PHASE EQUILIBRIA IN COMPLEX NON-IDEAL SYSTEMS

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PHASE EQUILIBRIA IN COMPLEX NON-IDEAL SYSTEMS

Charles Fuller Bethea

ABSTRACT

The industrial development of the unit operation of liquid-liquid extraction has been retarded by the extensive pilot plant studies and equipment evaluations necessary for the proper design of prototype units. Additional delays have been encountered due to the lack of a simple means of evaluating the results of pilot-sized equipment. In most cases, this has required the laborious and time consuming task of experimental determination of the phase equilibria for the system in use.

The purpose of this research was to extend the present-known means for obtaining phase equilibria in complex non-ideal systems; to formulate prediction methods whereby ternary phase equilibria, usually laboriously determined in the laboratory, might be estimated from easily obtainable binary liquid-liquid solubility measurements; and to test these estimations by comparison with reliable experimental equilibrium measurements.

Accordingly, experimental liquid-liquid equilibria were determined for ten different ternary systems involving the five different hydrocarbon pairs: cyclohexane-n-heptane, cyclohexane-isooctane, cyclohexane-cetane, cyclohexane-octene-1, and octene-1-n-heptane. Each of the hydrocarbon pairs was chosen either to illustrate the effect of molecular weight or to illustrate separations between hydrocarbon types such as naphthene-paraffin, naphthene-isoparaffin, naphthene-olefin, or olefin-

paraffin. Each was studied at one or more of the three temperature levels of 30, 60, and 90°C. with furfural as the selective solvent.

Experimental mutual solubility data were determined for the seven hydrocarbon-solvent binary pairs, furfural-cyclohexane, furfural-n-heptane, furfural-isooctane, furfural-cetane, furfural-octene-1, furfural-benzene, and furfural-toluene. These data were utilized to make activity coefficient calculations based both on van Laar and Scatchard-Hamer equations for one or more of the temperatures 30, 60, and 90°C. Where activity coefficients were desired at temperatures above the critical solution temperature of the binary pair, i.e., at complete miscibility, extrapolations were made based on the assumption that the differential heats of solution were constant. The validity of the assumption was supported by data which indicated the heats of solution were constant at the temperatures below the critical solution temperature.

An estimation method was developed and demonstrated for estimating phase equilibria in ternary systems from binary solubility data or a binodal solubility curve, and an activity coefficient equation. The method is based on the equality of activities in coexisting equilibrium phases, on the assumption that the activity coefficient of a component in a solution with a selective solvent is a function only of the binary solvent-hydrocarbon activity coefficient curve and the total hydrocarbon content of the solution, and on the assumption that the furfural content in a ternary solution may be estimated from the furfural content of the two binary furfural-hydrocarbon solutions.

The use of the estimation methods showed a precision of an equal order of magnitude regardless of whether the calculations were initiated from the solvent phase or from the hydrocarbon phase provided

that the calculations converged rapidly to a solution. Where rapid convergence was not obtained, advantage was gained by initiating calculations from the solvent phase.

The use of activity coefficients calculated with the van Laar equations showed a better correlation than those calculated with the Scatchard-Hamer equations when the estimation method was applied to the system cyclohexane-n-heptane-furfural at 30°C. However, with the system cyclohexane-cetane-furfural at 30°C., the use of the van Laar equations showed advantage in one concentration range and the use of Scatchard-Hamer equations showed advantage in the other.

The estimated equilibria based on the van Laar activity-coefficient equations showed good to excellent agreement with experimental equilibria for the systems cyclohexane-n-heptane-furfural, cyclohexane-isooctane-furfural, and octene-1-n-heptane-furfural at all the temperatures studied over the range of 30, 60, and 90°C. The estimated equilibria for cyclohexane-cetane-furfural showed progressive improvement with increased temperature for 30, 60 and 90°C. The discrepancy at low temperatures was apparently a molecular weight or shape effect, but the improved agreement with experimental data at 60 and 90°C. suggests the presence of a temperature coefficient.

Estimated and experimental equilibria for cyclohexane-octene-1-furfural were not in as good agreement, with regard to the difficulty of separation, as the other systems of this study. The estimations were conservative, however, and would be of value in engineering design work.

CHAPTER I

INTRODUCTION

Recent developments in liquid-liquid extraction have provided industry with a powerful and versatile tool. Separations that have been physically or economically unfeasible by conventional means of fractional distillation, absorption, adsorption, or crystallization, are now often easy to attain by use of solvent extraction. Some of the inherent advantages of liquid-liquid extraction over conventional separation means, such as fractional distillation, have been demonstrated by Varteressian and Fenske (1) with the separation of methylcyclohexane and n-heptane. Well-known applications of liquid-liquid extraction in the refining of lubricating oils, have recently been extended to include the separation of olefins and acetylenes for chemicals manufacture, the separation of carbon black feed stocks from highly refractory refinery residues, the purification of drugs and fine chemicals, and the preparation of aviation gasoline blend stocks.

The industrial development of liquid-liquid extraction has been retarded by the extensive pilot-plant studies and equipment evaluations necessary to guide the design of prototype units. The delays were due largely to lack of a means to evaluate the results of the pilot-sized equipment. This, in most cases, required the laborious and time consuming task of experimental determination of the phase equilibria

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(1) Varteressian, K. A. and Fenske, M. R., Ind. Eng. Chem. 29, 270 (1937).

for the system in use.

Thus, there is a considerable need for a simple and reliable method for estimating phase equilibria in complex non-ideal systems. A method is desired that might be based on vapor pressures, liquid-liquid solubilities, or other easily obtainable experimental data, and yet have a sufficiently sound theoretical basis to warrant extrapolation into systems involving variations in the nature of the selective solvent, the temperature of operation, the molecular weights of constituents and the hydrocarbon types.

The literature is abundant with so-called methods for the interpolation and prediction of tie-line data for use in liquid-liquid extraction. The International Critical Tables (2) and Sherwood (3) describe methods for the construction of conjugate lines for extending phase equilibria. Brancker, Hunter, and Nash (4) and Bachman (5) treat the interpolation and estimation of tie-line data. However, none of these methods amount to more than an interpolation of the existing data, and all require at least two sets of equilibrium tie-lines and knowledge of the equilibrium saturation curves. Moreover, they were developed for systems containing only two nonconsolute components, one of which was usually water, and are of limited value for systems containing two or more nonconsolute pairs or for systems with substantial miscibility of

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(2) International Critical Tables, Vol. III, 1st. ed., p. 398, New York, McGraw-Hill Book Co.

(3) Sherwood, T. K., Absorption and Extraction, 1st. ed., p. 242, New York, McGraw-Hill Book Co., 1937.

(4) Brancker, A. V., Hunter, T. G., and Nash, A. W., Ind. Eng. Chem., Anal. Ed., 12, 35 (1940).

(5) Bachman, I., Ind. Eng. Chem., Anal. Ed., 12, 38 (1940).

the nonconsolute components.

Othmer and Tobias (6) studied the results of Brancker, et al. (4) and Bachman (5) and through utilization of the Nernst distribution law (7), as revised by Hand (8), derived a plot for tie-line interpolation in systems with substantial miscibility. However, the previous restrictions to aquous systems and to only two nonconsolute components were still apparent. They then derived an expression (9) for the prediction of tie-line data based on the partial pressures of ternary liquid systems. The expression involved several assumptions as well as knowledge of vapor pressure data, and even then proved to be good only when the two nonconsolute components remained almost immiscible when the third component was added.

Darwent and Winkler (10) noted a reference by Brancker, Hunter, and Nash (4) relating to the applicability of the tie-line interpolation method of Sherwood (3) to the data of Varteressian and Fenske (11) on a hydrocarbon-type system. They were then inspired to determine whether the

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(3) Sherwood, op. cit., p. 242.

(4) Brancker, Hunter, and Nash, op. cit., p. 35.

(5) Bachman, op. cit., p. 38.

(6) Othmer, D. F., and Tobias, P. E., Ind. Eng. Chem. 34, 693 (1942).

(7) Nernst, Z., Physik Chem., 8, 110 (1891).

(8) Hand, D. B., J. Phys. Chem., 34, 1961 (1930).

(9) Othmer, D. F., and Tobias, P. E., Ind. Eng. Chem., 34, 696 (1942).

(10) Darwent, B. De B., and Winkler, C. A., J. Phys. Chem. 47, 442 (1943)

(11) Varteressian, K. A. and Fenske, M. R., Ind. Eng. Chem. 28, 928 (1936).

method was generally applicable and independent of temperature. Their results were good only for hydrocarbon mixtures which contained large amounts of paraffin and were far removed from the plait point.

Hildebrand (12) has proposed a method for predicting ternary liquid equilibria from only the activities of the binary solutions. The results, at low concentration, compare favorably with observed data, but are restricted to immiscible solvents. Carlson and Colburn (13) extended the Hildebrand (12) proposal in the formulation of a method for the evaluation of partition coefficients in liquid-liquid systems from binary activity coefficient curves. Again, however, the method was restricted to low mutual solubilities. Treybal (14) also extended the Hildebrand proposal (12) by modifying the abscissa of activity coefficient-composition curves to account for an "effective solute concentration" in systems restricted as above to one pair of nonconsolute components. Vapor-liquid equilibria for the two consolute pair of components, or activity coefficients derived therefrom, and knowledge of the liquid-liquid solubility curve are required for the method. Even so, the agreement with experimental equilibria is only fair.

Campbell (15) applied the Freundlich equation to the correlation of data relating to the distribution of a solute between any two phases.

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(12) Hildebrand, J. H., Solubility of Non-Electrolytes, 2nd ed., p. 184, New York, Reinhold Publishing Corp., 1936.

(13) Carlson, H. C. and Colburn, A. P., Ind. Eng. Chem., 34, 581 (1942).

(14) Treybal, R. E., Ind. Eng. Chem., 36, 875 (1944).

(15) Campbell, J. A., Ind. Eng. Chem., 36, 1158 (1944).

The correlation was good, but the method required two sets of equilibrium data and therefore should be considered only with the other means for interpolation.

Dryden (16) applied a hyperbolic equation derived by Varteressian and Fenske (11) to show a method of correlating equilibrium relations between conjugate phases on a solvent-free basis. Three sets of equilibrium data were required to establish the method. Fourteen systems were tested and four failed to correlate.

Brown (17) noted the usefulness of the activity coefficient concept in the extension of binary and ternary data involving two equilibrium phases. He made use of binary liquid-liquid solubility data and the van Laar equations (13) to calculate the van Laar constants and the so-called selectivity of the separation. His term selectivity was actually a sort of partition coefficient based on the extremities of activity coefficient-composition graphs and the assumption that it was a constant.

The author (18), working under the direction of K. H. Hachmuth of the Phillips Petroleum Company in 1948, was able to satisfactorily predict the equilibria for the system ethane-ethylene-acetonitrile some time before the experimental determinations were made at Princeton

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(11) Varteressian, K. A., and Fenske, M K., Ind. Eng. Chem., 28, 928 (1936).

(13) Carlson and Colburn, op. cit., p. 581.

(16) Dryden, C. E., Ind. Eng. Chem., 35, 492 (1943).

(17) Brown, T. F., Ind. Eng. Chem., 40, 103-6 (1948).

(18) Bethea, C. F., Unpublished Memorandum, Phillips Petroleum Company, 1949.

University (19). The comparison of these equilibria is shown in Figure 1. The prediction method differed from Brown's (17) in that the activity coefficient-composition curve was based on independently determined vapor-liquid equilibria. A different assumption was made regarding the activity coefficient of a component in solution, and the method was not restricted to constant selectivity.

Hachmuth (20) compared experimental (21) and predicted equilibria for the system cyclohexane-n-heptane-aniline as shown in Figure 2, and concluded that his predictions were better than the experimental data. The method differed significantly from that used in the acetonitrile system only in the method for determination of the activity coefficient-composition curve. Hachmuth derived and used his own equation (20, 22) for calculating activity coefficients from binary liquid-liquid solubility.

Pennington and Marwil (23) extended the method employed by Hachmuth (20) and Bethea (18) except that as with Brown (17) activity coefficients were evaluated from binary liquid-liquid solubilities and the

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(17) Brown, op. cit., p. 103.

(19) Sykes, H B., Phase Equilibrium in Condensed Ethane-Ethylene-Solvent Systems --- The Separation of Ethane and Ethylene by Liquid-Liquid Extraction, M. S. Thesis in Engineering, Princeton University, 1948.

(20) Hachmuth, K. H., Unpublished Fractionation Symposium, Phillips Petroleum Company, 1949.

(21) Hunter, T. G., and Brown, T. F., Ind. Eng. Chem., 39, 1343 (1947).

(22) Bethea, C. F., "A Correlation of Activity Coefficients for the Furfural-Water System," M. S. Thesis, Oklahoma Institute of Technology, Stillwater, Oklahoma, 1952.

(23) Pennington, E. N., and Marwil, S. J., Ind. Eng. Chem., 45, 1371 (1953).

SYSTEM: ETHANE-ETHYLENE-ACETONITRILE

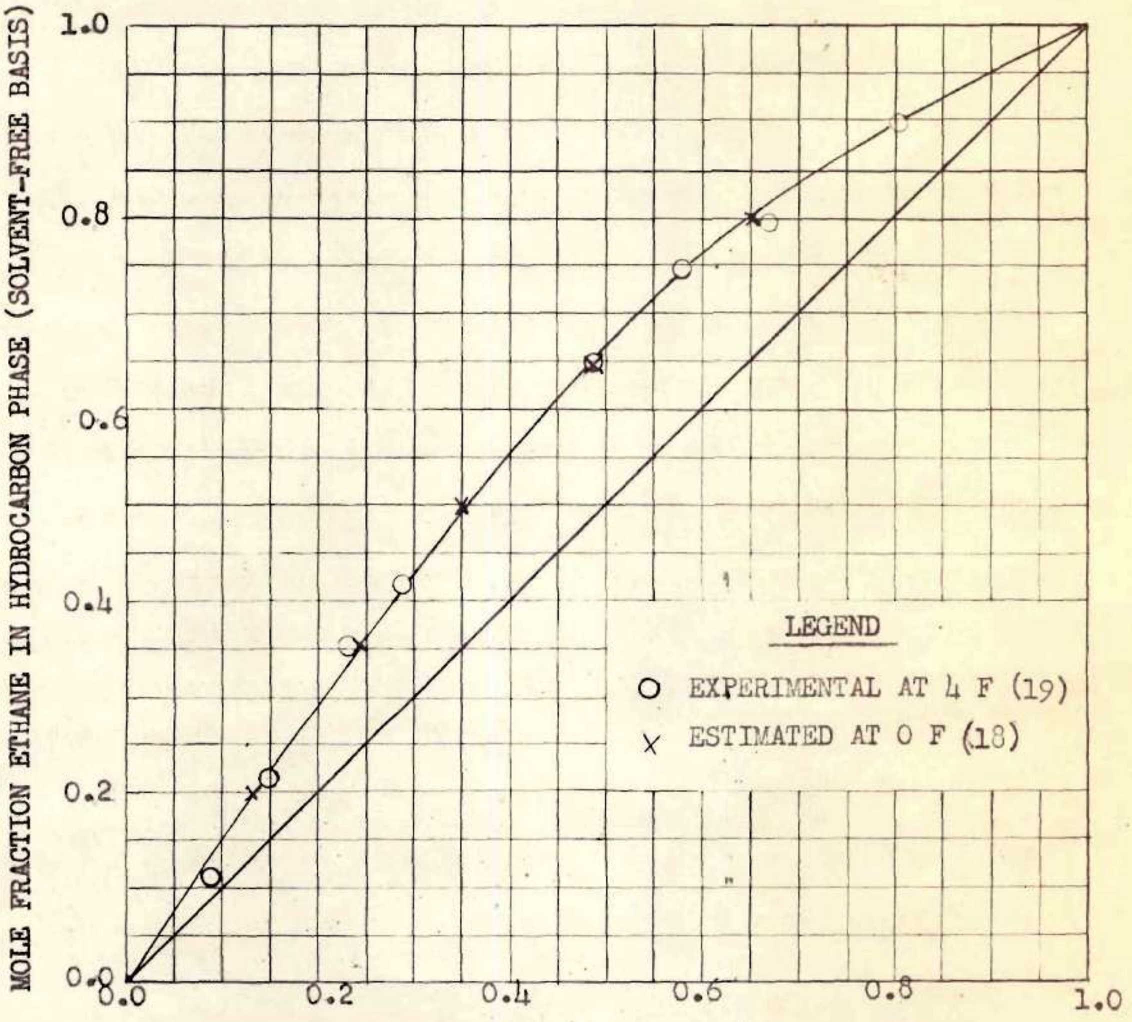

FIG. 1. ESTIMATED AND EXPERIMENTAL LIQUID-LIQUID EQUILIBRIA FOR ETHANE, ETHYLENE, AND ACETONITRILE.

SYSTEM: n-HEPTANE - CYCLOHEXANE - ANILINE AT 25 C.

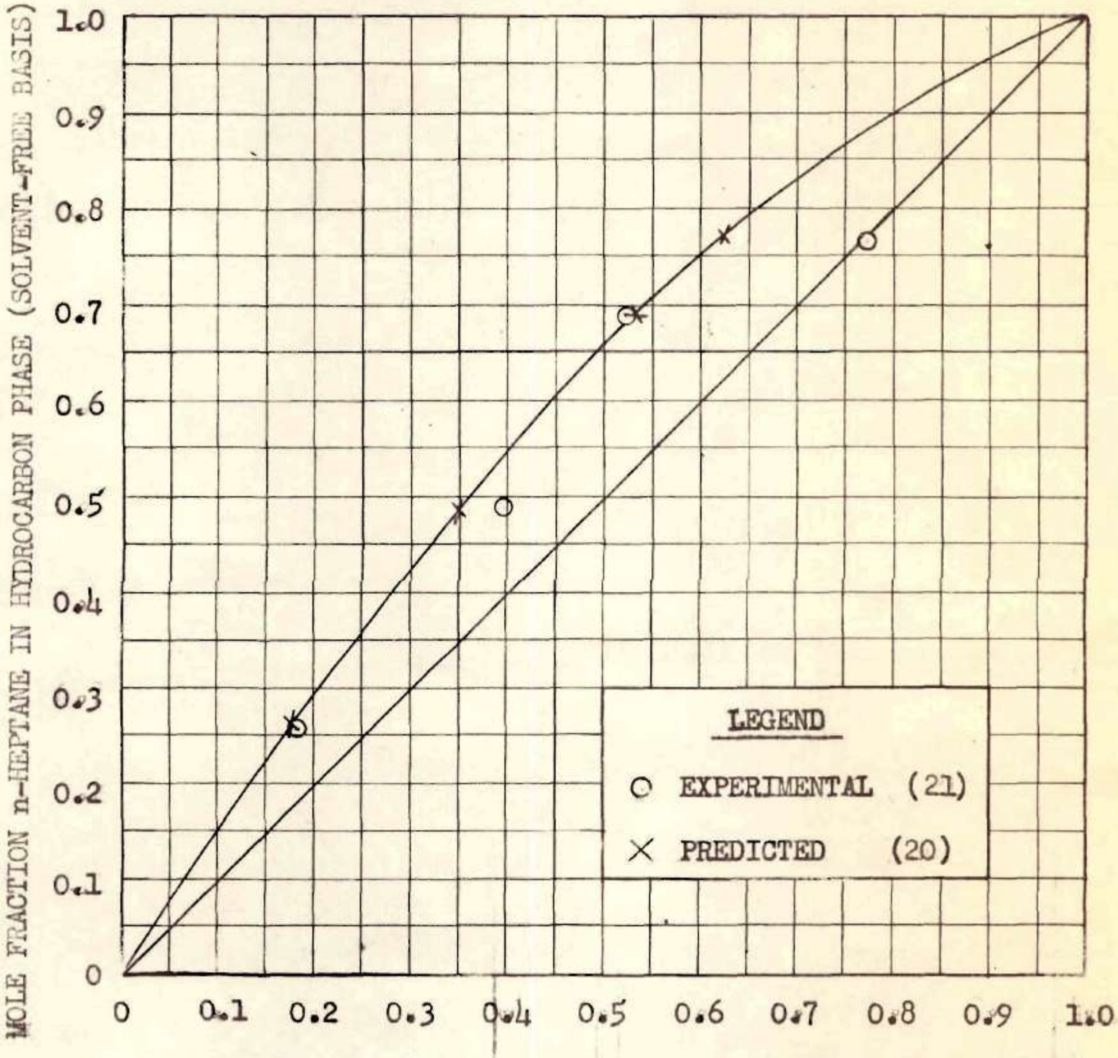

FIG. 2 . ESTIMATED AND EXPERIMENTAL LIQUID-LIQUID EQUILIBRIA FOR n-HEPTANE, CYCLOHEXANE, AND ANILINE.

van Laar equation (13). The investigators compared experimental and predicted equilibria for seven systems, five of which were taken from the literature (10, 11, 21, 24). Their separations involved only naphthenes and paraffins in the range of six to eight carbon atoms and at low temperatures. The authors recognized that some of their literature data were of questionable accuracy, and therefore were not able to formulate conclusions when the prediction method did not correlate well.

This disseration summarizes the results of a study to extend the estimation methods of Hachmuth, Bethea, and Pennington-Marwil, with modifications as necessary, to systems involving a variety of hydrocarbon types, temperatures, and molecular weights. Accordingly, reliable experimental phase equilibria were determined for ten ternary systems with furfural as the selective solvent and hydrocarbon pairs of the types: naphthene-paraffin, naphthene-isoparaffin, naphthene-olefin, and olefin-paraffin. These systems involved a variation in molecular weight from 84.16 (cyclohexane) to 226.44 (cetane), at temperatures of 30, 60, and 90°C. The experimental ternary equilibria are compared with ternary equilibria estimated by various methods from experimental binary liquid-liquid solubility measurements.

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(10) Darwent and Winkler, op. cit., p. 442.

(11) Varteressian, K. A., and Fenske, M. R., Ind. Eng. Chem., 28, 928 (1936).

(13) Carlson and Colburn, op. cit., p. 581.

(21) Hunter and Brown, op. cit., p. 1343.

(24) Herholsheimer, G., "Solvent Extraction of Low Molecular Weight Hydrocarbons," Ph.D. Thesis, The Pennsylvania State College, 1942.

CHAPTER II

THEORY OF PREDICTION METHOD

The prediction methods employed in this paper are based on the general equilibrium equations of thermodynamics, activity coefficient relationships derived therefrom, and certain assumptions regarding the activity coefficient of a component in non-ideal liquid solutions. However, before proceeding into the details of the prediction methods, it seems advisable to review some of the pertinent theory regarding equilibrium and activity coefficient equations.

A. Equilibrium Equations

In his celebrated paper "On the Equilibrium of Heterogeneous Substances," Josiah Willard Gibbs (25) developed as a general criterion of equilibrium the relation

$$dF = 0 \text{ at constant P and T where only P-V work is done} \qquad (1)$$

Here F is the total free energy of the system, and the derivative is with respect to all possible variations except those of P and T. Gibbs related the free energy function to the chemical potential by the expression

$$\mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{P,T,N_A ----} \qquad (2)$$

---

(25) Gibbs, J. W., Trans. Connecticut Acad., 3, 108-284, 343-524 (1875-1878).

This states that the chemical potential of any component in a phase is the rate at which the total free energy of that phase changes as one changes the amount of that particular component, keeping the pressure, temperature, and amounts of all the other components of the phase the same.

Since by definition

$$F = E - TS + pv. \tag{3}$$

On differentiation we obtain

$$dF = dE - TdS - SdT + pdV + Vdp$$

which, when simplified by the first law expression

$$dE - TdS + pdV = 0$$

becomes

$$dF = -SdT + vdp. \tag{4}$$

Equation 4 applies to any homogeneous solution of fixed composition. Consider a solution containing N_A, N_B, --- N_N moles of components A, B, --- N respectively. The number of moles of any component can be varied independently and will cause a change in the free energy of the solution. Thus,

$$dF = -SdT + Vdp + \frac{\partial F}{\partial N_A}dN_A + \frac{\partial F}{\partial N_B}dN_B + ---- + \frac{\partial F}{\partial N_N}dN_N \tag{5}$$

For phase equilibrium in two or more coexisting phases, we may substitute the Gibbs chemical potential expression (equation 2) into equation 5 and, designating different phases by primes, write

$$\begin{gathered} dF' = -S'dT + V'dp + \mu'_A dN'_A + \mu'_B dN'_B + ---- + \mu'_N dN'_N \\ dF'' = -S''dT + V''dp + \mu''_A dN''_A + \mu''_B dN''_B + ---- + \mu''_N dN''_N \end{gathered} \qquad (6)$$

for as many phases as there are in the system. In this expression the prime was dropped from temperature and pressure terms because of the condition of equilibrium. Now, if F represents the total free energy of the entire system, then

$$F = F' + F'' + F''' + ---- + F^Z \qquad (7)$$

and upon differentiation

$$dF = dF' - dF'' + dF''' + ---- + dF^Z \qquad (8)$$

Then by combining equations 6 and 8 and applying the general criterion of equilibrium (equation 1) we arrive at the relation

$$\begin{gathered} \mu'_A dN'_A + \mu'_B dN'_B + \mu'_C dN'_C + ---- + \mu'_N dN'_N + \\ \mu''_A dN''_A + \mu''_B dN''_B + \mu''_C dN''_C + ---- + \mu''_N dN''_N + \\ \mu^Z_A dN^Z_A + \mu^Z_B dN^Z_B + \mu^Z_C dN^Z_C + ---- + \mu^Z_N dN^Z_N = 0 \end{gathered} \qquad (9)$$

However, since the total mass of each component remains constant in a closed system we can write

$$dN'_A + dN''_A + dN'''_A + ---- dN^Z_A = 0 \qquad (10)$$

and a similar equation for each of the other components. Now, to satisfy both equations 9 and 10 it is necessary that

$$\mu'_A = \mu''_A = \mu'''_A = ----\mu^Z_A$$
$$\mu'_B = \mu''_B = \mu'''_B = ----\mu^Z_B \qquad (11)$$
$$\mu'_N = \mu''_N = \mu'''_N = ----\mu^Z_N$$

In other words, the necessary condition for equilibrium is that the chemical potentials of a given component shall be equal in all the phases.

