FOR PROGRAM 0040

Card No.	Word No.	Fortran Code	Actual Value
1	1	XAA	X''_{1a}
	2	XBA	X''_{2a}
	3	XCA	X''_{3a}
	4	YAA	X'_{1a}
	5	YBA	X'_{2a}
	6	YCA	X'_{3a}
	7	XX 0000 005X	Problem No.
	8	----	
2	1	BCA	B_{31}
	2	BAB	B_{12}
	3	BBC	B_{23}
	4	CCA	C_{31}
	5	CAB	C_{12}
	6	CBC	C_{23}
	7	DCA	D_{31}
	8	----	
3	1	DAB	D_{12}
	2	DBC	D_{23}
	3	XX 0000 005X	Problem No.
	4 - 8	----	
4	1	XAA	X''_{1b}
	2	XBA	X''_{2b}

TABLE XLVI (Continued)

Card No.	Word No.	Fortran Code	Actual Value
	3	XCA	X''_{3b}
	4	YAA	X'_{1b}
	5	YBA	X'_{2b}
	6	YCA	X'_{3b}
	7	00 0000 0000	
	8	----	
		⋮	
N 2	1	XAA	X''_{1n}
	2	XBA	X''_{2n}
	3	XCA	X''_{3n}
	4	YAA	X'_{1n}
	5	YBA	X'_{2n}
	6	YCA	X'_{3n}
	7	00 0000 0000	
	8	----	

TABLE XLVII

OUTPUT DATA FORMAT FOR PROGRAM 0040

Card No.	Word No.	Fortran Code	Actual Value
1	1	XAA	X''_{1a}
	2	XCA	X''_{3a}
	3 - 8	----	
2	1	XBA	X''_{2a}

TABLE XLVII (Continued)

Card No.	Word No.	Fortran Code	Actual Value
	2	XCA	X''_{3a}
	3 - 8	-----	
3	1	XAA	X''_{1a}
	2	XCA	X''_{3a}
	3 - 8	-----	
4	1	E	See Fortran program
	2	R	
	3	C	
	4	D	
	5 - 8	-----	
5	1	XAB	X''_{1b}
	2	XCB	X''_{3b}
	3 - 8	-----	
6	1	XBB	X''_{2b}
	2	XCB	X''_{3b}
	3 - 8	-----	
7	1	XAB	X''_{1b}
	2	XCB	X''_{3b}
	3 - 8	-----	
8	1	E	See Fortran program

TABLE XLVII (Continued)

Card No.	Word No.	Fortran Code	Actual Value
	2	R	
	3	C	
	4	D	
	5 - 8	----	

etc.

Machine Operation:

Console Settings:

Storage entry

70 1952 9999 - conditional punch for each iteration

+ no punch on each iteration

70 1952 9988 on line operation

70 1952 9999 off line operation

70 1952 9989 on line punch

Programmed	RUN
Half Cycle	RUN
Control	RUN
Display	UPPER
Overflow	SENSE
Error	STOP

Run New Problem Without Re-running Program:

1. Program stop. Set address selection switch to 1999
2. Control switch changed manual
3. Depress computer reset
4. Depress transfer

5. Return control switch to RUN
6. Depress program start
7. Feed next set of problem data

Running Time:

About 3 to 5 minutes for each tie-line calculation. If there are 10 tie-lines in each problem to be evaluated, then about 40 minutes is required.

Program 0045

Conversion of Mole Fraction to Weight Fraction

Purpose of Program:

This program is developed for the purpose of conversion of mole fraction to weight fraction, a reverse process of the program 0021. This process can be omitted if the solubility curve and tie lines are plotted on the base of mole fraction.

Flow Diagram: Table XLVIII

Program Language: IBM 650 Fortran

Program: Table XLIX

Input and Output Data:

Data are in floating point system. The detail formats for input data and for output data are as shown in Table LI and Table LII respectively.