In this study it was found convenient to treat equilibrium through use of activity rather than chemical potential. Therefore, it was necessary to establish the relationships between them. The fugacity of any component of a solution $\overline{f}_i$ may be defined by the equation

$$d\mu_i = RTd\ln\overline{f}_i \qquad (12)$$

Integrating between two isothermal states

$$\mu_i - \mu^\circ_i = RT\ln\frac{\overline{f}_i}{f^\circ_i} \qquad (13)$$

where μ°_i and f°_i represent the chemical potential and fugacity, respectively, of component i in some arbitarily chosen initial standard state of pressure and concentration. Hence they are functions only of the temperature. Now the activity of a component in a solution may be defined by the equation

$$\overline{a}_i = \frac{\overline{f}_i}{f^\circ_i} \qquad (14)$$

This may be substituted into equation 13 as follows:

$$\mu_i - \mu^\circ_i = RT\ln\overline{a}_i \qquad (15)$$

If one chooses to designate μ°_i and f°_i as the chemical potential and fugacity respectively of pure component i as a liquid at the temperature and pressure of the system, it is apparent from equations 11 and 15 that at equilibrium in coexisting phases

$$\bar{a}'_i = \bar{a}''_i = \bar{a}'''_i = \text{----}\bar{a}^Z_i \qquad (16)$$

for as many components as there are in the system.

The above selection of standard state is the usual one for materials that are normally liquid. It was convenient to use that state in this report so as to be able to utilize the activity coefficient equations of Carlson and Colburn (13) and Hachmuth (20), also based on that reference state. Equation 16 relates the exact condition of equilibrium reported by Hildebrand (12), and utilized by Brown (17), Bethea (18), Hachmuth (20), and Pennington and Marwil (23). The expression is thermodynamically rigorous.

B. Activity Coefficient Equations

1. General Equations.--The term activity coefficient is by definition

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(12) Hildebrand, op. cit., p. 184.

(13) Carlson and Colburn, op. cit., p. 581.

(17) Brown, op. cit., p. 103.

(18) Bethea, C. F., Unpublished Memorandum, Phillips Petroleum Company, 1949.

(20) Hachmuth, op. cit., p. 83.

(23) Pennington and Marwil, op. cit., p. 1371.

$$\gamma_i = \frac{\bar{a}_i}{X_i} \tag{17}$$

or is the activity of equation 16 divided by mole fraction. This is utilized in the formulation of the activity coefficient form of the Gibbs-Duhem equation, expressed for binary mixtures as follows:

$$X_1\left(\frac{\partial \ln \gamma_i}{\partial X_i}\right)_{T\ P} = -X_2\left(\frac{\partial \ln \gamma_2}{\partial X_1}\right)_{T\ P} \tag{18}$$

This equation is thermodynamically rigorous in the differential form, but the magnitudes of the slopes are difficult to determine precisely. Therefore, studies have been made to obtain convenient mathematical solutions of the differential equation. Wohl (26) has developed some general equations that contain the three constants A, B, and $\frac{q_1}{q_2}$. These equations may be resolved into either the van Laar, Margules, or Scatchard-Hamer equations if the proper choice of the $\frac{q_1}{q_2}$ term is made. The Wohl equations are

$$\begin{aligned} \log \gamma_1 &= Z_2^2\left[A + 2\left(B\frac{q_1}{q_2} - A\right)Z_1\right] \\ \log \gamma_2 &= Z_1^2\left[B + 2\left(A\frac{q_2}{q_1} - B\right)Z_2\right] \end{aligned} \tag{19}$$

Here the $\frac{q_1}{q_2}$ ratio is an empirical constant. However, it is sometimes called the ratio of effective or generalized molal volumes because of its relation to Z, termed the effective volume fraction. The relations are

$$Z_1 = \frac{X_1}{X_1 + \frac{q_2}{q_1}X_2}$$

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(26) Wohl, K., Trans. Am. Inst. Chem. Engrs., <u>42</u>, 215-50 (1946).

and

$$Z_2 = \frac{X_2 \frac{q_2}{q_1}}{X_1 + \frac{q_2}{q_1} X_2}$$

The A and B constants are the values for log γ_1, and γ_2 at the mole fraction of component one (X_1) equal to zero and unity respectively. By the use of various assumptions regarding the ratio of the effective molal volumes $\frac{q_2}{q_1}$, the number of empirical constants may be reduced to two - A and B.

Margules (27) in effect assumed that $\frac{q_2}{q_1} = 1.0$. With this assumption equations 19 reduce to the familiar Margules equations as modified by Carlson and Colburn (13)

$$\log \gamma_1 = X_2^2 \left[A - 2(B-A)X_1 \right] = (2B-A)X_2^2 + 2(A-B)X_2^3$$
$$\log \gamma_2 = X_1^2 \left[B - 2(A-B)X_2 \right] = (2A-B)X_1^2 + 2(B-A)X_1^3 \qquad (20)$$

Scatchard (28) and co-workers (29, 30) took the effective molal volumes as equal to the actual molal volumes of the pure components. On this basis $\frac{q_2}{q_1} = \frac{V_2}{V_1}$ and equations 19 reduce to what is termed the Scatchard-Hamer equations.

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(13) Carlson and Colburn, op. cit., p. 581.

(27) Margules, M. Sitzber, Akad. Wiss. Wien. Math. naturw, Klasse, II, 104, 1243-78 (1895).

(28) Scatchard, G., Chem. Rev., 8, 321 (1931).

(29) Scatchard, G. and Prentiss, S. S., J. Am. Chem. Soc., 56, 1486 (1934).

(30) Scatchard, G. and Hamer, W. J., J. Am. Chem. Soc., 57, 1805 (1935).

$$\log \gamma_1 = Z_2^2\left[A + 2\left(B \frac{V_1}{V_2} - A\right)Z_1\right]$$
$$\log \gamma_2 = Z_1^2\left[B + 2\left(A \frac{V_2}{V_1} - B\right)Z_2\right] \qquad (21)$$

If it is assumed that $\frac{q_1}{q_2} = \frac{A}{B}$ equations 19 reduce to the form developed by van Laar (31, 32) as rearranged by Carlson and Colburn (13).

$$\log \gamma_1 = AZ_2^2 = \frac{AX_2^2}{\left(\frac{A}{B}X_1 - X_2\right)^2}$$
$$\log \gamma_2 = BZ_1^2 = \frac{BX_1^2}{\left(X_1 + \frac{B}{A}X_2\right)^2} \qquad (22)$$

2. Evaluation of Constants by Liquid-Liquid Solubility.--For systems that form two liquid phases the empirical constants A and B of equations 20, 21, and 22 may be evaluated from binary liquid-liquid solubility measurements. Substituting $\bar{a}_i = \gamma_i X_i$ from equation 17 into the condition for equilibrium (equation 16), and designating the liquid phases by primes one obtains

$$\frac{\gamma_1'}{\gamma_1''} = \frac{X_1''}{X_1'}$$

and (23)

$$\frac{\gamma_2'}{\gamma_2''} = \frac{X_2''}{X_2'}$$

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(13) Carlson and Colburn, op. cit., p. 581.

(31) van Laar, J. J., Z. phys. Chem., 72, 723 (1910).

(32) van Laar, J. J., Z. phys. Chem., 185, 35 (1929).

Taking the logarithms of both sides of these equations and substituting into the Scatchard-Hamer equations (equation 21) we get

$$\log\frac{\gamma_1'}{\gamma_1''} - \log\frac{X_1''}{X_1'} - A\left[\left[\frac{2BV_1}{AV_2} -1\right]\left[(Z_2')^2-(Z_2'')^2\right]-2\left[\frac{BV_1}{AV_2} -1\right]\left[(Z_2')^3-(Z_2'')^3\right]\right]$$

$$\log\frac{\gamma_2'}{\gamma_2''} = \log\frac{X_2''}{X_2'} = B\left[\left[\frac{2AV_2}{BV_1} -1\right]\left[(Z_1')^2-(Z_1'')^2\right]-2\left[\frac{AV_2}{BV_1} -1\right]\left[(Z_1')^3-(Z_1'')^3\right]\right]$$

These two equations may be divided and solved for $\frac{A}{B}$ and A to give

$$\frac{A}{B} = \frac{\left[\frac{2V_1}{V_2}\log\frac{X_2''}{X_2'}\right]\left[(Z_2')^2-(Z_2'')^2-(Z_2')^3-(Z_2'')^3\right]+}{\left[\frac{2V_2}{V_1}\log\frac{X_1''}{X_1'}\right]\left[(Z_1')^2-(Z_1'')^2-(Z_1')^3+(Z_1'')^3\right]+}$$

$$\frac{\left[\log\frac{X_1''}{X_1'}\right]\left[(Z_1')^2-(Z_1'')^2-2(Z_1')^3+2(Z_1'')^3\right]}{\left[\log\frac{X_2''}{X_2'}\right]\left[(Z_2')^2-(Z_2'')^2-2(Z_2')^3+2(Z_2'')^3\right]}$$

and

$$A = \frac{\log\frac{X_1''}{X_1'}}{\left[\frac{2V_1-\frac{A}{B}V_2}{\frac{A}{B}V_2}\right]\left[(Z_2') -(Z_2'')^2\right] - \left[\frac{2V_1-(2)(\frac{A}{B})(V_2)}{\frac{A}{B}V_2}\right]\left[(Z_2')^3-(Z_2'')^3\right]} \qquad (24)$$

When $V_1 = V_2$, substitution into equation 24 will give the solution to the Margules equations 20.

By a similar procedure, a solution for the van Laar constants may be obtained as:

$$\frac{A}{B} = \frac{\left(\frac{X_1'}{X_2'} + \frac{X_1''}{X_2''}\right)\left(\frac{\log \frac{X_1'}{X_1''}}{\log \frac{X_2'}{X_2''}}\right) - 2}{\frac{X_1'}{X_2'} + \frac{X_1''}{X_2''} - \frac{2X_1'X_1'' \log \frac{X_1''}{X_1'}}{X_2'X_2'' \log \frac{X_2'}{X_2''}}}$$

and (25)

$$A = \frac{\log \frac{X_1''}{X_1'}}{\frac{1}{\left(1 + \frac{A}{B}\frac{X_1'}{X_2'}\right)^2} - \frac{1}{\left(1 + \frac{A}{B}\frac{X_1''}{X_2''}\right)^2}}$$

These expressions are of considerable importance because of the ease with which mutual solubility of this type may be determined. They provide a simple method for the evaluation of the activity coefficient - composition curves used in this paper.

3. Effect of Temperature.--Hougen and Watson (33) have derived an expression for the effect of temperature on activity coefficient as follows:

$$\left(\frac{\partial \ln \gamma}{\partial T}\right)_p = \left(\frac{\partial \ln f_1}{\partial T}\right)_p - \left(\frac{\partial \ln f_1^\circ}{\partial T}\right)_p = \frac{(H_1^* - \overline{H}_1) - (H_1^* - H_1^\circ)}{RT^2} = -\frac{\overline{H}_1 - H_1^\circ}{RT^2} \quad (26)$$

where the quantity $\overline{H}_1 - H_1^\circ$ is the partial molal enthalpy relative to the pure components at the temperature of the solution or the differential heat of solution. When the differential heat of solution is positive, indicating heat absorption on solution, the activity coefficient is decreased by an increase in temperature. Carlson and Colburn (13)

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(13) Carlson and Colburn, op. cit., p. 581.

(33) Hougen, O. A. and Watson, K. M., Chemical Process Principles, Part 2, p. 661, John Wiley & Sons, Inc., New York.

noted that as a general rule systems of organic liquids with positive deviations from Raoult's law ($\gamma > 1$) have positive values for the differential heat of solution, and systems with negative deviations have negative heats of solution. Thus, activity coefficients for systems of organic liquids, having either positive or negative deviations from Raoult's law, approach unity as the temperature rises and thus approach Raoult's law as a limit.

If the assumption is made that the differential heat of solution is constant, equation 26 may be integrated to give

$$\ln \gamma_1 = \frac{\overline{H}_1 - H_1^\circ}{RT} + f(p) \qquad (27)$$

If the above assumptions are valid a graph of log γ versus $\frac{1}{T}$ should give a straight line. This provides a convenient method for extrapolating activity coefficients, calculated from liquid-liquid solubility measurements and one of the equations 20, 21, or 22, to temperatures above the critical solution temperature for the binary pair.

4. Limitations of Activity Coefficient Curves.--At this point it would be advisable to call attention to the limitations imposed by the use of the binary liquid-liquid solubilities in evaluating activity coefficient curves. First, equation 23, relating activity coefficients and mutual solubilities, is in the ratio form. This imposes the condition that the curves derived by substitution of this expression into the Margules, van Laar, Schatchard-Hamer, or Hachmuth equations will exhibit only the correct ratio of the activity coefficients at the values of the mutual solubility, and may not give the correct absolute value of either. This is apparent when it is seen that each of the above expressions for calculating activity coefficient

composition curves gives a different curve. Thus, the absolute value of the activity coefficient at any given mole fraction hydrocarbon (or solvent) will ordinarily be different with the different equations. The ratio of activity coefficients, at the two compositions given by the mutual solubilities, will however be the same for all of the expressions.

This situation becomes somewhat clearer with systems of low or moderate mutual solubilities. In such cases one of the activity coefficients of equation 23 will approach unity, regardless of the mathematical expression employed, and the calculated activity coefficient of the other will be nearly the same at the mutual solubility composition for all of the cases. Nevertheless, some error in activity coefficients might be expected if any composition is far removed from that of the mutual solubility.

Second, the range of compositions between those of the mutual solubilities constitutes an unreal region of the curve where only heterogeneous mixtures can exist. However, the mathematical expressions for the activity coefficient-composition curves, such as equations 20 through 22, do not account for this, and do permit the calculation of a curve in this region. Nevertheless, one should note that this is purely an extrapolation into an unreal region and be guided accordingly.

In this work it becomes necessary to make this type of extrapolation in order to evaluate the activity coefficients in ternary mixtures. This is analogous to the well-known extrapolations of the fugacity of pure hydrocarbon vapors into regions where they can exist only as liquids.

C. Prediction Theory

1. Distribution Coefficient.--Activity coefficient composition curves are easily calculated for binary mixtures from knowledge of the mutual solubil-

ity and utilization of one of the equations 20, 21, or 22 above. On the other hand, the equivalent-type equations for ternary and quarternary systems are complicated and frequently do not match experimental data well. The binary activity coefficients could be employed for ternary or more complex mixtures if some information were available on the effect of the additional component on the activity coefficients of the original two. This study utilizes the basic assumption that the activity coefficient of a component in a solution with a selective solvent is a function only of the binary solvent-component activity coefficient curve and the total amount of hydrocarbon (or solvent) present in the solution. In other words, a hydrocarbon in 0.8 mole fraction solvent exhibits an activity coefficient independent of the nature of the other hydrocarbons present in a manner analogous to partial pressure in an ideal gas mixture. Thus, the above hydrocarbon in 0.8 mole fraction solvent has the same activity coefficient regardless of whether said hydrocarbon is the only hydrocarbon present or is only a part of the total hydrocarbon fraction. This is equivalent to stating that the effect of the hydrocarbons on each other is negligible compared to the effect of the solvent. This assumption may be combined with equation 23 and the composition of one equilibrium phase to calculate the other. Thus rewriting equations 23

$$\begin{aligned} X_1'' &= X_1'\left(\frac{\gamma_1'}{\gamma_1''}\right) \\ X_2'' &= X_2'\left(\frac{\gamma_2'}{\gamma_2''}\right) \end{aligned} \qquad (23)$$

Here the ratio of activity coefficients is frequently called the distribution coefficient, partition coefficient, or simply the K constant. It is obtained from the appropriate binary hydrocarbon - solvent activity coefficient curve at the known (or estimated) total hydrocarbon content of the phase, and is the factor by which the composition of a given component in one phase may be calculated from the known composition in the other. This is illustrated by the same calculations in Appendix III.

2. Hydrocarbon (or Solvent) Contents.--Since the purpose of this study is to formulate a method for estimating phase equilibria from binary liquid-liquid solubilities, some relationships must be determined for the solvent contents of the equilibrium ternary phases. The establishment of the solvent content of one equilibrium phase will ordinarily fix the other by successive approximation and equation 23. Of course, the better the method for approximating the hydrocarbon content of the first phase, the more likely the estimated equilibria will be to correlate with experimental data. Bethea (18) drew a smooth curve between the two binary compositions on a graph with mole per cent hydrocarbon as ordinate and mole fraction ethylene (solvent-free basis) as abscissa in such a manner that the calculated solvent phase was also a smooth curve. Hachmuth (20) effectively drew a straight line between the binary hydrocarbon compositions on the same graph. Pennington and Marwil (23) assumed linearity of the hydrocarbon phase on a graph representing mols of solvent per mole of hydro-

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(18) Bethea, C. F., Unpublished Memorandum, Phillips Petroleum Company, 1949.

(20) Hachmuth, op. cit., p. 83.

(23) Pennington and Marwil, op. cit., p. 1371.

carbon as ordinate and mole per cent hydrocarbon A (solvent-free basis) as abscissa (34). A study of the nature of these curves for several systems indicates that the Pennington-Marwil assumption more nearly approaches the experimental data and should therefore be the most useful. However, in this work it was noted that the assumption of linearity of the solvent phase gave equivalent results as assumed linearity of the hydrocarbon phase for all cases where good correlations were obtained. Moreover, the solvent phase assumption gave a better correlation in some of the systems with discrepancies.

In those systems involving only one pair of nonconsolute components (i.e., above the critical solution temperature for one hydrocarbon-solvent pair), it was necessary to assume knowledge of the binodal curve to apply the prediction method. This is because one of the two solvent-hydrocarbon binary pairs is completely miscible. It follows, therefore, that only one of the two sets of binary solubility data needed in the above procedures for estimating the solvent content of the ternary solutions is available.

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(34) Maloney, J. O. and Schubert, A. E., A. I. Ch.E. <u>36</u>, 741 (1940).

CHAPTER III

EXPERIMENTAL EQUIPMENT AND MATERIALS

A. Experimental Equipment

The most important parts of the experimental equipment used in this investigation are shown in Figures 3 through 6. The equipment is classified according to its use in (1) solubility measurements or (2) ternary equilibrium measurements as follows.

1. Solubility Measurements.--Figure 3 is a view of the cloud point apparatus and analytical balance used in determining the mutual solubility of the solvent (furfural) and a variety of hydrocarbons. A detailed inspection will reveal the jacketed inner tube, thermometer, variable speed stirrer, and speed control unit of the cloud point apparatus. All thermometers were -10°C. to 110°C., graduated to 1°C. and calibrated to an estimated 0.1°C. with a Bureau of Standards calibrated thermometer, or -10°C. to 315°C., graduated to 1°C. and calibrated to an estimated 0.1°C. with the Bureau of Standards calibrated thermometer. The analytical balance was a Voland type with a reciprocal sensitivity of 0.54 mg. empty and 1.38 mg. at 100 grams load. The balance weights were calibrated against standards from the U. S. Bureau of Standards.

2. Ternary Equilibria.--Some of the equipment used in determining the ternary equilibria is shown in Figures 4, 5, and 6. Figure 4 is a close-up photograph of the calibrated Pyrex equilibrium cell with ground glass stopper, and the Hyde-type mercury seal stirrer used for maintaining a vapor seal during equilibrium. Figure 5 is an overall view of the

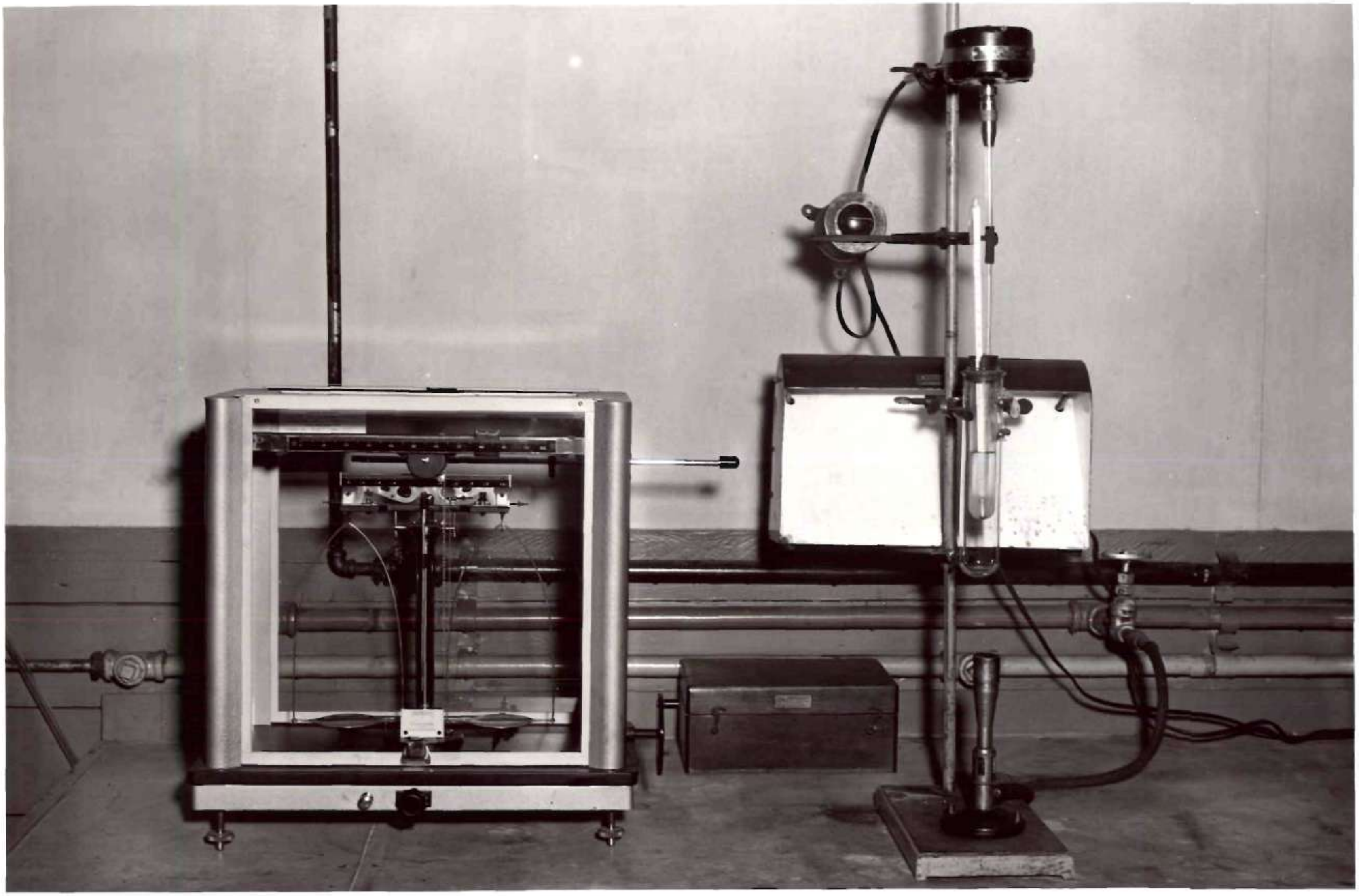

FIG. 3. CLOUD POINT APPARATUS AND ANALYTICAL BALANCE

equilibrium cell as situated in one of the constant temperature baths. It shows the stirrer, heaters, and control unit for the bath, and the variable speed stirrer and control unit for the equilibrium cell. Figure 6 is a photograph of the five-decimal-place, Bausch and Lomb, precision sugar refractometer used to determine the composition of hydrocarbon blends.

A Todd precision fractionator (35), complete with accessories, was utilized in analysis to separate the hydrocarbons from the solvent. The one-inch diameter fractionating column used was equivalent to thirty equilibrium stages.

B. Materials

The hydrocarbons and solvent used in this work were as follows:

1. Hydrocarbons.--The seven hydrocarbons utilized in this study were benzene, cyclohexane, n-heptane, octene-1, 2,2,4-trimethylpentane (isooctane), hexadecane (cetane), and toluene. All except the toluene and cetane were Phillips pure grade products (36) and were donated by the Phillips Petroleum Company. The cetane, although donated by Phillips, was a pure grade product of the DuPont Company. The toluene was a reagent grade Merck product. These materials were used without further purification.

The above hydrocarbons were selected as typical of several hydro-

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(35) Todd, F., Ind. and Eng. Chem., Anal. Ed. 17, 175 (1945).

(36) Phillips 66 Hydrocarbons, Third Edition, 1947, Phillips Petroleum Company, Bartlesville, Oklahoma.

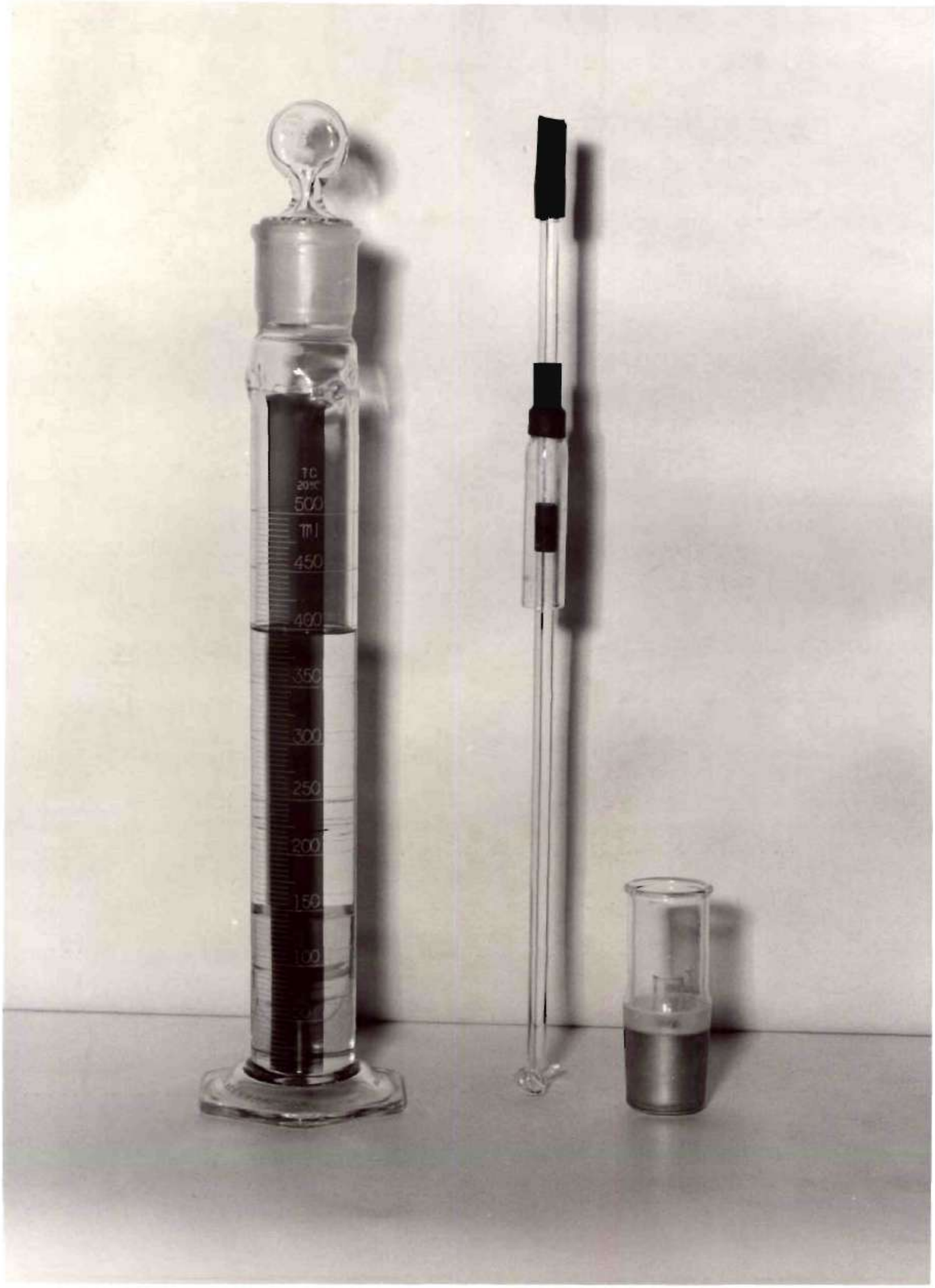

FIG. 4. PYREX EQUILIBRIUM CELL AND MERCURY SEAL STIRRER

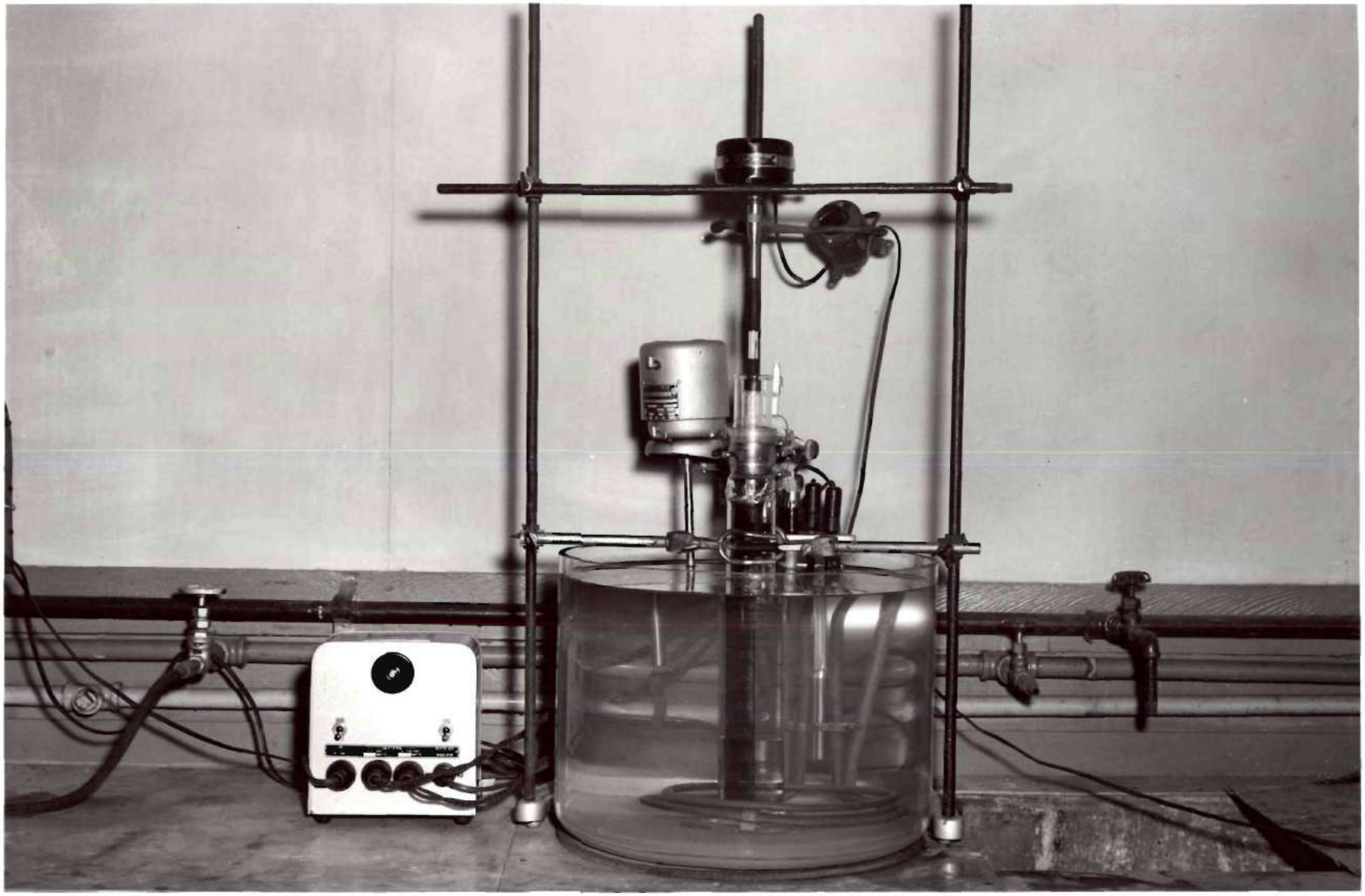

FIG. 5. CONSTANT TEMPERATURE BATH, EQUILIBRIUM CELL, AND ACCESSORIES

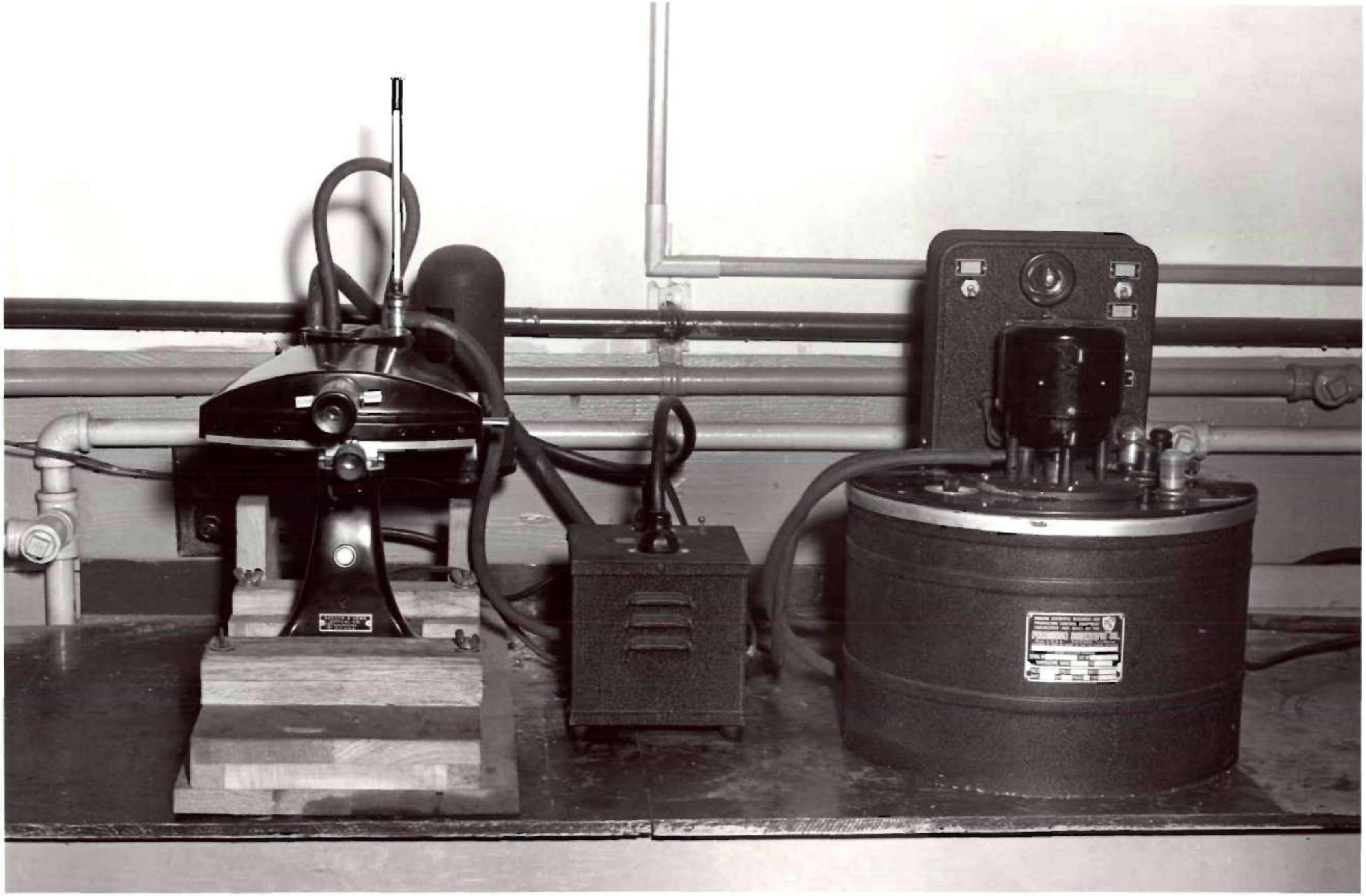

FIG. 6. FIVE-DECIMAL-PLACE PRECISION REFRACTOMETER

carbon types - two n-paraffins with considerable difference in molecular weight, an isoparaffin, a n-olefin, a naphthene, and an aromatic. Individual members of each type were selected which exhibited desirable properties of boiling point and refractive index so as to facilitate subsequent fractionation and analysis.

2. Solvent.--Quaker Oats Company technical grade furfural was purchased as the selective solvent for this research.

This material was purified by vacuum distillation in a Vigreaux distillation unit and a clear, polymer-free distillate was obtained. However, it was used only when the purity was verified by refractive index determination.

The values of the refractive index of pure furfural were determined at various temperatures and are listed in Table 1. The value at 20°C. is in agreement with the Quaker Oats Company value (37), but does not agree with the International Critical Tables (38) for this temperature. Literature data at the other temperatures were not available.

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(37) Furfural as a Selective Solvent, Tech. Div., Quaker Oats Co., 1940.

(38) International Critical Tables, Vol. VII, 1st. ed., p. 36.

Table 1. Refractive Index - Temperature Data for Purified Furfural

Temperature °C.	Refractive Index n_D^T
15	1.5286
20	1.5261
25	1.5237
30	1.5211
35	1.5187

CHAPTER IV

EXPERIMENTAL PROCEDURES

A. Equilibrium-Cell Measurements

1. Equilibrium.--Predetermined weights of hydrocarbon or hydrocarbon blend and furfural were charged to the equilibrium cell. The Hyde-type mercury-seal stirrer was then placed in position, the assembly placed in the constant-temperature bath, and the heterogeneous mixture stirred vigorously for at least 30, 60, or 90 minutes for temperature levels of 30°C., 60°C., or 90°C. respectively. This procedure allowed ample opportunity for the attainment of thermal and phase equilibrium.

Actually, temperature measurements showed that thermal equilibrium was attained in less than thirty minutes, even at a temperature level of 90°C., but it was not deemed advisable to modify the procedure. The attainment of phase equilibrium was verified by tests that showed no change in hydrocarbon-phase composition after room-temperature agitation for fifteen minutes. Additional tests were made with a hydrocarbon system of considerable difference in molecular weight (cyclohexane and cetane) to determine whether false equilibria due to concentration barriers would be encountered. Accordingly, in the cyclohexane-cetane-furfural runs, equilibrium was approached with furfural and a blend of the hydrocarbons, with furfural saturated initially with cyclohexane, and with a solvent saturated initially with cetane. The results of these tests indicated that liquid-liquid phase equilibria may be obtained by fifteen minutes of vigorous agitation at the desired temperature regardless of the direction of approach to equilibrium with respect to concentration.

After the attainment of phase equilibrium the mercury-seal stirrer was withdrawn from the cell, the ground-glass stopper placed in position, and the mixture allowed to settle for at least thirty minutes before withdrawing samples for analysis. The volumes of the two phases were then recorded for subsequent material-balance calculations.

Samples of the hydrocarbon phase were taken first in all cases, and the excess of hydrocarbon phase then withdrawn, and the solvent phase samples taken. All samples were secured by pressuring the sample, with the use of a rubber squeeze bulb, into an appropriate preheated pipette. Care was taken to preheat the pipettes slightly warmer than the solution, to secure the samples as rapidly as possible, and to allow the solution to stand fifteen to twenty minutes before withdrawing another sample. Thus, the equilibrium conditions were not altered.

2. Hydrocarbon-Phase Samples.--Three tests were made with samples from the hydrocarbon phase. The first was the determination of density of the phase, the second the determination of the furfural content of the phase, and the third the determination of the hydrocarbon composition of the phase. The density of the hydrocarbon phase was determined by placing the sample in a previously calibrated pycnometer, attaining thermal equilibrium and obtaining the weight of the sample. The furfural content of the hydrocarbon phase was obtained by a modification of the procedure outlined by Bryant and Smith (39). This involved the

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(39) Bryant, W. M. D., and Smith, D. M., J. Am. Chem. Soc., 57, 57-61 (1935).

addition of hydroxylamine hydrochloride solution with a pyridine-bromophenol-blue indicator solution to the sample, allowing thirty minutes for the reaction liberating hydrochloric acid to complete itself, and back titrating the liberated acid with standardized sodium hydroxide.

Considerable difficulty was experienced with the above procedure as described in the literature because the blank was on the basic side of the end point and this made the titrations tedious and uncertain. The neutralization of the blank by the addition of standardized hydrochloric acid produced additional complications in the added water, and the end point was not satisfactory. The difficulties were surmounted, however, when it was discovered that the color of the blank could be altered to the end point of the indicator by diluting the indicator solution to two liters with 95 per cent ethanol rather than to one liter as prescribed in the procedure. This simple modification produced a sharp and precise end point in what had previously been an onerous and uncertain procedure.

The hydrocarbon analysis of the hydrocarbon phase was obtained by the determination of the refractive index of a solvent-free sample. This third sample from the hydrocarbon phase was treated by washing with an equal volume of 20 weight per cent aqueous sodium bisulfite, and two equal volumes of water. The composition of the solvent-free hydrocarbon was then read from one of the predetermined calibration curves (see Appendix I). The only exception to this method for determining hydrocarbon composition was made with the system furfural-cyclohexane-cetane. Here the cyclohexane and cetane were fractionated separately from the furfural, one being an overhead product and the other a bottoms, and were therefore measured directly after removal of residual quantities of furfural.

3. Solvent-Phase Samples.--Two samples of the solvent phase were taken for analysis. The first was used for the determination of the phase density in a manner similar to that used with the hydrocarbon phase. The second sample was charged to the thirty-stage fractionator, and the dissolved hydrocarbons separated from the furfural by close fractionation with reflux ratios in the range between 3 to 1 and 10 to 1. The overhead hydrocarbon distillate was then washed with sodium bisulfite to remove final traces of furfural, the volume measured in place, the density determined by pycnometer method, and the purity of the final solvent-free fraction determined by refractive index. The only exception to this procedure was, as before, with the system cyclohexane-cetane-furfural. Here the cyclohexane and cetane were obtained as separate fractions, one as overhead and the other as bottoms, and were again measured directly after removal of the final traces of furfural.

The above procedures for the equilibrium-cell runs provided a method by which complete material balances on all three components could be obtained. These balances were made after each run, and were generally in the range of 95-105 per cent of all components. It was soon evident, however, that the analysis of one or both of the phases could be considerably in error, and the overall material balance still be almost perfect. Similarly, it was possible for equilibrium phase analysis to be correct and the overall balances to be in error. Therefore, no great significance was attached to the fact that one run had a slightly better or worse material balance than another in evaluating the data.

B. Solubility Measurements

Samples for the determination of binary solubilities by the cloud point method were prepared by weighing the portions of the furfural-hydrocarbon blend into the removal inner-tube-assembly of the cloud point apparatus. The tube assembly was then placed in the apparatus, the stirrer adjusted for vigorous agitation, and the sample heated to some 5 to 10°C. above the solution temperature. The temperature, corresponding to the solution temperature of the mixture, was then observed by cooling the stirred homogeneous solution until the mixture first separated into two phases. This point, called the cloud point, was indicated by the distinct change in the solution from clear (or faint haziness) to turbid. The procedure was repeated as often as necessary to obtain a precise values, to an estimated ± 0.1°C., and to insure that the readings were constant. The inner tube, complete with thermometers and stirrer, was then reweighed and the evaporation loss determined. This loss, computed as hydrocarbon loss, was never sufficient to change the hydrocarbon composition by 0.1 per cent.

The evaporation losses were maintained at the above-mentioned almost-insignificant figure by the close clearance between the stirring rod and the stirrer bearing, the only source of loss, and the speed at which the cloud points were obtained. The determination of high-temperature cloud points was followed by a rapid quench of the sample to prevent further loss before the final weighing.

The polymer content of the furfural had a considerable bearing on the temperature, and the sharpness of the cloud point determinations. Discrepancies in the cloud point values were obtained between samples with freshly purified furfural and samples with two-day-old furfural. This was experimentally observed even though there was no perceptible change in the refractive index (to four decimal places) of the furfural, or in the solubility as determined in the equilibrium cell. Further, there was a marked decrease in the sharpness of the test when the furfural had aged as much as one day at room temperature. To minimize this error, all cloud point tests were made with furfural that was freshly purified on the day of use.

The cloud point solubility values at any given temperature were obtained by interpolation on a semilogarithmic graph in which the logarithm of the solute concentration was plotted as ordinate and the temperature as abscissa. Here the solute concentration refers to the concentration of the component in minor concentration, and is not to be confused with the term solvent used throughout this paper to designate the selective solvent, irrespective of its concentration. The semilogarithmic type of of graph was preferred to the usual arithmetic temperature-composition graphs, sometimes referred to as T-X curves, because of its facility for interpolation.

Actually, binary liquid-liquid solubility measurements were made both in the cloud point apparatus and the equilibrium cell. This duplication of data provided an independent check on the two procedures, and resulted in the discovery of the sensitiveness of the cloud point method with respect to the age, or polymer content, of the furfural. Thereafter, the cloud point data, as interpolated to the appropriate temperature, were used as checks on the results of the equilibrium-cell binary system measurements.

CHAPTER V

EXPERIMENTAL DATA AND RESULTS

The experimental data obtained in this work on liquid-liquid systems have been classified as (A) Binary Solubilities and (B) Ternary Equilibria. These follow.

A. Binary Solubilities

Binary liquid-liquid solubility measurements were made both in the cloud-point apparatus and in the equilibrium cell. The cloud-point data were interpolated to the appropriate temperatures of the equilibrium-cell measurements, and the two sets of data are compared in Table 2. The agreement is considered generally good, and in only a few cases was it deemed advisable to repeat equilibrium-cell binary measurements. These are indicated in the table where two sets of equilibrium-cell values are listed at any one temperature.

The mutual solubility data obtained in the cloud-point apparatus are discussed and compared with available literature data as follows:

1. Furfural-Cyclohexane.--The mutual solubility of furfural and cyclohexane as obtained in this investigation and as reported by Marwil and Pennington (23) are compared in Figure 7. The agreement between the two sets of data is generally good, particularly in the furfural-rich phase, but some unexplained scatter is noted in the Marwil-Pennington data for the cyclohexane-rich phase in the range of 20 to 40°C. The

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(23) Pennington and Marwil, op. cit., p. 1371.

Table 2. Comparison of Solubility Values by
Cloud Point and Equilibrium Cell Measurements

		Mol Fr. Hydroc. in Solvent Phase		Mol Fr. Solvent in Hydroc. Phase	
System	Temp.	Cloud Point	Equil.Cell	Cloud Point	Equil.Cell
Furfural-Cyclohexane	30°C.	0.149	0.144 0.149	0.063	0.065 0.064
	60°C.	0.318	0.309	0.206	0.195
	90°C.	Completely Miscible		Completely Miscible	
Furfural-n-Heptane	30°C.	0.059	0.060 0.057	0.058	0.060 0.060
	60°C.	0.111	0.109	0.131	0.128
	90°C.	0.269	0.254	0.352	0.334
Furfural-Cetane	30°C.	0.0054	0.0050	0.080	0.082
	60°C.	0.0126	0.0123	0.156	0.152
	90°C.	0.029	0.027	0.295	0.289
Furfural-Isooctane	30°C.	0.048	0.046	0.060	0.061
Furfural-Octene-1	30°C.	0.110	0.116 0.117	0.137	0.137 0.140
	60°C.	0.281	0.278	0.400	0.383
Furfural-Benzene	10-100°C.	Completely Miscible		Completely Miscible	
Furfural-Toluene	10-100°C.	Completely Miscible		Completely Miscible	

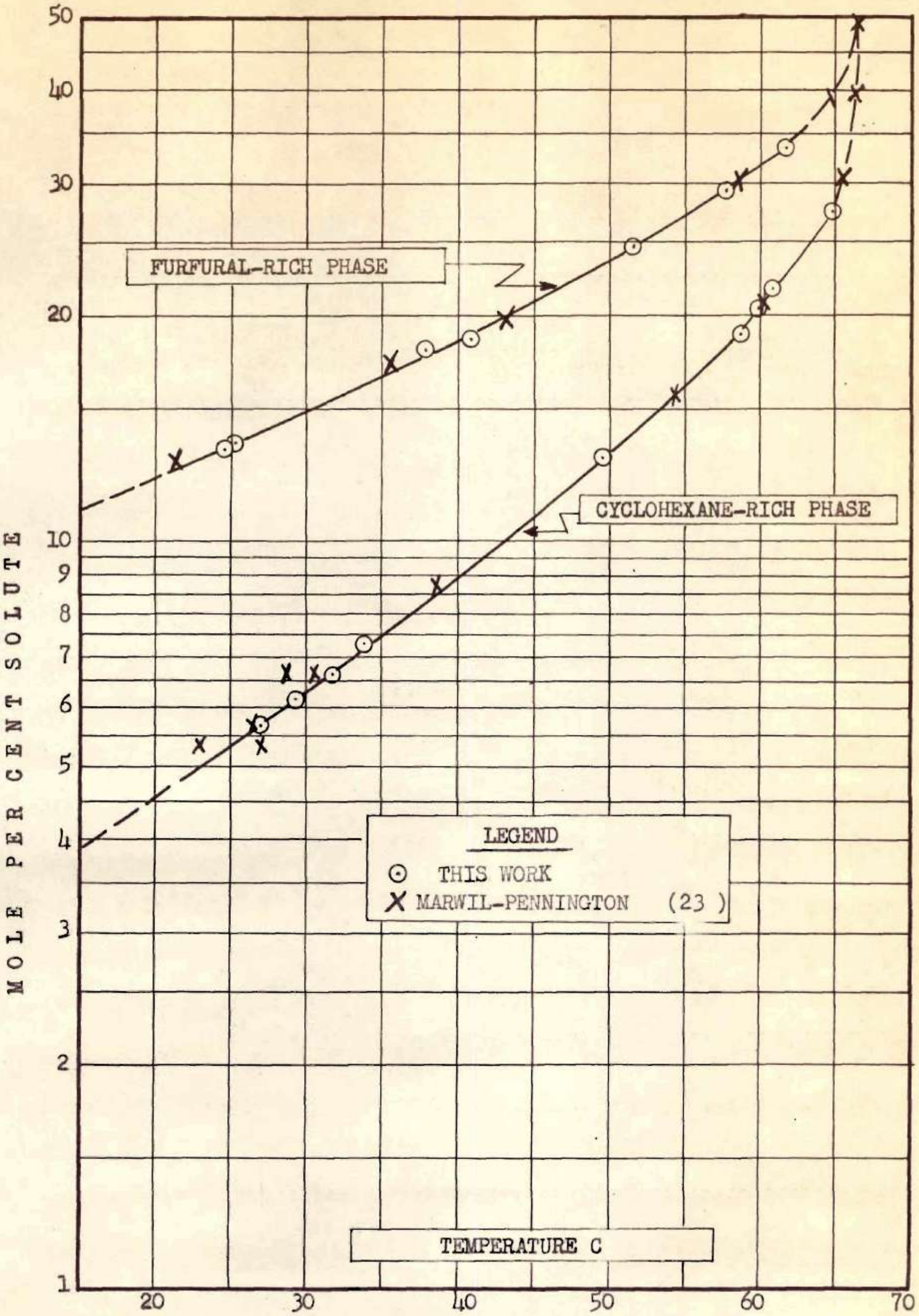

FIG. 7. MUTUAL SOLUBILITY FOR FURFURAL AND CYCLOHEXANE

data of this work, on the other hand, are quite consistent over the same temperature range, and should therefore be more reliable. A tabulation of these data is shown in Table 20, Appendix II.