Punch Instruction: Same as program 0021

Machine Operation: Same as program 0021

TABLE XLVIII

FLOW DIAGRAM OF PROGRAM 0045 - CONVERSION OF MOLE FRACTION TO WEIGHT FRACTION

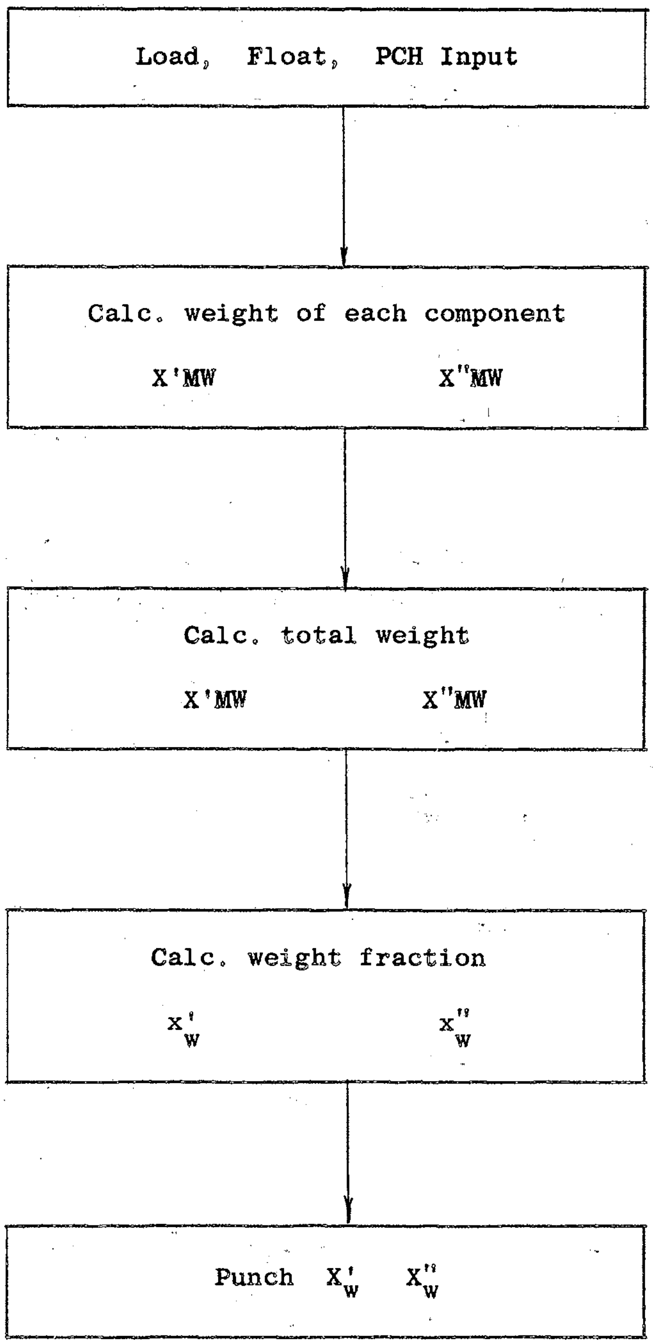

TABLE XLIX

PROGRAM 0045

```
C 0000 0 CONVERSION OF MOLE FRACTION
C 0000 0 TO WEIGHT FRACTION
     1 0 READ,XAA,XBA,XCA,AMW,BMW,CMW
     2 0 W=(XAA*AMW)+(XBA*BMW)+(XCA*
     2 1 CMW)
     3 0 XWAA=(XAA*AMW)/W
     4 0 PUNCH,XWAA
     5 0 XWBA=(XBA*BMW)/W
     6 0 PUNCH,XWBA
     7 0 XWCA=(XCA*CMW)/W
     8 0 PUNCH,XWCA
     9 0 READ,XAA,XBA,XCA,AMW,BMW,CMW
    10 0 IF(AMW)12,12,2
    12 0 END
```

TABLE L

INPUT DATA FORMAT

Card No.	Word No.	Fortran Code	Actual Value
1	1	XAA	X_{1a}
	2	XBA	X_{2a}
	3	XCA	X_{3a}
	4	AWM	MW_1
	5	BWM	MW_2
	6	CWM	MW_3
	7	----	
	8	----	
2	1	XAA	X_{1b}
	2	XBA	X_{2b}
	3	XCA	X_{3b}
	4	AWM	MW_1
	5	BWM	MW_2
	6	CWM	MW_3
	7	----	
	8	----	

etc.

TABLE LI

OUTPUT FORMAT FOR PROGRAM 0045

Card No.	Fortran Code	Actual Value
1	XWAA	x_{w1a}
2	XWBA	x_{w2a}
3	XWCA	x_{w3a}
4	XWAA	x_{w1b}
5	XWBA	x_{w2b}
6	XWCA	x_{w3b}
etc.		

VITA

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