2. Furfural-n-Heptane.--The mutual solubility of furfural and n-heptane, as obtained in this work, are compared with those reported by Marwil and Pennington (23) and Herbolsheimer (24) in Figure 8. The agreement between these data are good, especially for the solvent phase. However, the data of this work for the hydrocarbon-rich phase seem in better agreement with Marwil-Pennington's data than with Herbolsheimer's. A tabulation of these data is shown in Table 21, Appendix II.

3. Furfural-Hexadecane (Cetane).--The mutual solubility of furfural and cetane are shown in Figure 9. No data were available in the literature for a comparison, but the experimental data seem consistent and reliable. A tabulation of the data is made in Table 23, Appendix II.

4. Furfural-2,2,4-Trimethyl Pentane (Isooctane).--The mutual solubility of furfural and the isooctane 2,2,4-trimethyl pentane are compared in Figure 10 with the Marwil-Pennington (23) data for furfural and "isooctane." Judging from the close agreement of the data it must be assumed that the same isooctanes were employed in the two studies. Here again, however, a slight scatter is noted in the literature data at temperatures below 40°C. The experimental data are tabulated in Table 22, Appendix II.

5. Furfural-Octene-1.--The mutual solubility of furfural and octene-1 are shown in Figure 11 and are tabulated in Table 24, Appendix II. No

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(23) Pennington and Marwil, op. cit., p. 1371.

(24) Herbolsheimer, op. cit.

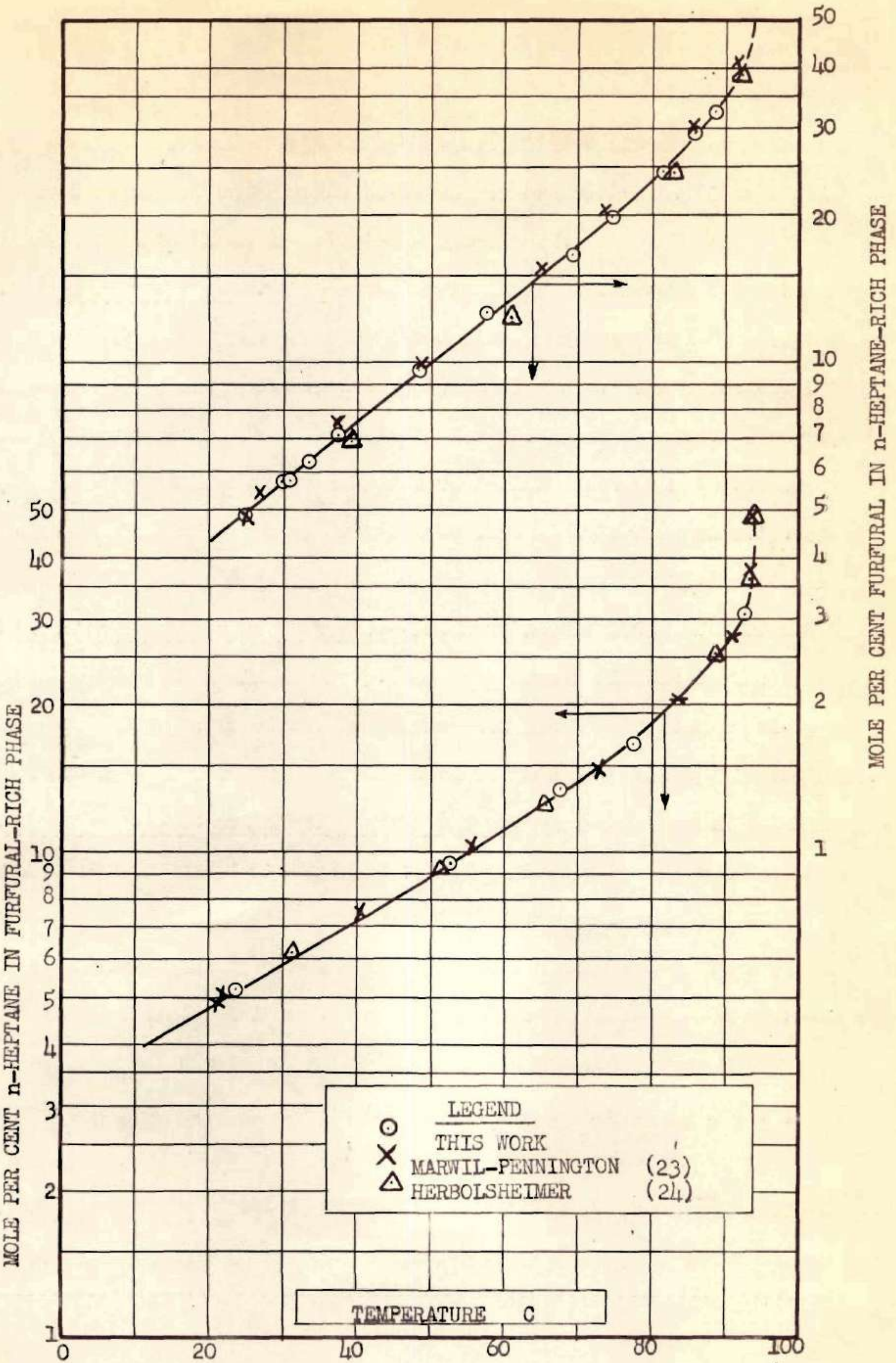

FIG. 8 . MUTUAL SOLUBILITY FOR FURFURAL AND n-HEPTANE.

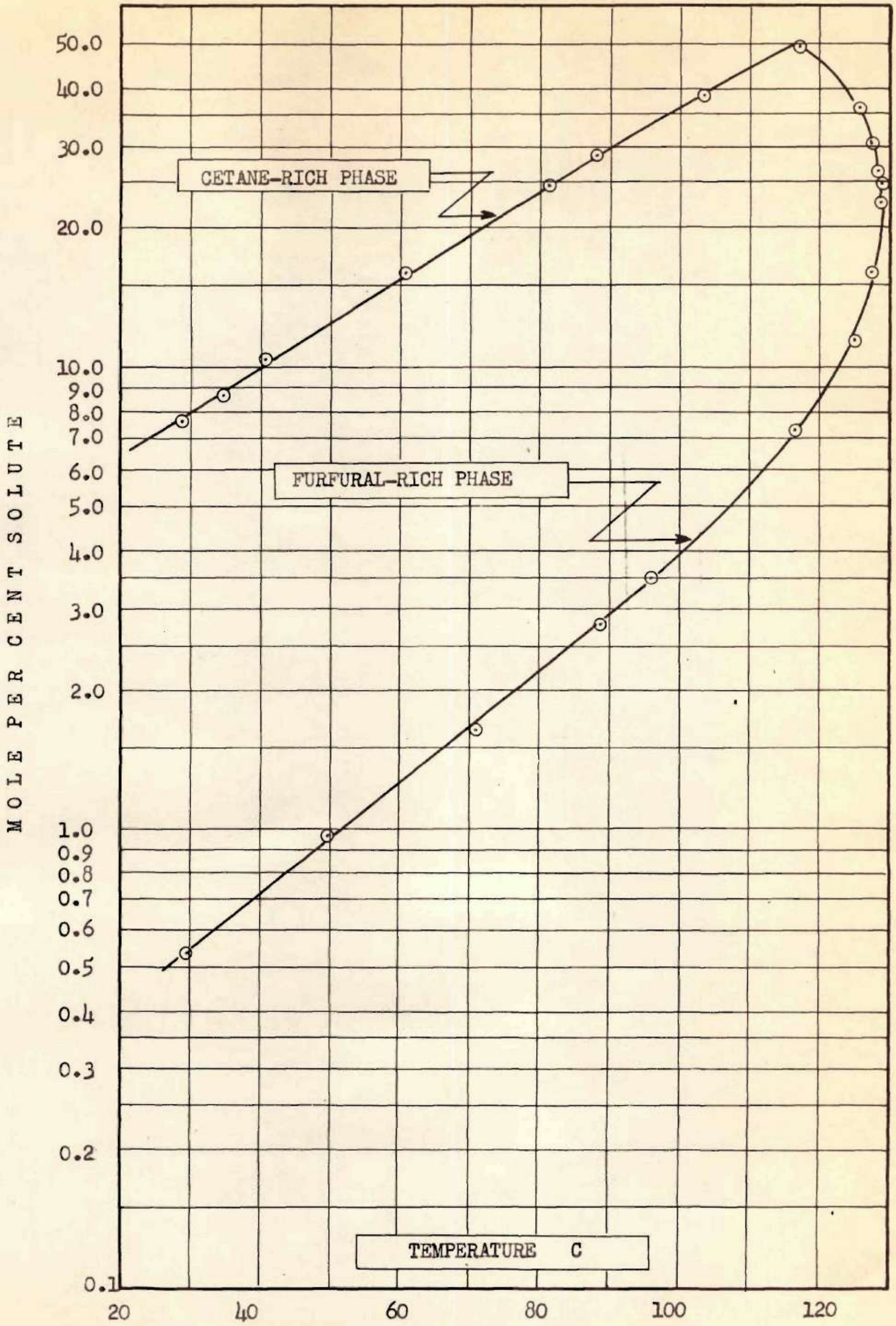

FIG. 9 . MUTUAL SOLUBILITY FOR FURFURAL AND CETANE.

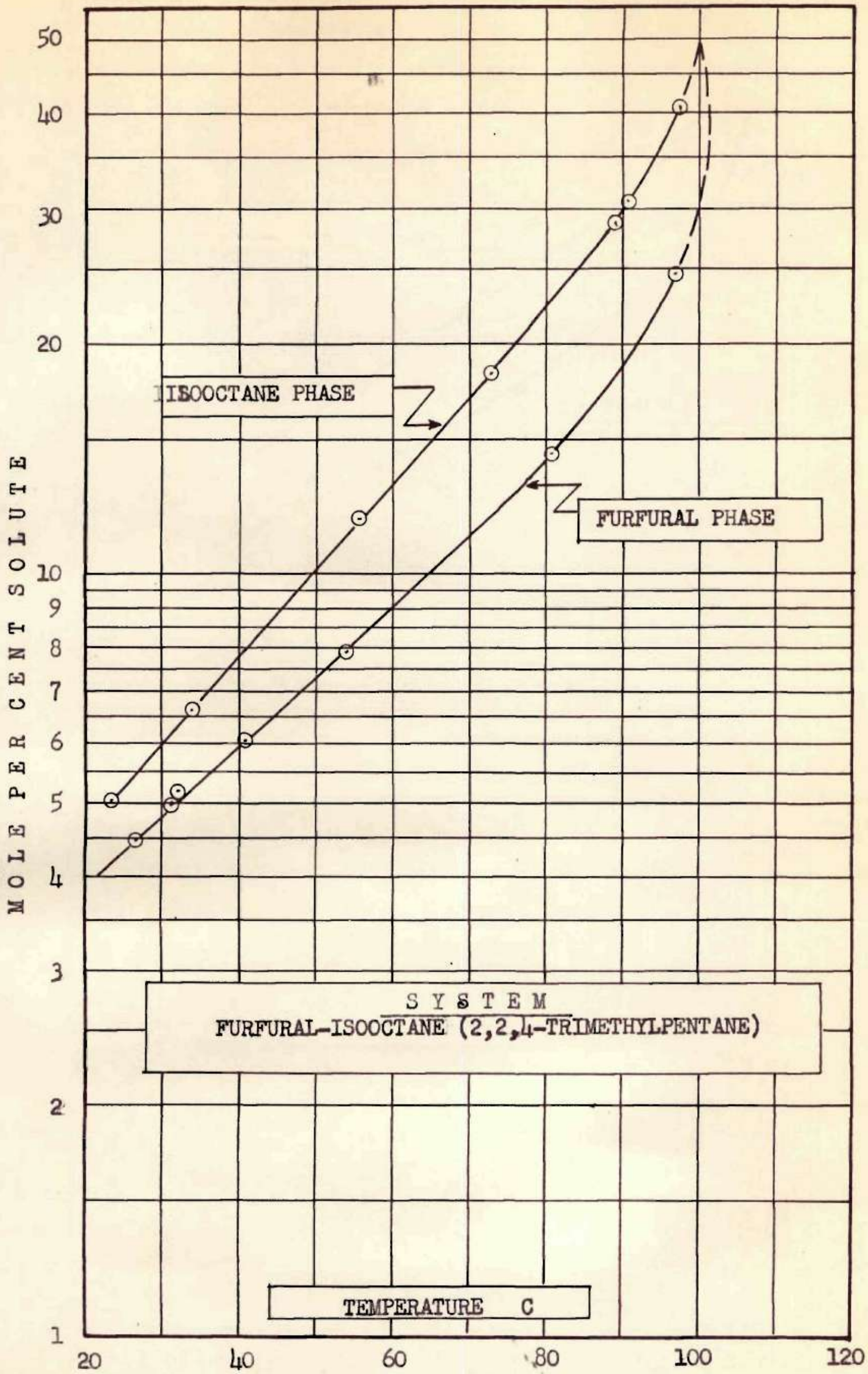

FIG. 10. MUTUAL SOLUBILITY FOR FURFURAL AND ISOOCTANE.

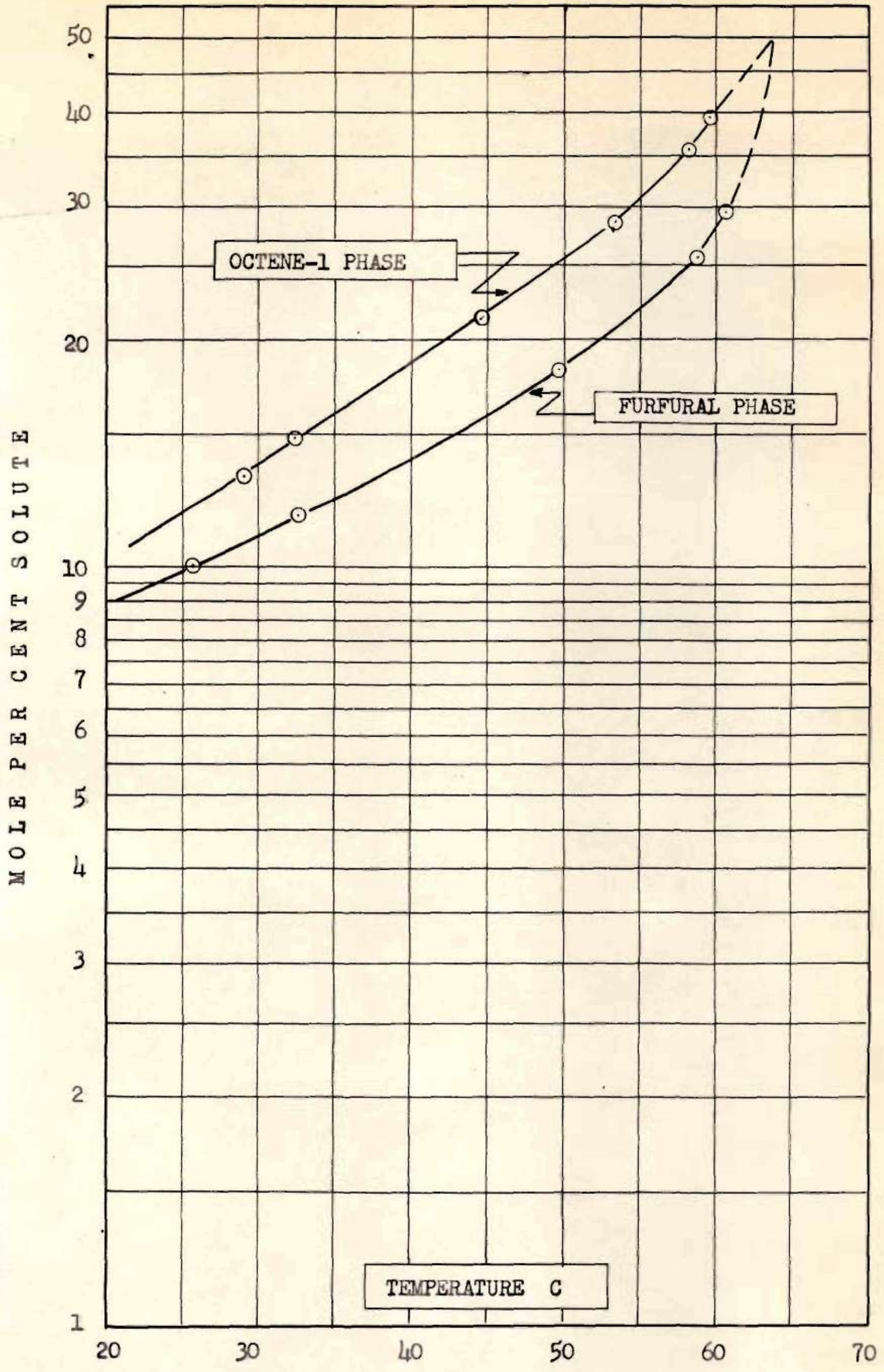

FIG. 11 . MUTUAL SOLUBILITY FOR FURFURAL AND OCTENE-1.

literature data are available for comparison.

B. Ternary Equilibria

Ternary liquid-liquid equilibria for a variety of hydrocarbons with furfural were obtained in the equilibrium all at one or more of the temperature levels 30°C., 60°C., and 90°C. These data have been plotted on triangular graph paper for inspection.

1. Cyclohexane-n-Heptane-Furfural.--Liquid-liquid phase equilibria for cyclohexane-n-heptane-furfural were obtained at temperatures of 30°C., 60°C., and 90°C. These are shown in the triangular graphs of Figures 12, 13, and 14 and are tabulated in Table 32, Appendix II.

These hydrocarbons were selected as typical of a naphthene-paraffin system in which the molecular weights approach that of the solvent. The molecular weights are 84.16, 100.20, and 96.08 respectively for cyclohexane, n-heptane, and furfural. The substituted naphthene methylcyclohexane, with molecular weight 98.18, had been considered for study, but was not selected because of the unknown effect of paraffinic substitution. However, some data for the system methylcyclohexane-n-heptane-furfural are available in Herbolsheimer's paper (24).

The equilibria of this study at 30°C. may be compared in Figure 11 with the data of Marwil and Pennington (23). The agreement between these independent sets of data is only fair. The Marwil and Pennington data show considerable scatter in the solvent phase.

The phase diagrams as shown in Figures 12 and 13 for temperatures of 30°C. and 60°C. are typical of systems involving two nonconsolute

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(23) Pennington and Marwil, op. cit., p. 1371.

(24) Herbolsheimer, op. cit.

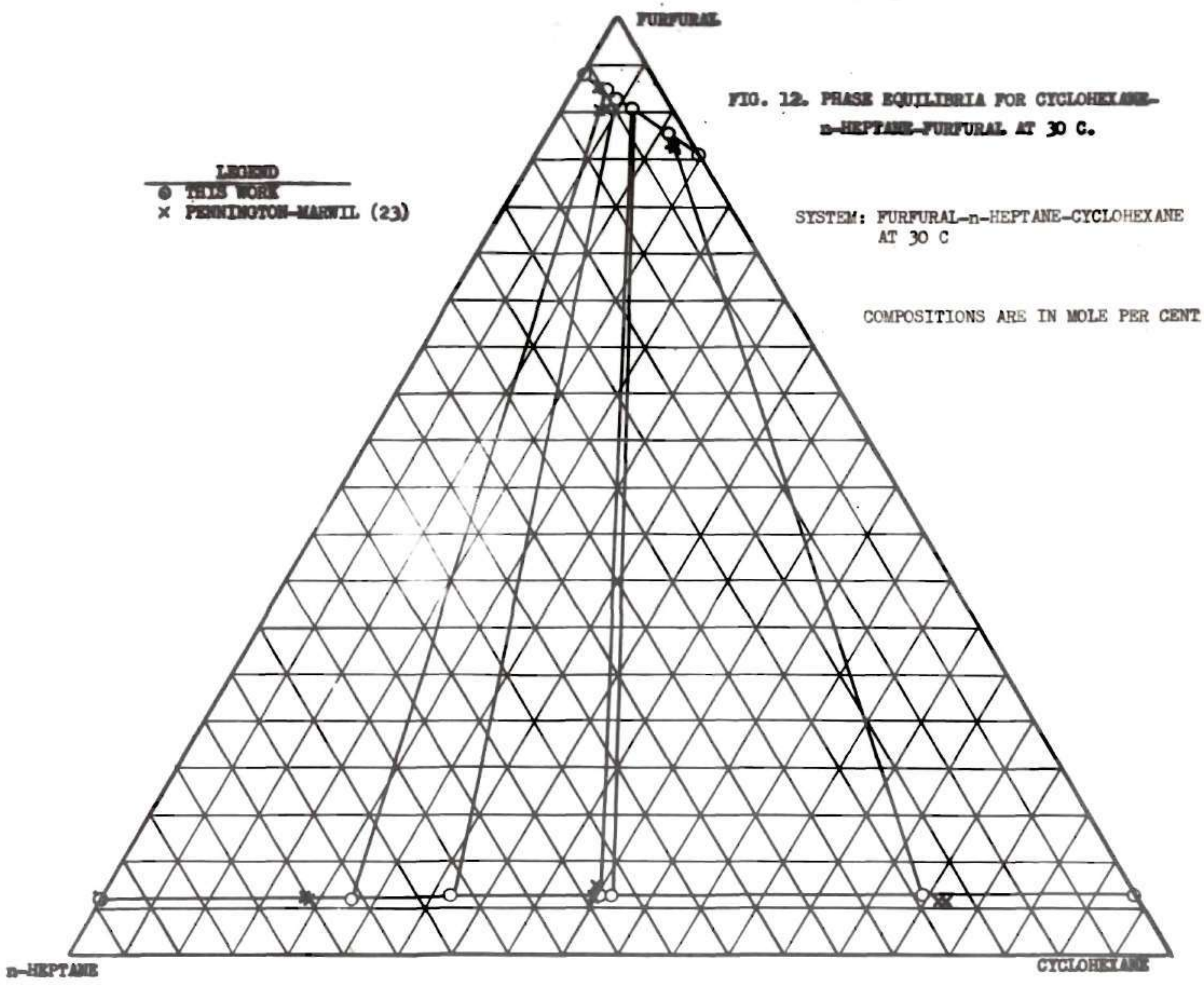

FIG. 12. PHASE EQUILIBRIA FOR CYCLOHEXANE-n-HEPTANE-FURFURAL AT 30 C.

SYSTEM: FURFURAL-n-HEPTANE-CYCLOHEXANE
AT 30 C

COMPOSITIONS ARE IN MOLE PER CENT

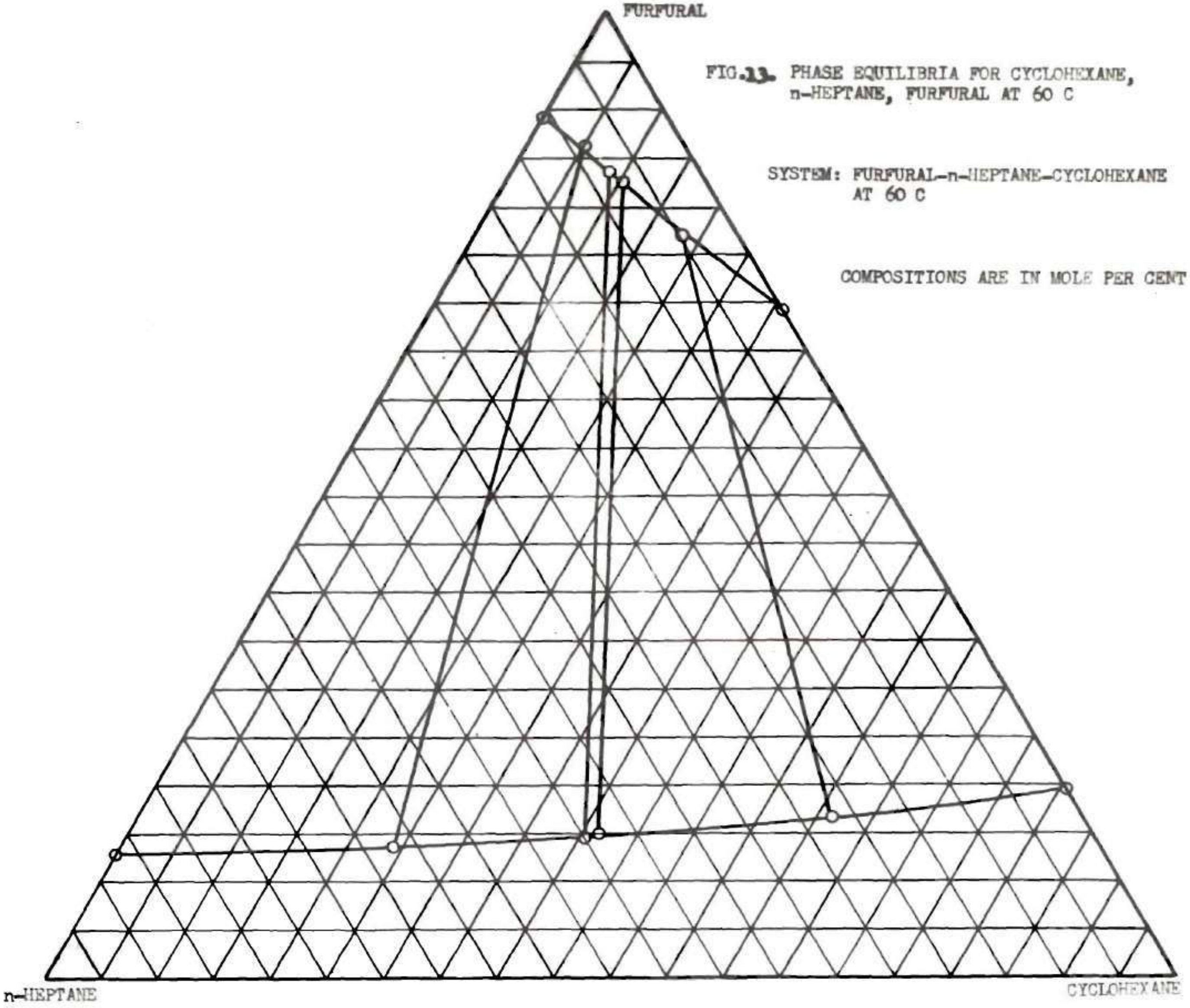

FIG.13. PHASE EQUILIBRIA FOR CYCLOHEXANE, n-HEPTANE, FURFURAL AT 60 C

SYSTEM: FURFURAL-n-HEPTANE-CYCLOHEXANE AT 60 C

COMPOSITIONS ARE IN MOLE PER CENT

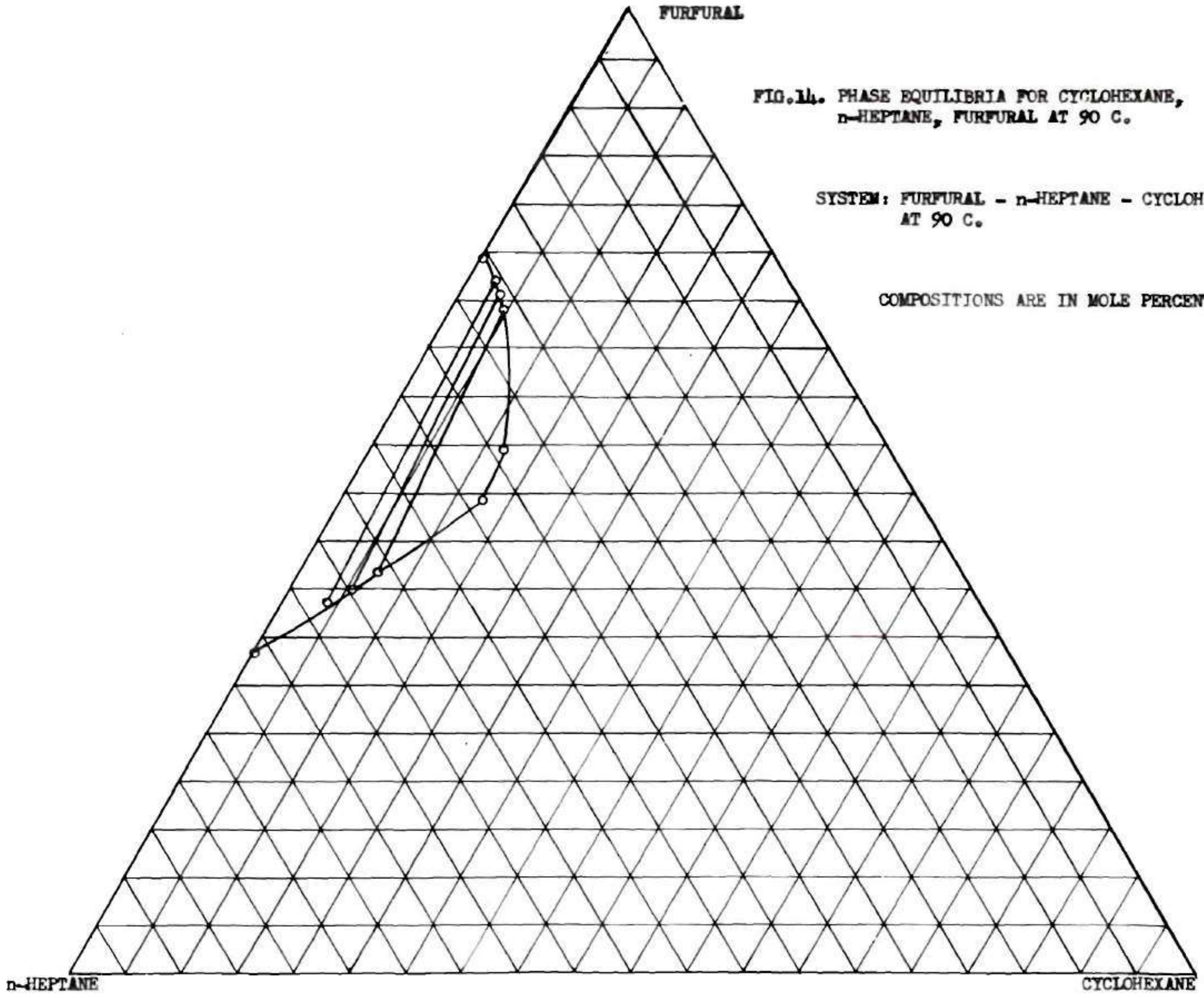

FIG. 14. PHASE EQUILIBRIA FOR CYCLOHEXANE, n-HEPTANE, FURFURAL AT 90 C.

SYSTEM: FURFURAL - n-HEPTANE - CYCLOHEXANE AT 90 C.

COMPOSITIONS ARE IN MOLE PERCENT

binary pairs, i.e., furfural-cyclohexane and furfural-n-heptane. On the other hand, the diagram of Figure 14 for 90°C. is typical of systems with only one nonconsolute binary pair, i.e., furfural-n-heptane. This difference is due, of course, to having passed through the critical solution temperature for cyclohexane and furfural in the vicinity of 67°C.

2. Cyclohexane-Isooctane-Furfural.--Liquid-liquid phase equilibria for cyclohexane-2,2,4-trimethylpentane (isooctane)-furfural were obtained at 30°C. These are shown in the triangular graph of Figure 15, and are tabulated in Table 33, Appendix II.

These hydrocarbons were chosen to illustrate a typical naphthene-isoparaffin separation in systems with molecular weights of the same order of magnitude as the solvent. For a strict comparison with the data on cyclohexane-n-heptane-furfural it would have been desirable to use an isoheptane or n-octane in this study. The former would illustrate the comparison between n- and isoparaffins of the same molecular weight, and the latter would determine whether the expected molecular weight effect might be evident with adjacent members of a homologous series. However, the solubility and selectivity differences between n- and isoparaffins of the same molecular weight and between adjacent members of a homologous series are usually slight. Therefore, an isooctane was selected for use in this study in the anticipation that significant changes might be apparent with the combination of the change in structure and the increase in molecular weight. The use of the n-octane or n-nonane were considered, but both were rejected because of the increased difficulty of quantitative recovery of these higher boiling materials from furfural by fractionation.

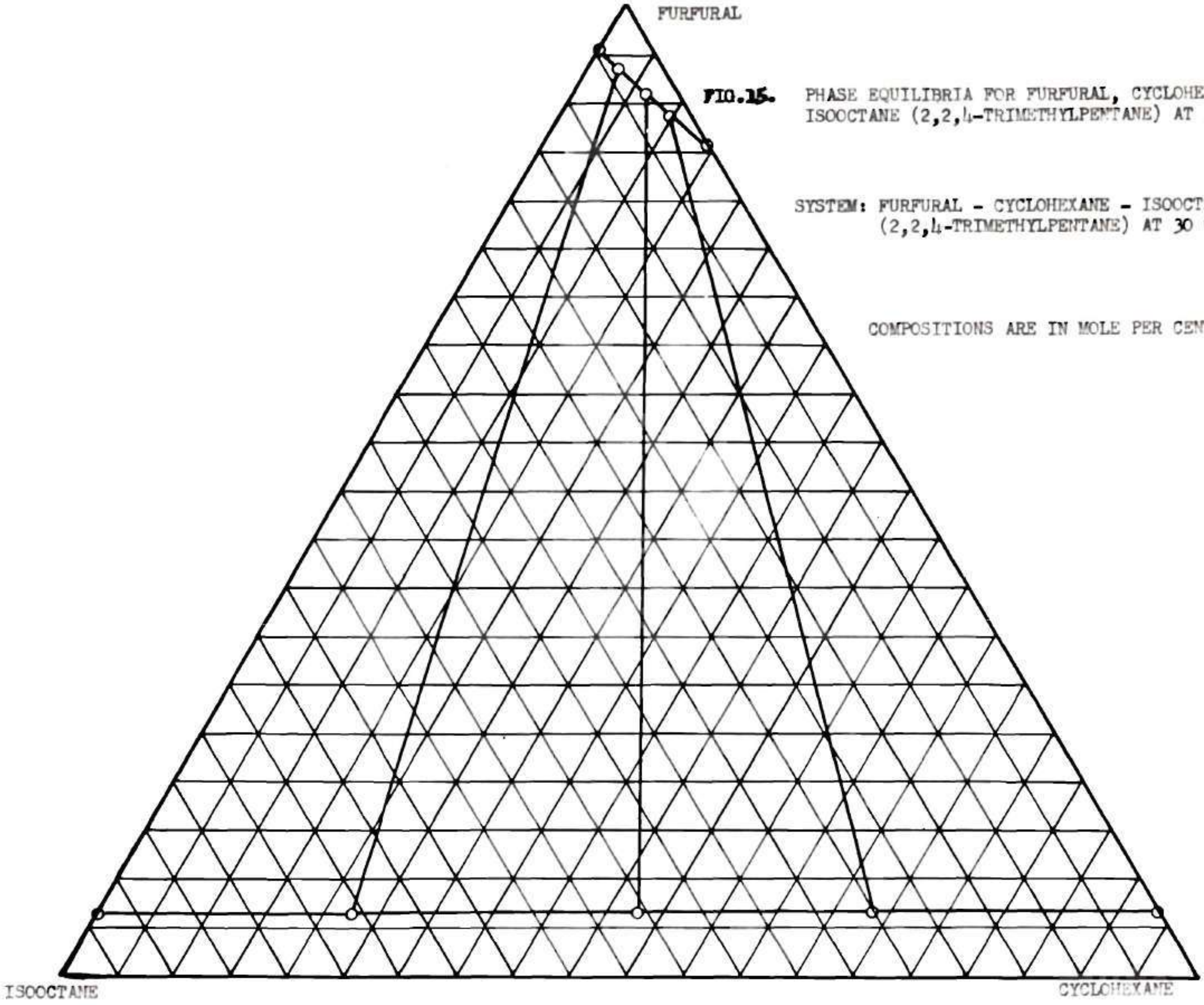

FIG. 15. PHASE EQUILIBRIA FOR FURFURAL, CYCLOHEXANE, ISOOCTANE (2,2,4-TRIMETHYLPENTANE) AT 30 C

SYSTEM: FURFURAL - CYCLOHEXANE - ISOOCTANE
(2,2,4-TRIMETHYLPENTANE) AT 30 C

COMPOSITIONS ARE IN MOLE PER CENT

3. Cyclohexane-Cetane-Furfural.--Liquid-liquid phase equilibria for cyclohexane-hexadecane (cetane)-furfural were obtained at the temperatures of 30°C., 60°C., and 90°C. These are shown in the triangular graphs of Figures 16, 17, and 18, and are tabulated in Table 34, Appendix II.

These hydrocarbons were selected so as to extend the study of the effect of molecular weight in naphthene-paraffin separations. The previous two systems had treated only C_7 and C_8 paraffins; this system extended the data to a C_{16} paraffin. The use of other paraffins such as decane and dodecane were considered but rejected in this study because of the proximity of their boiling points with that of furfural. However, with efficient fractionation it should be possible to obtain nearly quantitative recovery of dodecane from furfural. This component should certainly be included in any later studies.

All three temperature levels of 30°C., 60°C., and 90°C. were employed with this system as in the cyclohexane-n-heptane separation so as to determine whether the expected molecular weight effects might have a temperature coefficient. Further, the area of heterogeneity for cyclohexane-n-heptane-furfural at 90°C. was disappointingly small because of the proximity to the furfural-n-heptane critical solution temperature. For cetane-furfural, on the other hand, the temperature of 90°C. is considerably below the critical solution temperature, and a much larger area of heterogeneity was expected and obtained (see Figure 18).

4. Octene-1-n-Heptane-Furfural.--Liquid-liquid phase equilibria for octene-1-n-heptane-furfural were obtained at the temperature levels of 30°C. and 60°C. These are shown in the triangular graphs, Figures 19 and 20, and are tabulated in Table 35, Appendix II.

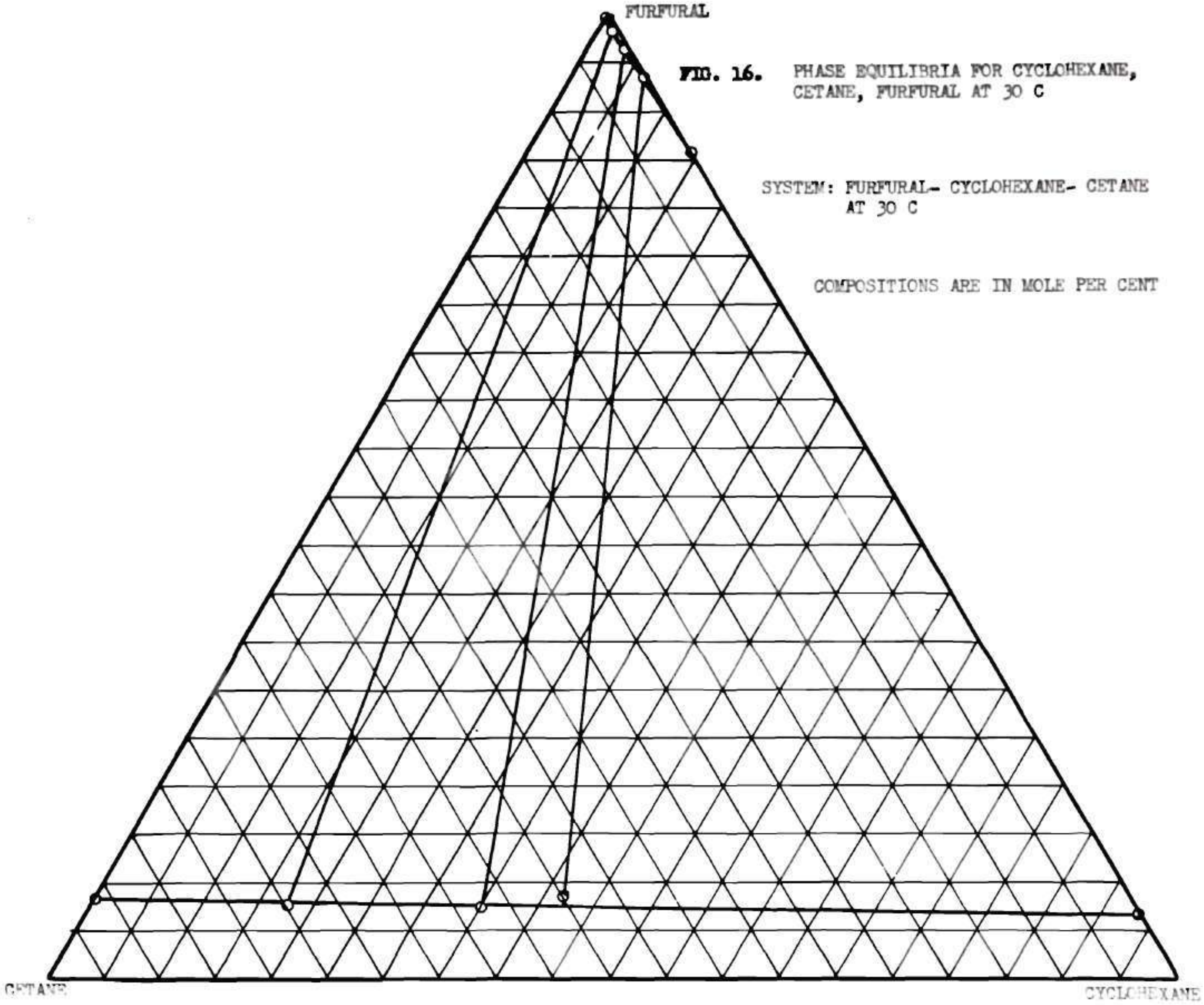

FIG. 16. PHASE EQUILIBRIA FOR CYCLOHEXANE, CETANE, FURFURAL AT 30 C

SYSTEM: FURFURAL- CYCLOHEXANE- CETANE
AT 30 C

COMPOSITIONS ARE IN MOLE PER CENT

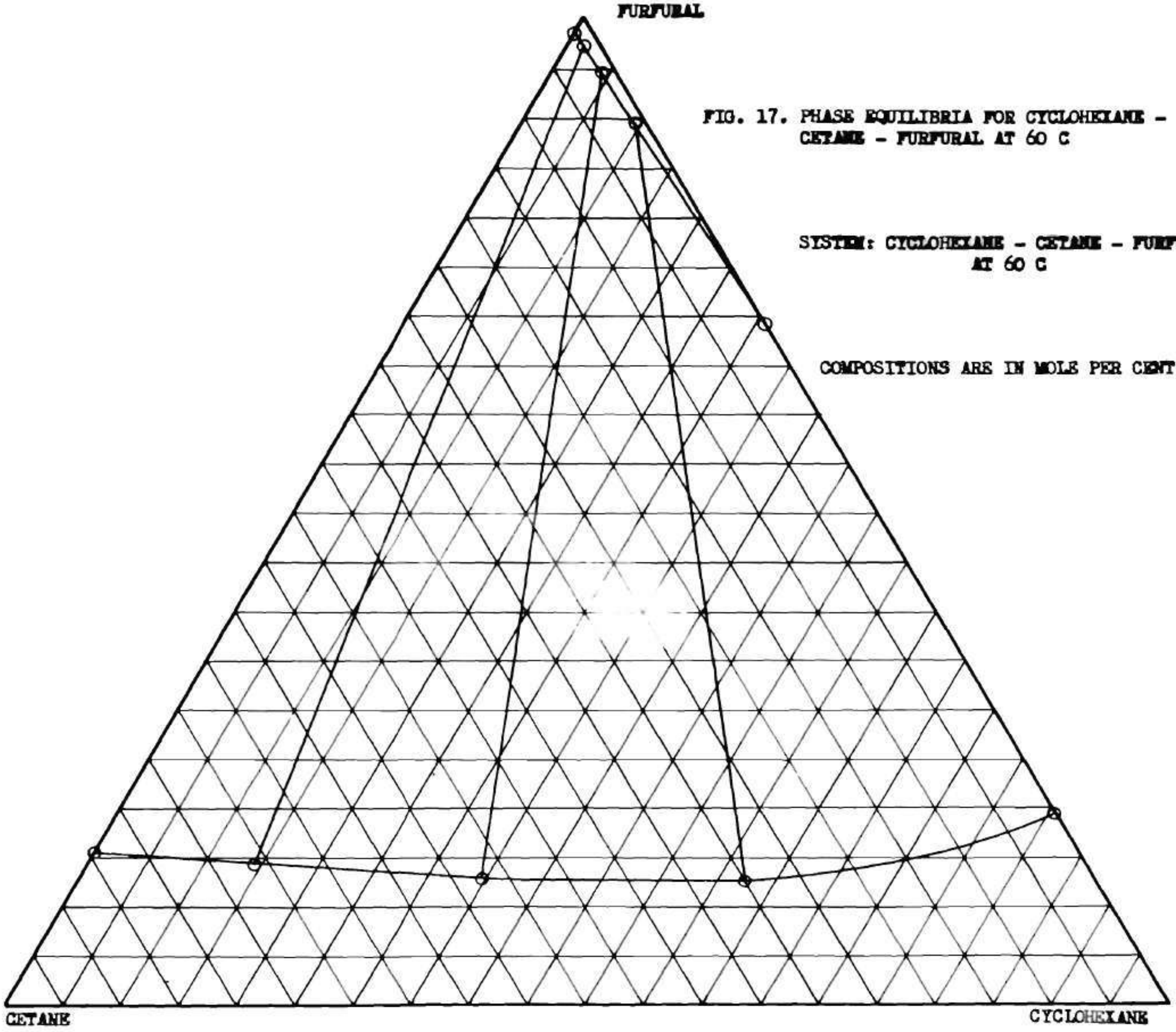

FIG. 17. PHASE EQUILIBRIA FOR CYCLOHEXANE - CETANE - FURFURAL AT 60 C

SYSTEM: CYCLOHEXANE - CETANE - FURFURAL AT 60 C

COMPOSITIONS ARE IN MOLE PER CENT

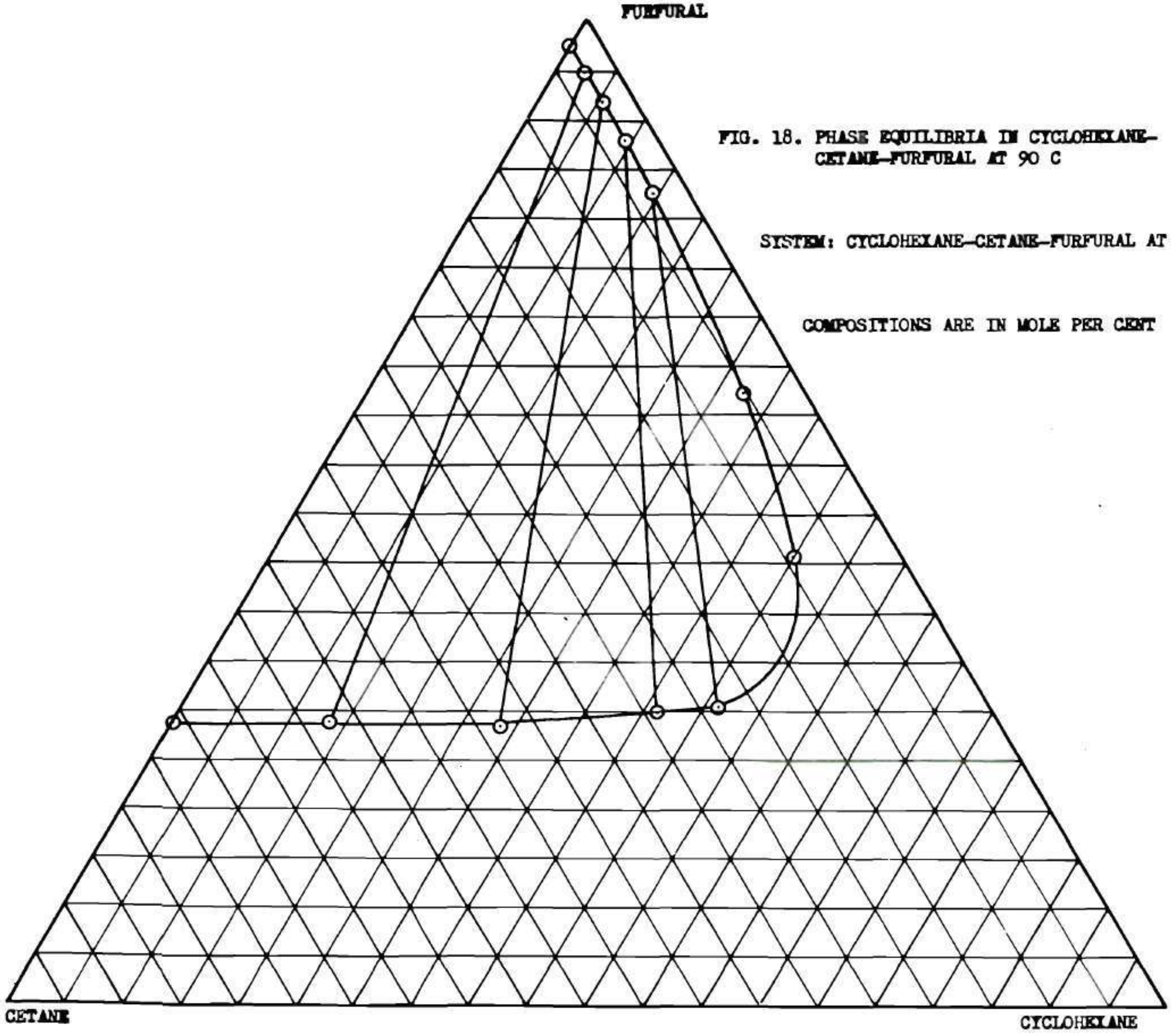

FIG. 18. PHASE EQUILIBRIA IN CYCLOHEXANE-CETANE-FURFURAL AT 90 C

SYSTEM: CYCLOHEXANE-CETANE-FURFURAL AT 90 C

COMPOSITIONS ARE IN MOLE PER CENT

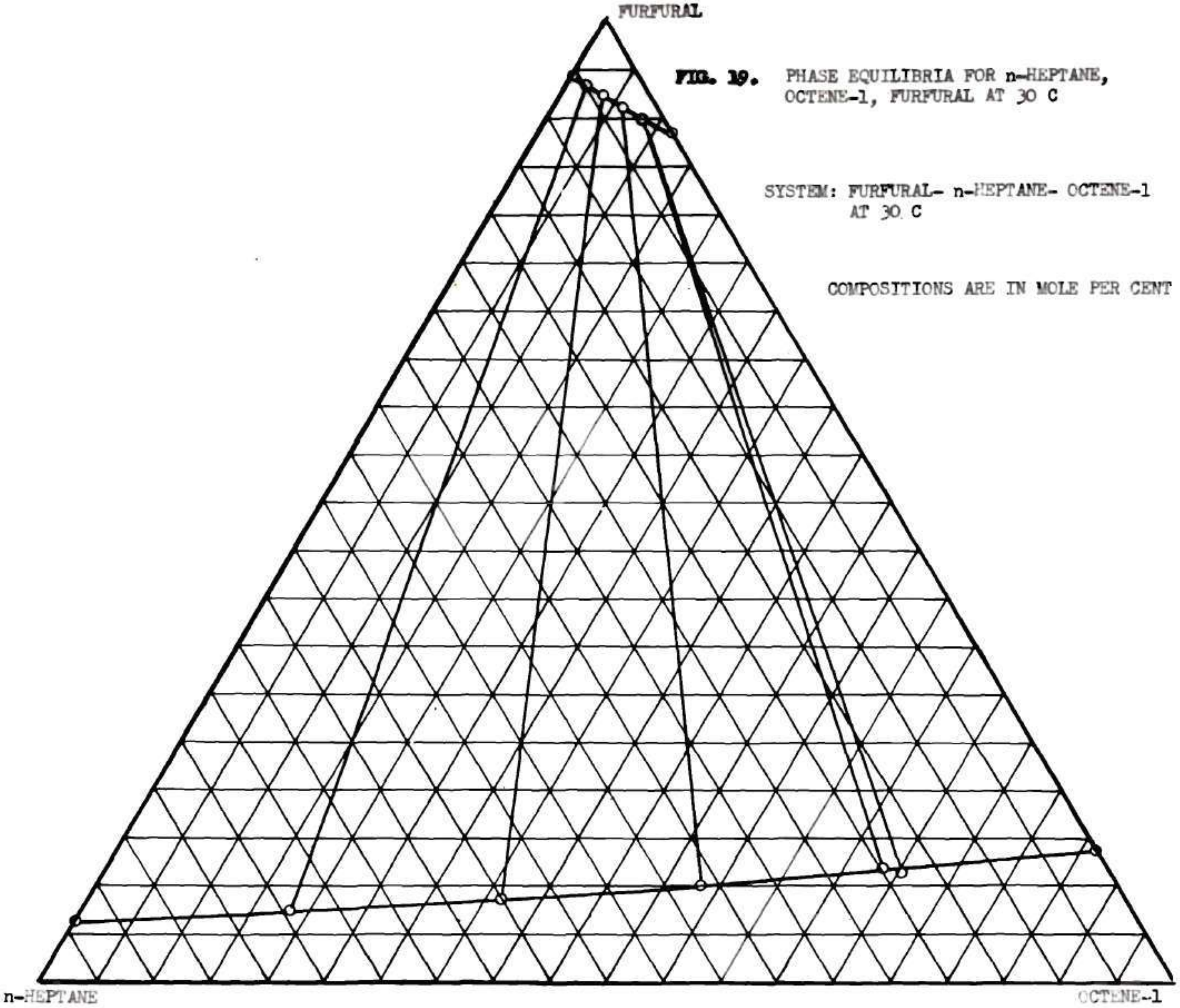

FIG. 19. PHASE EQUILIBRIA FOR n-HEPTANE, OCTENE-1, FURFURAL AT 30 C

SYSTEM: FURFURAL- n-HEPTANE- OCTENE-1
AT 30 C

COMPOSITIONS ARE IN MOLE PER CENT

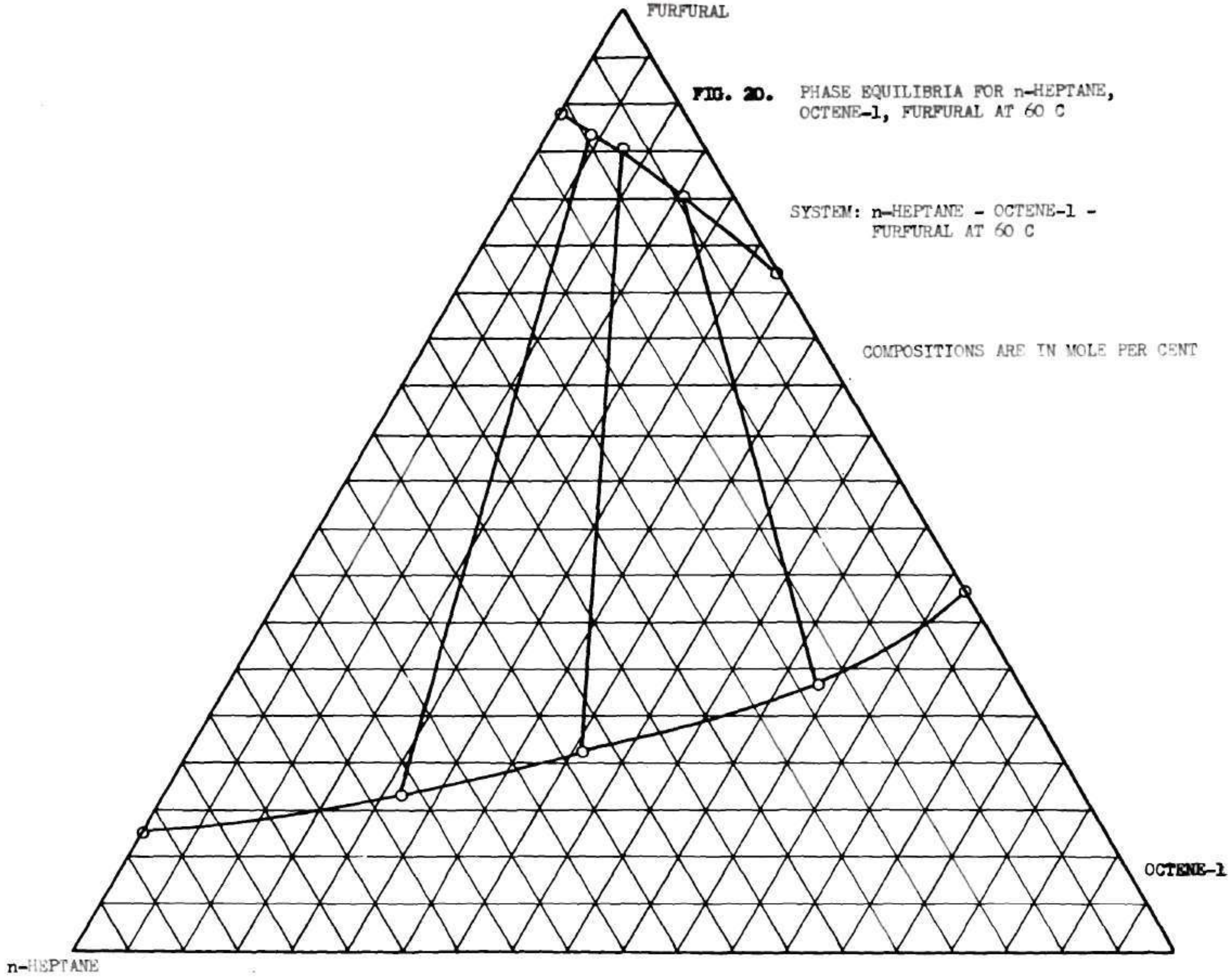

FIG. 20. PHASE EQUILIBRIA FOR n-HEPTANE, OCTENE-1, FURFURAL AT 60 C

SYSTEM: n-HEPTANE - OCTENE-1 - FURFURAL AT 60 C

COMPOSITIONS ARE IN MOLE PER CENT

These hydrocarbons were selected as typical of an olefin-paraffin separation with molecular weights in the same range as furfural. Use of the olefin heptene-1 was considered, but was rejected because the greatly decreased spread in refractive index would have necessitated use of another means of analysis.

This system was not studied at 90°C. because of its similarity with the system cyclohexane-n-heptane-furfural. The resulting phase diagram would also have had an extremely small region of heterogeneity.

5. Cyclohexane-Octene-1-Furfural.--Liquid-liquid phase equilibria for cyclohexane-octene-1-furfural were obtained at 30°C. These are shown in Figure 21 and are tabulated in Table 36, Appendix II.

These hydrocarbons were selected as typical naphthene-olefin systems. The use of other olefins, as heptane-1, or a substituted naphthene, as methylcyclohexane, would likely have served as well with certain restrictions on refractive index. However, the additional experimental work was not justified.

Naphthene-olefin separations are usually difficult to obtain by liquid-liquid extraction. An inspection of the tie-line slopes in Figure 21 shows that this system is no exception, even at the favorable temperature of 30°C. The selectivity would have been even smaller at the higher temperatures of 60°C. or 90°C., and the data were therefore not obtained.

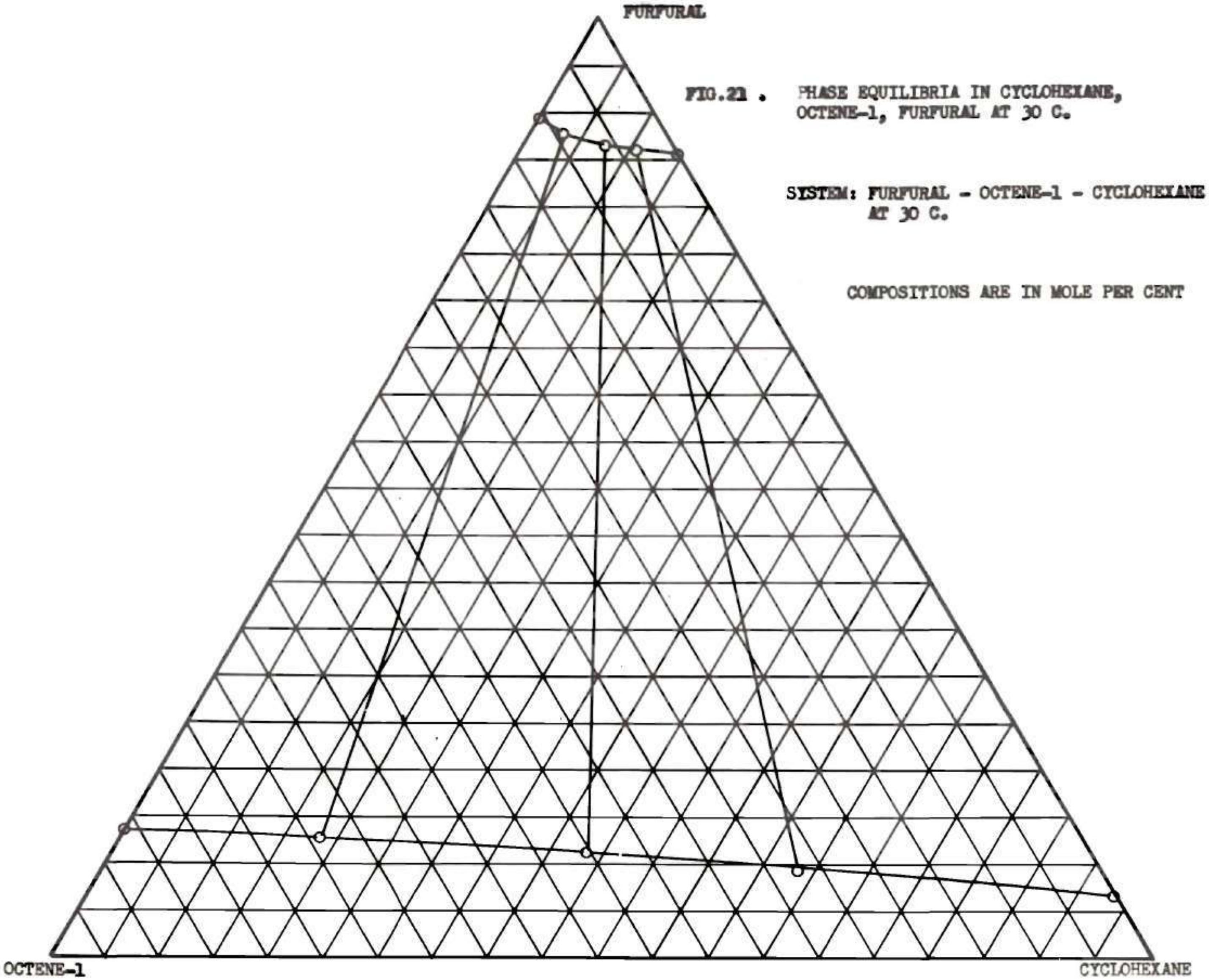

FIG.21 . PHASE EQUILIBRIA IN CYCLOHEXANE, OCTENE-1, FURFURAL AT 30 C.

SYSTEM: FURFURAL - OCTENE-1 - CYCLOHEXANE AT 30 C.

COMPOSITIONS ARE IN MOLE PER CENT

CHAPTER VI

ACTIVITY COEFFICIENT CORRELATIONS

Numerous methods are available for calculating activity coefficients in binary systems from the mutual solubility of coexisting liquid-liquid phases. Some of these as the Margules, Scatchard-Hamer, van Laar, and Hachmuth equations are discussed in Chapter II. Each is a particular solution of the Gibbs-Duhem differential equation (equation 18, page 15).

Unfortunately, all of the above-mentioned equations are complicated (see equations 24 and 25 on pages 18 and 19), and their solutions time comsuming. The use of any of the five equations (the Hachmuth equations have two forms) with the mutual solubility of Table 2, would result in different activity coefficient curves and different A and B constants (the terminals of the curves). The predicted equilibrium for each of the ten systems investigated in this research would then be displaced, depending upon which of the five activity coefficient correlations was employed for the binary pairs. Moreover, the application of one equation for one binary pair and another for the other pair would increase the number of variations exponentially.

A detailed study of each of the possible variation was considered beyond the scope of this work. Instead, in the absence of information demonstrating the reliability of one method over another for predicting the activity coefficients, it was decided to employ the more-widely-known van Laar equations (equations 22 and 25) for the initial prediction of all equilibria. This was followed by predictions for isolated systems based on the Scatchard-Hamer activity coefficient equations (equations 21 and 24).

A. van Laar Activity Coefficient Calculations

1. Cyclohexane-Furfural.--The van Laar activity coefficients for cyclohexane in furfural have been calculated from the mutual solubility at temperature levels of 15, 30, 45, and 60°C. These calculations made use of the general van Laar expressions (equation 22) with the A and B constants that were obtained by the solution of equation 25. This is illustrated by Sample Calculation A in Appendix III for cyclohexane in furfural at 30°C.

In this study activity coefficients were needed at the temperatures of 30, 60, and 90°C. However, the temperature of 90°C. is considerably above the critical solution temperature for furfural and cyclohexane, which occurs at approximately 67°C. In order to obtain these data, it was necessary to extrapolate the activity coefficients calculated for temperatures of 15, 30, 45, and 60°C. to 90°C. on a graph representing the logarithm of the activity coefficients (for given concentrations) as ordinate and the reciprocal absolute temperature, $°K^{-1}$, as abscissa. This is equivalent to a graphical solution of equation 27, which will result in a straight line if the differential heats of solution are constant. These curves are shown in Figure 22, indicating that the differential heats of solution are constant over the temperature range employed. The absolute value of these heats of solution can, therefore, be evaluated from the slopes of the lines.

The extrapolated van Laar activity coefficient values at 90°C.

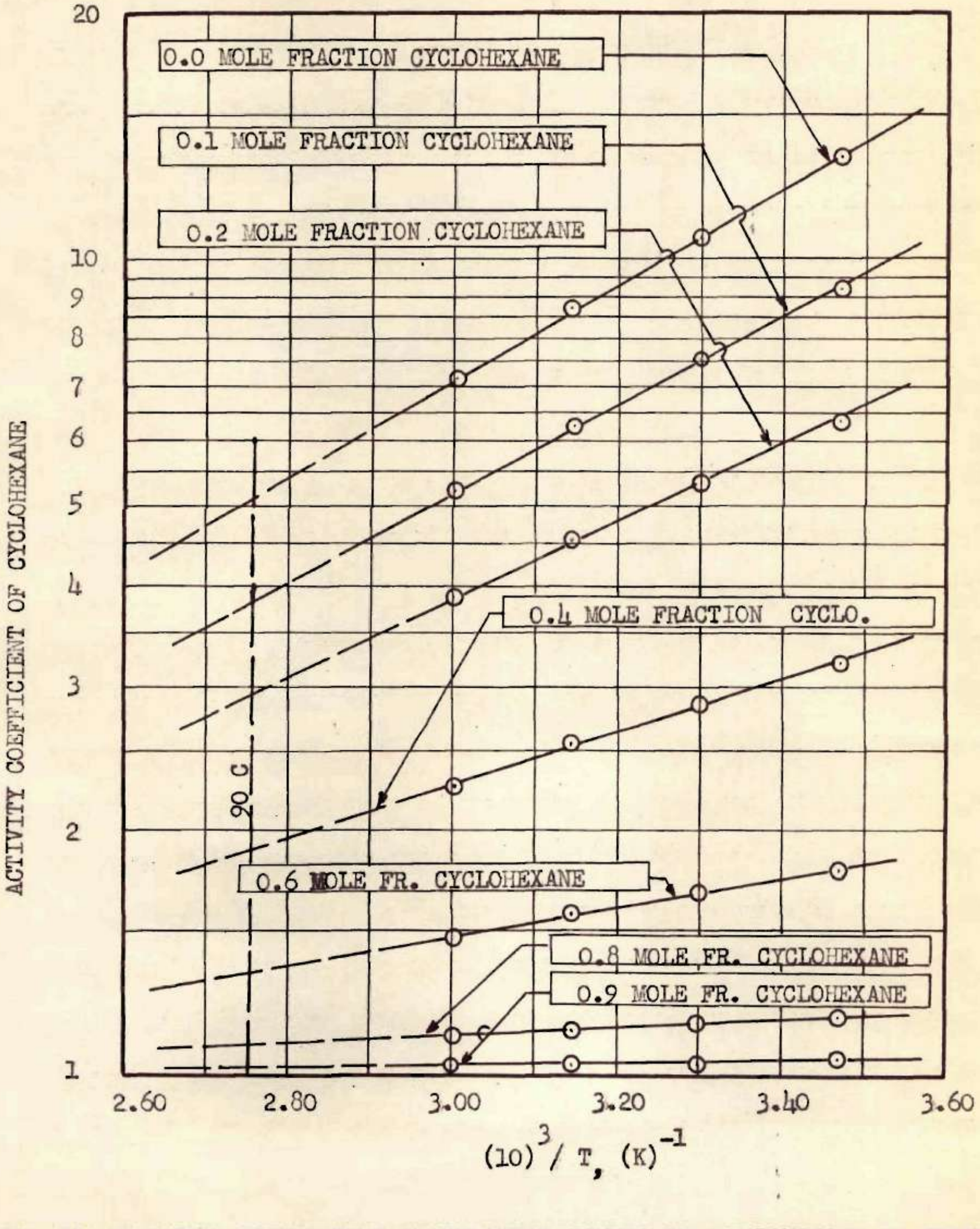

FIG. 22. ACTIVITY COEFFICIENT-TEMPERATURE CURVES FOR CYCLOHEXANE IN FURFURAL
(van Laar Equations)

are tabulated in Table 25, Appendix II, with the mutual solubility, van Laar constants, and activity coefficient data for temperatures of 15, 30, 45, and 60°C. The activity coefficient data for cyclohexane in furfural at 30, 60 and 90°C. from this table are shown in Figure 23. Here the cross marks on the curves designate the compositions given by the mutual solubility at the temperature obtaining. These are joined by dotted lines which show the locus of points representing the mutual solubilities.

2. n-Heptane-Furfural.--The van Laar activity coefficients for n-heptane in furfural have been calculated from the mutual solubility at temperature levels of 30, 60, and 90°C. A summary of the mutual solubility, van Laar constants, and van Laar activity coefficient data for these three temperatures is made in Table 26, Appendix II. The van Laar activity coefficient data for n-heptane in furfural taken from this table are shown in Figure 24.

3. Isooctane-Furfural.--The van Laar activity coefficient data for 2,2,4-trimethylpentane (isooctane) in furfural have been calculated from the mutual solubility at the temperature of 30°C. A summary of these activity coefficient data, mutual solubility, and van Laar constants is made in Table 27, Appendix II. The van Laar activity coefficient data for this isooctane in furfural have been taken from this table and are shown in Figure 25.

4. Cetane-Furfural.--The van Laar activity coefficients for hexadecane (cetane) in furfural have been calculated from the mutual solubility at the temperature levels of 30, 60, and 90°C. A summary of the mutual solubility, van Laar constants, and van Laar activity cofficients for these temperatures is made in Table 28, Appendix II. The van Laar

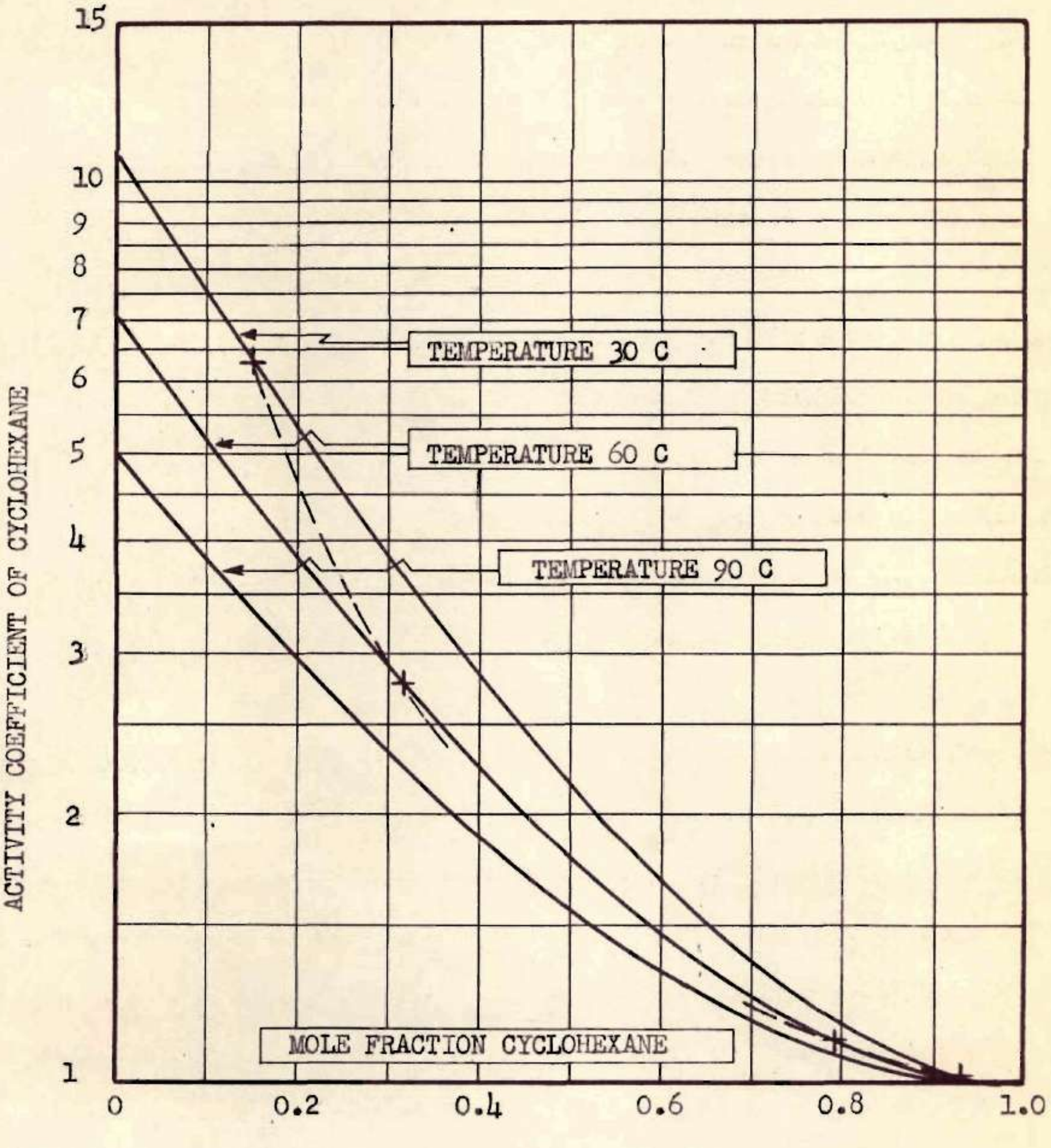

FIG. 23. ACTIVITY COEFFICIENT CURVES FOR CYCLOHEXANE IN FURFURAL (van Laar Equations)

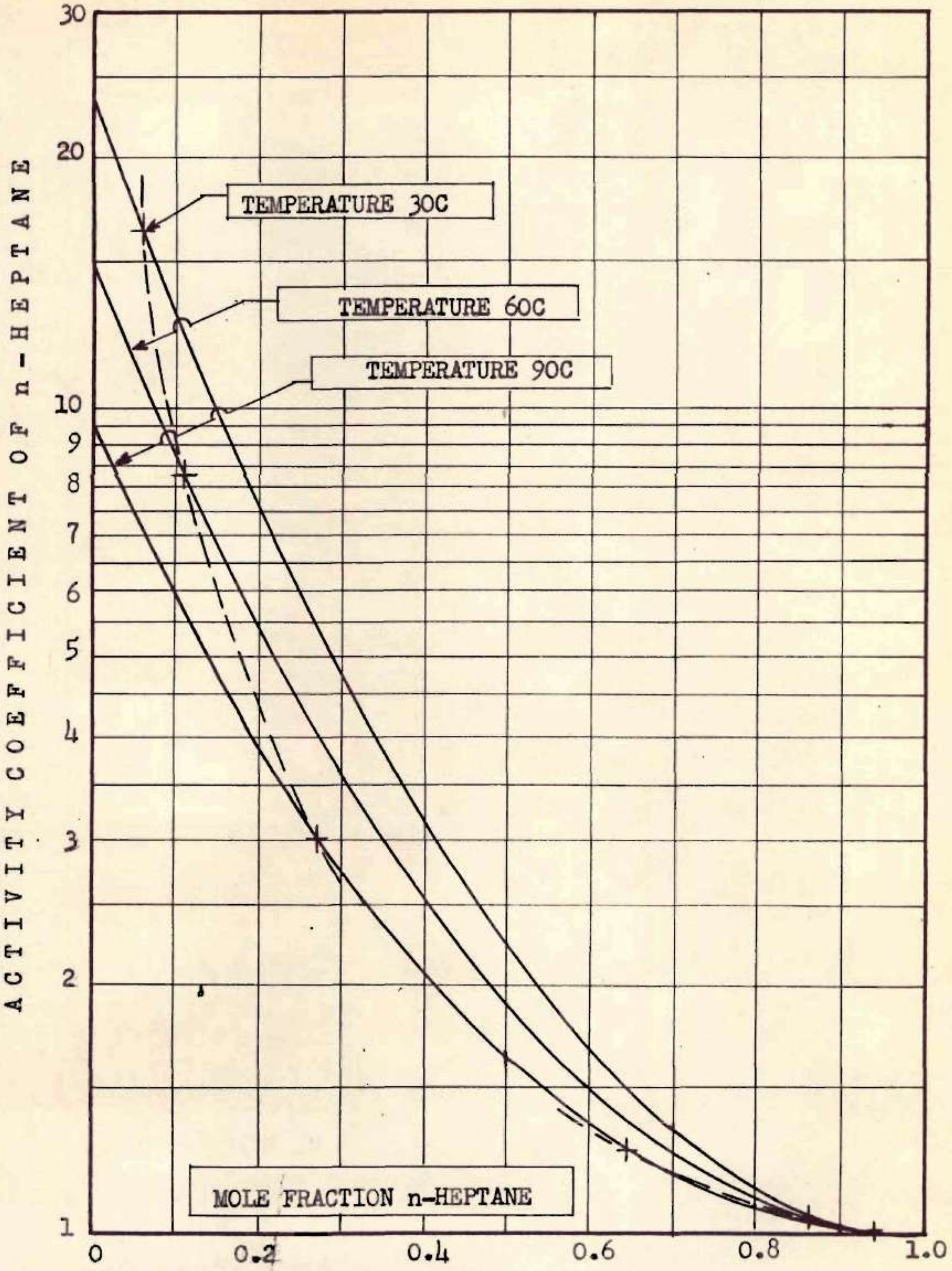

FIG. 24 . ACTIVITY COEFFICIENT CURVES FOR n-HEPTANE IN FURFURAL.
(van Laar Equations)

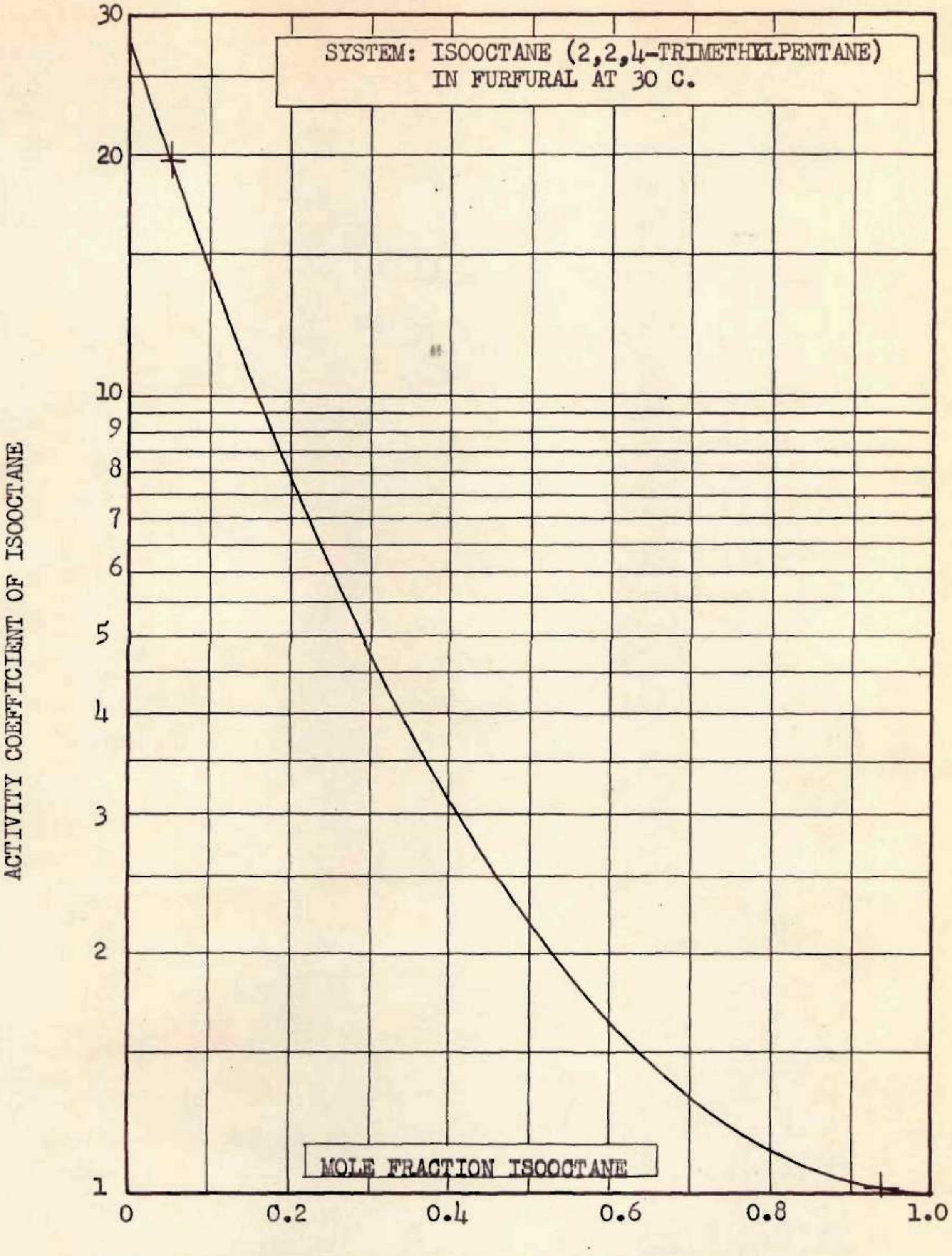

FIG. 25. ACTIVITY COEFFICIENT CURVE FOR ISOOCTANE IN FURFURAL.
(van Laar Equations)

activity coefficients for cetane in furfural have been taken from this table and are shown in Figure 26.

5. Octene-1-Furfural.--The van Laar activity coefficients from octene-1 in furfural have been calculated from the mutual solubility at the temperature levels of 30 and 60°C. A summary of these activity coefficients, mutual solubility, and van Laar constants is made in Table 29, Appendix II. The activity coefficients data from this table are shown in Figure 27.

B. Scatchard-Hamer Correlations

As was discussed in Chapter II, the van Laar equations for activity coefficients are based on the assumption that the effective molal volumes are in the ratio of the van Laar constants A and B. On the other hand, the Scatchard-Hamer equations are premised on the effective volumes being in the ratio of the actual molal volumes. The vast difference in these two assumptions indicates that there might be some systems for which the van Laar equations would apply, and others for which the Scatchard-Hamer equations would apply.

The large difference in molecular weight (and molar volume) between cetane and furfural indicated that the Scatchard-Hamer equations might be useful for this correlation. However, since these correlations are applied to the separation of hydrocarbon pairs, consistency of method would dictate that the activity coefficient for the furfural-cyclohexane system also be recorrelated with this equation. The additional recorrelation of only one more paraffin-furfural system, say for n-heptane-furfural, would provide a direct comparison of the correlation methods for two naphthene-paraffin separations.

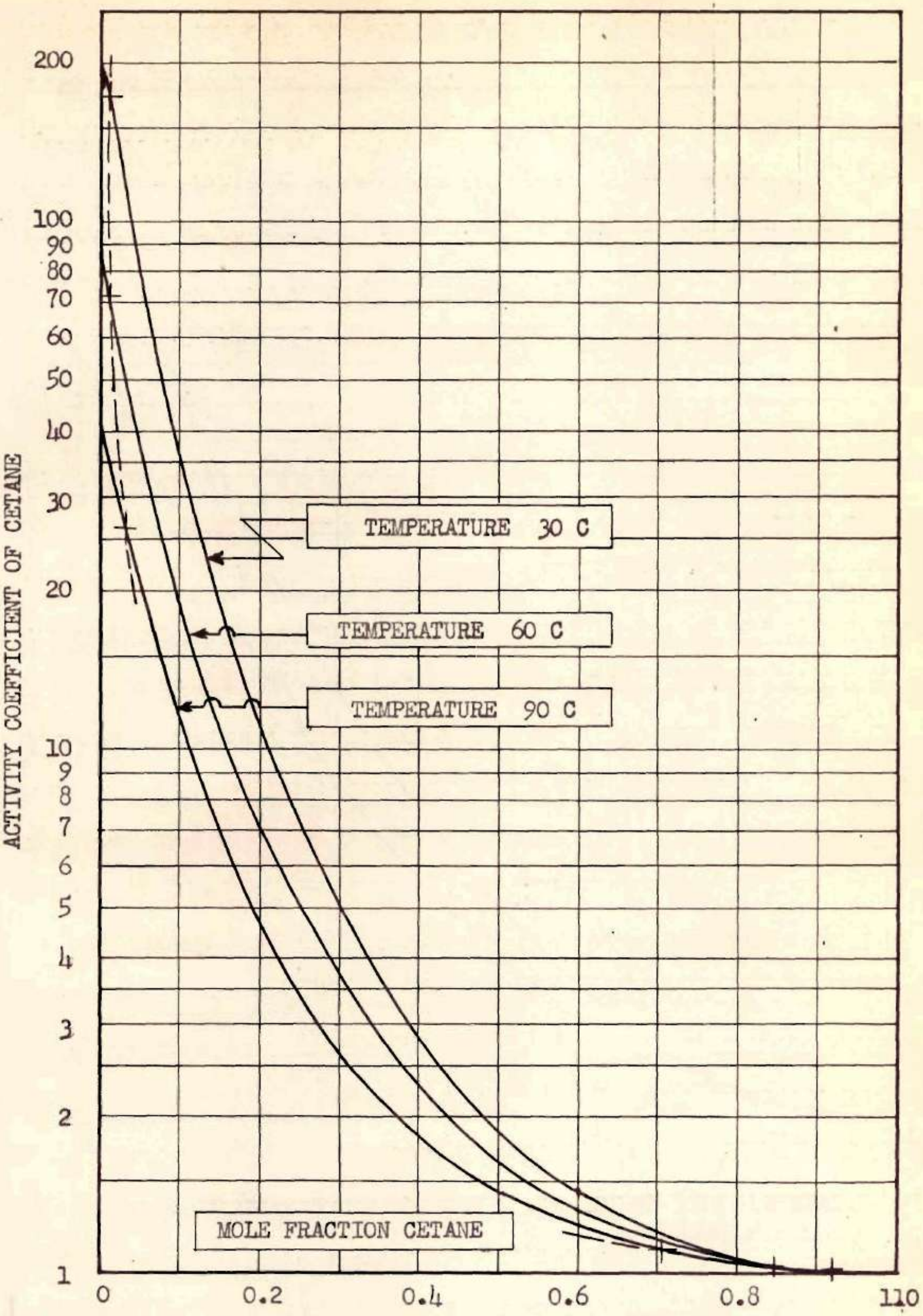

FIG.26 . ACTIVITY COEFFICIENT CURVES FOR CETANE IN FURFURAL.
(van Laar Equations)

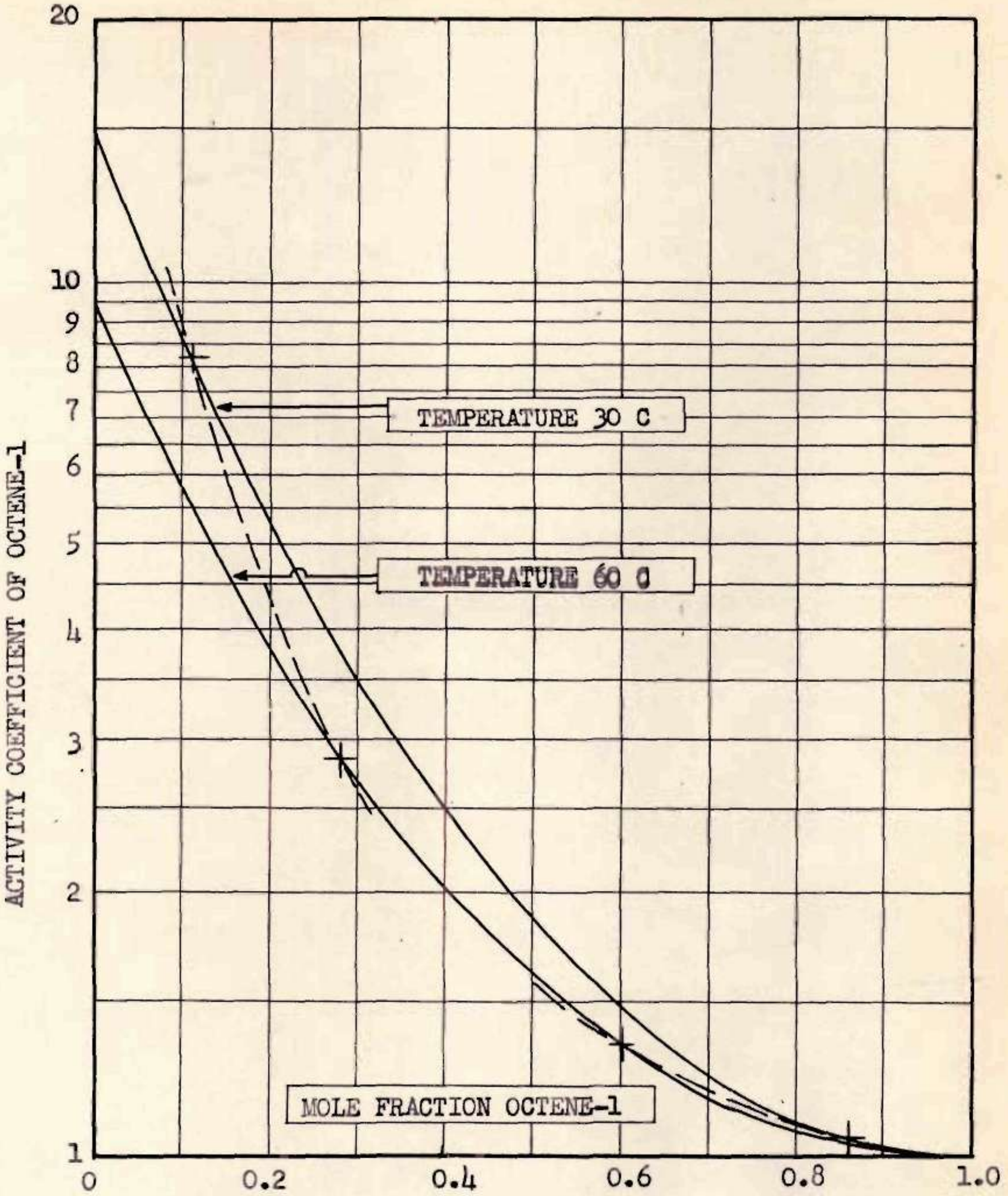

FIG. 27. ACTIVITY COEFFICIENT CURVES FOR OCTENE-1 IN FURFURAL.
(van Laar Equations)

Accordingly, the Scatchard-Hamer equations (equations 24) have been applied for the calculation of activity coefficients for the three binary systems furfural-cetane, furfural-cyclohexane, and furfural-n-heptane at 30°C. The activity coefficients for the hydrocarbons in furfural are shown in Figure 28. They may be compared with the van Laar activity coefficients shown in Figures 23, 24, and 26. It is apparent from these curves that the values for the activity coefficients, at the compositions representing the saturated hydrocarbon-rich phases, are very nearly the same for both the van Laar and Scatchard-Hamer equations. This was explained in Chapter II for systems with low or moderate mutual solubilities. However, the curves show considerable deviation as one approaches zero hydrocarbon content, and at the terminals of the curves the van Laar equation gives an activity coefficient that is over 40 per cent greater than that given by the Scatchard-Hamer expression for cyclohexane in furfural at 30°C.

A summary of the mutual solubility, Scatchard-Hamer constants, and Scatchard-Hamer activity coefficient data for the above three hydrocarbons in furfural is made in Table 30, Appendix II.

The application of the Scatchard-Hamer equations required an evaluation of the molal volumes of the constituents at 30°C. These were calculated from the density data at other temperatures given in Perry (40), and application of the estimation method of Watson (41). The critical properties needed in the Watson method were obtained from

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(40) Perry, John H., Chemical Engineers Handbook, Third Edition, pp. 139-141, 204, McGraw-Hill Book Co., New York, 1950.

(41) Watson, K. M., Ind. Eng. Chem., <u>35</u>, 398 (1943).

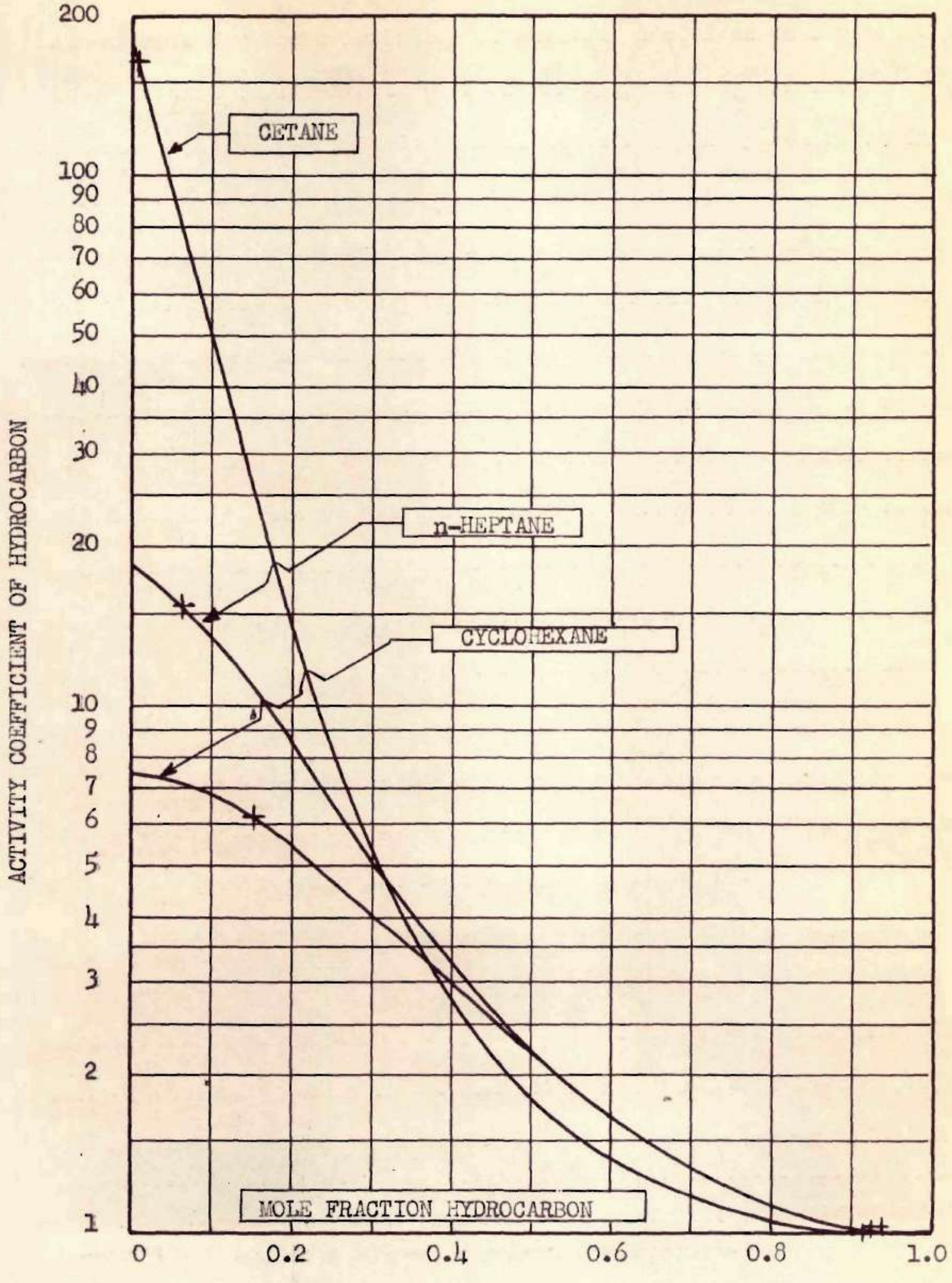

FIG. 28. ACTIVITY COEFFICIENTS AT 30 C FOR HYDROCARBONS IN FURFURAL
(SCATCHARD-HAMER EQUATIONS)

Bethea (22) for furfural, from Perry (40) for cyclohexane, from Hougen and Watson (33) for hexadecane, and from Phillips Hydrocarbons (36) for n-heptane. A summary of these data and results is shown in Table 31, Appendix II.

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(22) Bethea, C. F., M. S. Thesis, p. 21, O.I.T., 1952.

(33) Hougen and Watson, Chemical Process Principles, p. 507.

(36) Phillips Hydrocarbons, p. 147, Phillips Petroleum Company, Bartlesville, Okla., 1949.

(40) Perry, John H., Chemical Engineers Handbook, Third Edition, pp. 139-141, 204, McGraw-Hill Book Co., New York, 1950.

CHAPTER VII

COMPARISON OF EXPERIMENTAL AND ESTIMATED DATA

The experimental equilibria obtained in this work are shown in Tables 32 through 36. These data constitute ten different phase diagrams for five different ternary systems at three different temperature levels. They are compared in the following sections with the equilibria calculated with the estimation methods described in Chapter II and illustrated by Sample Calculations B, C, D, and E in Appendix III.

In order to facilitate the comparison of the experimental and estimated equilibria, all calculations were initiated from the experimental value of the hydrocarbon composition (on a solvent-free basis) in either the solvent-rich or hydrocarbon-rich phase. It is to be emphasized that this selection of an experimental composition was only a matter of convenience, and does not restrict the estimation method in any way. Any other compositions could have been assumed for a starting point, but they would not have provided the direct comparison with the experimental data.

The comparison of the estimated and experimental equilibria is shown both in tables and on graphs. The graphs are of the X-Y equilibrium type commonly used in the representation of vapor-liquid equilibria. Here, however, the co-ordinates represent the hydrocarbon compositions (on a solvent-free basis) in the hydrocarbon-rich and solvent-rich phases. Such graphs are of considerable utility because they show at a glance the relative ease, or difficulty, of the separation of the two hydrocarbons.

The tables employed in these comparisons show both the X-Y equilibria and the mole fraction furfural in the solvent-rich and hydrocarbon-rich phases. They provide the additional comparison of the estimated and experimental solvent contents in the two liquid phases.

A. Cyclohexane-n-Heptane-Furfural

Experimental equilibria for the system cyclohexane-n-heptane-furfural were obtained at the three temperatures of 30, 60, and 90°C. These are compared with estimated equilibria as follows:

1. Equilibria at 30°C.--The experimental equilibria for cyclohexane-n-heptane-furfural at 30°C. are compared with estimated equilibria based both on van Laar and Scatchard-Hamer activity coefficients as shown in Figure 29 and Table 3. The estimation method is illustrated in detail by Sample Calculation B, Appendix III, showing the calculation of the Run 5 phase equilibria for the van Laar case given in Table 3.

The estimations based on the van Laar equations seem in much better agreement with the experimental data for this system than those based on the Scatchard-Hamer equations. An inspection of Table 3 will show that the solvent-phase compositions were estimated from the hydrocarbon-phase compositions of the given experimental runs. Accordingly, only one value for $\frac{X_N}{(1-X_F)_{Hc}}$, representing mole fraction cyclohexane in the solvent-free hydrocarbon phase, is given in the spaces alloted to Exp. (experimental data) and Est. (estimated data) - regardless of the basis for activity coefficients. Similarly, the same value for $(X_F)_{Hc}$, representing the mole fraction furfural in the hydrocarbon phase, was estimated in the two cases. This is explained in Chapter II, i.e.,

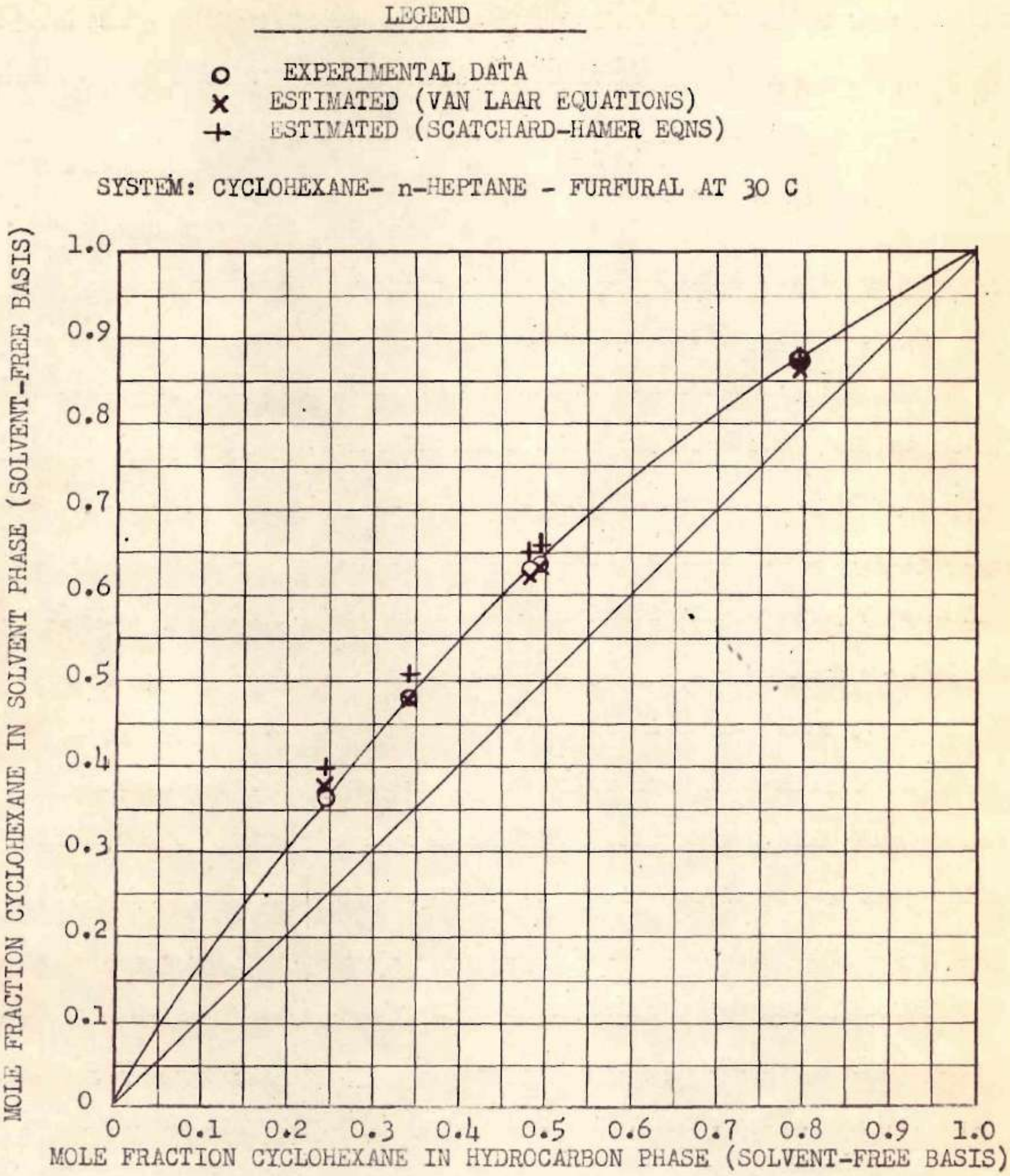

FIG. 29. X-Y EQUILIBRIA IN CYCLOHEXANE - N -HEPTANE - FURFURAL AT 30 C.

Table 3. Comparison of Experimental and Estimated Equilibria for Cyclohexane-n-Heptane-Furfural at 30°C.

Composition	Run 4		Run 8		Run 9		Run 5		Run 6	
	Exp.	Est.	Exp.	Est.	Exp.	Est.	Exp.	Est.	Exp.	Est.
A. Based on van Laar Activity Coefficients										
$(\frac{X_N}{1-X_F})_{Hc}$	0.244*		0.344*		0.482*		0.495*		0.795*	
$(\frac{X_N}{1-X_F})_{Sol.}$	0.362	0.374	0.481	0.480	0.631	0.624	0.636	0.634	0.874	0.866
$(X_F)_{Hc}$	0.060	0.059	0.063	0.060	0.066	0.060	0.064	0.061	0.063	0.062
$(X_F)_{Sol.}$	0.922	0.924	0.915	0.915	0.904	0.904	0.903	0.903	0.877	0.873
B. Based on Scatchard-Hamer Activity Coefficients										
$(\frac{X_N}{1-X_F})_{Hc}$	0.244*		0.344*		0.482*		0.495*		0.795*	
$(\frac{X_N}{1-X_F})_{Sol.}$	0.362	0.396	0.481	0.510	0.631	0.645	0.636	0.655	0.874	0.877
$(X_F)_{Hc}$	0.060	0.059	0.063	0.060	0.066	0.060	0.064	0.061	0.063	0.062
$(X_F)_{Sol.}$	0.922	0.916	0.915	0.909	0.904	0.895	0.903	0.894	0.877	0.866

Where: X_N = mole fraction naphthene (cyclohexane)

X_F = mole fraction furfural

$\frac{X_N}{1-X_F}$ = mole fraction naphthene (solvent free basis)

Subscripts Hc, Sol. refer to hydrocarbon and solvent phase respectively.

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*The experimental hydrocarbon-phase composition (solvent free basis) is also the basis, or starting point, for the estimation.

the assumption is made that the curve representing mols of solvent per mole of hydrocarbon versus mole fraction cyclohexane (solvent-free basis) is linear for the starting or known phase, regardless of the activity coefficient correlation basis.

2. Equilibria at 60°C.--The experimental equilibria for cyclohexane-n-heptane-furfural at 60°C. are compared with estimated equilibria based on van Laar activity coefficient curves as shown in Figure 30 and Table 4. The estimated equilibria were calculated in two ways - one starting with experimental compositions in the hydrocarbon phase, the other starting with experimental compositions in the solvent phase. These are illustrated in Sample Calculation C, Appendix III, for the equilibria of Run 15 shown in Table 4. Figure 30 shows excellent agreement of the experimental with estimated X-Y equilibria, regardless of which phase was used to initiate calculations. Table 4 shows the estimated values for mole fraction furfural in the solvent and hydrocarbon phases to be slightly in error, but the error is independent of which phase was used to initiate calculations, and not of practical engineering significane.

3. Equilibria at 90°C.--The experimental equilibria for cyclohexane-n-heptane-furfural at 90°C. are compared with estimated equilibria based on van Laar activity coefficient curves and extrapolations therefrom shown in Figure 31 and Table 5. As mentioned previously, this temperature is above the critical solution temperature for the binary pair, furfural-cyclohexane, and the previous methods for estimating the furfural content of the starting phases cannot be employed. Therefore, it was necessary to assume knowledge of the binodal curve in order to calculate the tie-line data. However, these curves are not difficult to

SYSTEM: FURFURAL - CYCLOHEXANE - n-HEPTANE

TEMPERATURE 60 C

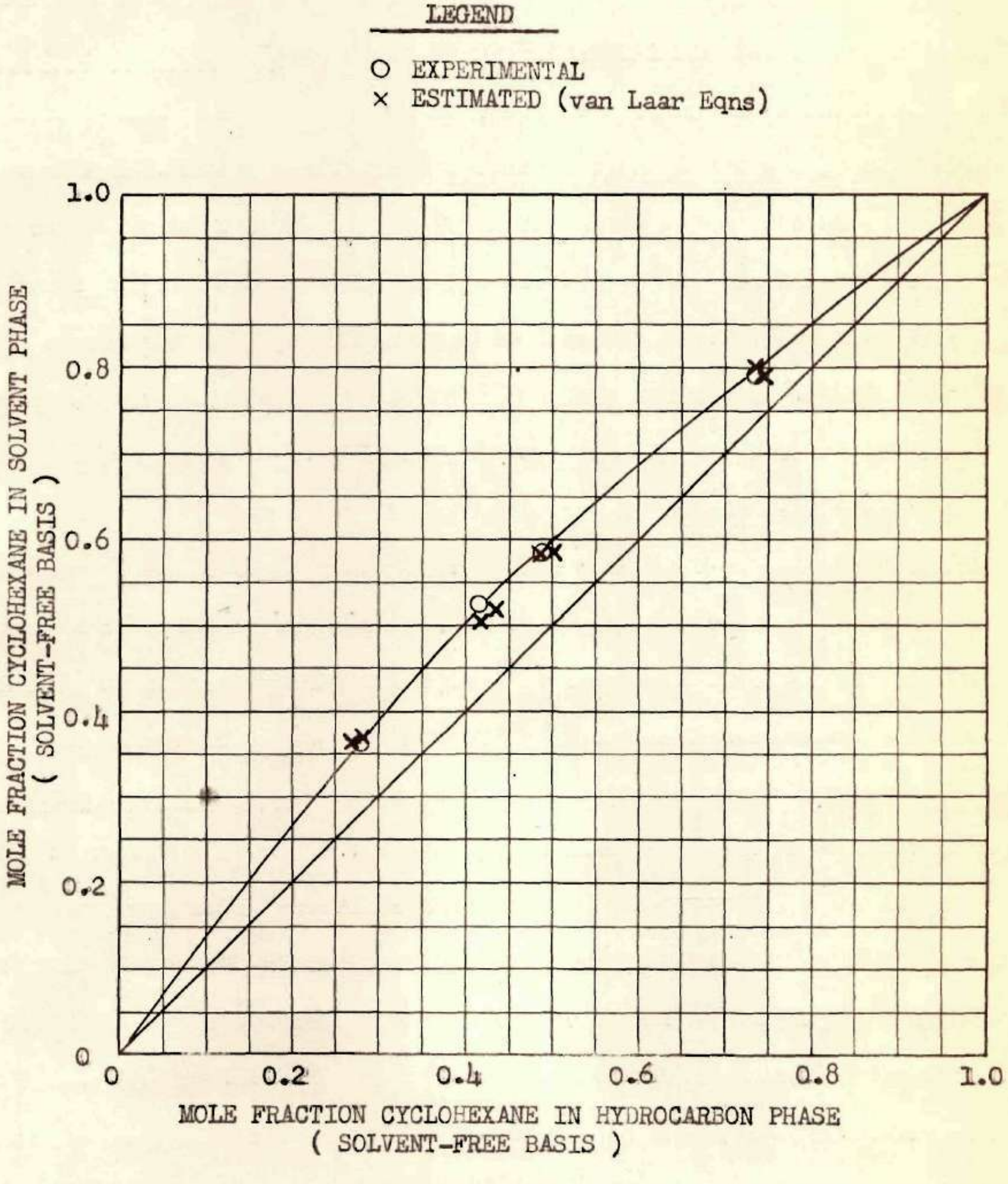

FIG. 30. X-Y EQUILIBRIA IN CYCLOHEXANE - n-HEPTANE - FURFURAL AT 60 C

Table 4. Comparison of Experimental and Estimated*
Equilibria for Cyclohexane-n-Heptane-Furfural at 60°C.

A. Estimations Based on the Experimental Hydrocarbon-Phase Composition (Solvent-Free Basis)

Composition	Run 15		Run 14		Run 13		Run 16	
	Exp.	Est.	Exp.	Est.	Exp.	Est.	Exp.	Est.
$(\frac{X_N}{1-X_F})_{Hc}$	0.280		0.416		0.489		0.737	
$(\frac{X_N}{1-X_F})_{Sol.}$	0.365	0.371	0.529	0.505	0.588	0.583	0.791	0.805
$(X_F)_{Hc}$	0.138	0.153	0.145	0.164	0.150	0.170	0.167	0.187
$(X_F)_{Sol}$	0.862	0.849	0.837	0.820	0.828	0.815	0.770	0.767

B. Estimations Based on the Experimental Solvent-Phase Composition (Solvent-Free Basis)

Composition	Run 15		Run 14		Run 13		Run 16	
	Exp.	Est.	Exp.	Est.	Exp.	Est.	Exp.	Est.
$(\frac{X_N}{1-X_F})_{Sol.}$	0.365		0.529		0.588		0.791	
$(\frac{X_N}{1-X_F})_{Hc}$	0.280	0.272	0.416	0.432	0.489	0.496	0.737	0.745
$(X_F)_{Hc}$	0.138	0.153	0.145	0.165	0.150	0.170	0.167	0.188
$(X_F)_{Sol.}$	0.862	0.854	0.837	0.831	0.828	0.820	0.770	0.771

*Based on van Laar activity coefficients.

SYSTEM : CYCLOHEXANE - n-HEPTANE - FURFURAL AT 90 C

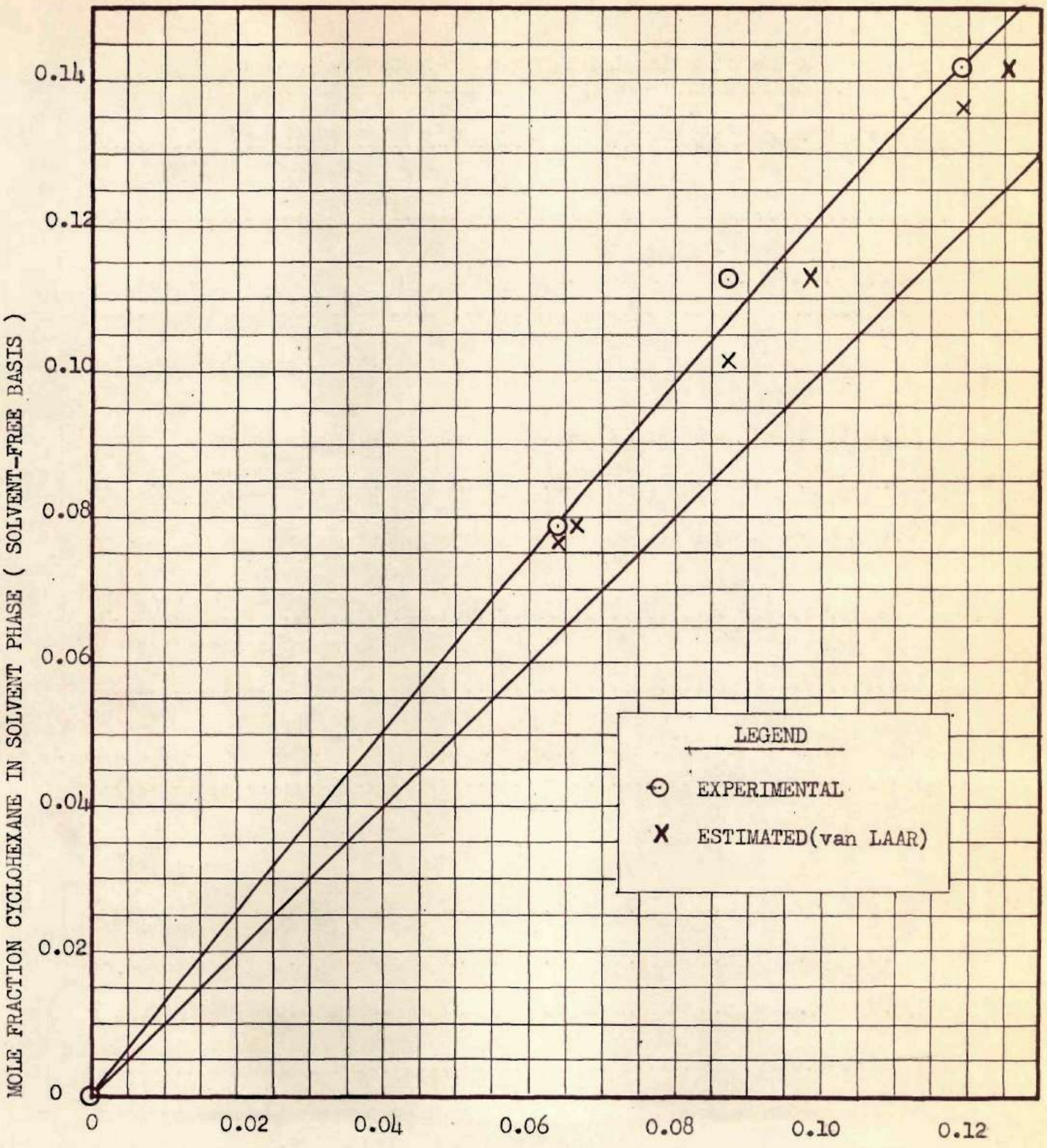

FIG. 31. X-Y EQUILIBRIA IN CYCLOHEXANE - n-HEPTANE - FURFURAL AT 90 C

Table 5. Comparison of Experimental and Estimated*
Equilibria for Cyclohexane-n-Heptane-Furfural at 90°C.

A. Estimations Based on the Experimental Hydrocarbon-Phase Composition

Composition	Run 19		Run 18		Run 20	
	Exp.	Est.	Exp.	Est.	Exp.	Est.
$(\frac{X_N}{1-X_F})_{Hc}$	0.064		0.087		0.119	
$(\frac{X_N}{1-X_F})_{Sol.}$	0.079	0.0766	0.113	0.1016	0.142	0.1360
$(X_F)_{Hc}$	0.385		0.401		0.416	
$(X_F)_{Sol.}$	0.725	0.722	0.705	0.710	0.693	0.698

B. Estimations Based on the Experimental Solvent-Phase Composition

Composition	Run 19		Run 18		Run 20	
	Exp.	Est.	Exp.	Est.	Exp.	Est.
$(\frac{X_N}{1-X_F})_{Sol.}$	0.079		0.113		0.142	
$(\frac{X_N}{1-X_F})_{Hc}$	0.064	0.0665	0.087	0.0985	0.119	0.1255
$(X_F)_{Hc}$	0.385	0.384	0.401	0.406	0.416	0.425
$(X_F)_{Sol.}$	0.725		0.705		0.693	

*Based on van Laar activity coefficients.

locate, and the additional requirement does not seriously limit the estimation method. Sample Calculation D, Appendix III, illustrates this type calculation with the estimation of the phase equilibria for Run 19 shown in Table 5.

Figure 31 shows excellent agreement between the experimental and estimated X-Y equilibria considering the scatter in the experimental data and the long extrapolations necessary to obtain the 90°C. activity coefficients for cyclohexane in furfural as shown in Figure 22. Further, it appears that the estimations were made with equal precision regardless of the phase selected to initiate calculations. Table 5 shows excellent agreement between estimated and experimental solvent contents. This is as it should be, since knowledge of the binodal curve is necessary. The slight differences are brought about by interpolation to find the extremity of a tie-line on the known binodal curve.

B. Cyclohexane-Isooctane-Furfural

Experimental equilibria for the system cyclohexane-2,2,4-trimethylpentane (isooctane)-furfural were obtained only at 30°C. These data are compared with estimated equilibria based on van Laar activity coefficient data as shown in Figure 32 and Table 6. The calculations were initiated with the hydrocarbon phase only.

The agreement of the experimental and estimated X-Y equilibria shown in Figure 32 is excellent. In addition, Table 6 shows that the experimental solvent contents of the two phases are in close agreement with those of the estimation method. The overall correlation for this system gives added confidence in the estimation method.

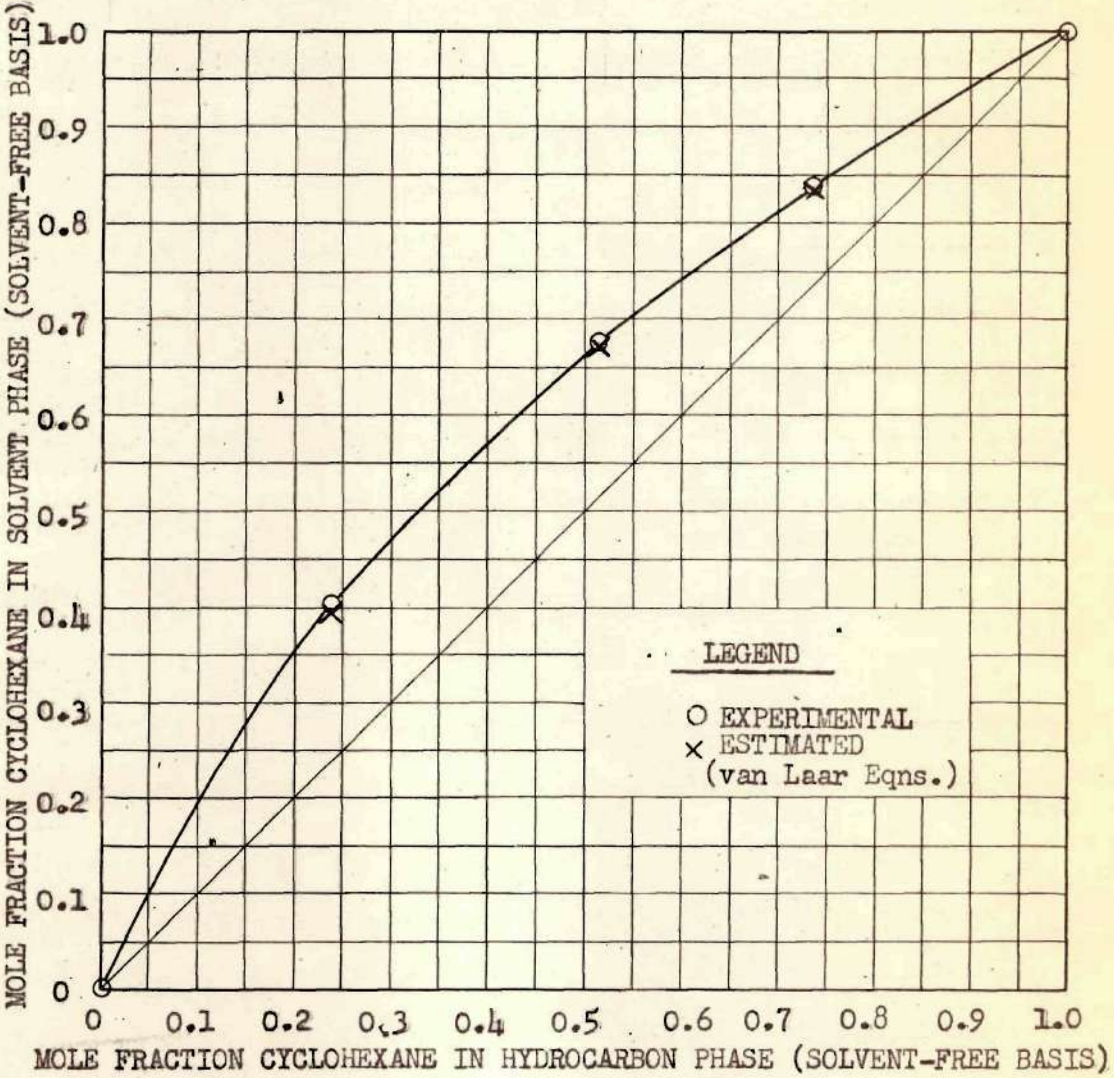
SYSTEM: FURFURAL - ISOOCTANE (2,2,4-TRIMETHYLPENTANE) - CYCLOHEXANE AT 30 C

FIG. 32. X-Y EQUILIBRIA IN ISOOCTANE - CYCLOHEXANE - FURFURAL AT 30 C

Table 6. Comparison of Experimental and Estimated* Equilibria for Cyclohexane-2,2,4-Trimethylpentane (Isooctane)-Furfural at 30°C.

Composition	Run 50		Run 49		Run 51	
	Exp.	Est.	Exp.	Est.	Exp.	Est.
$\left(\frac{X_N}{1-X_F}\right)_{Hc}$	0.238**		0.511**		0.731**	
$\left(\frac{X_N}{1-X_F}\right)_{Sol.}$	0.402	0.392	0.678	0.667	0.839	0.831
$(X_F)_{Hc}$	0.063	0.061	0.065	0.062	0.066	0.062
$(X_F)_{Sol.}$	0.934	0.932	0.909	0.906	0.885	0.883

X_N = Mole fraction naphthene (cyclohexane)

X_F = Mole fraction furfural

$\frac{X_N}{1-X_F}$ = Mole fraction naphthene (cyclohexane), on a solvent-free basis, in the designated phase.

Subscripts: Hc, Sol. refer to hydrocarbon and solvent phases respectively.

---

*Activity coefficients are based on van Laar equations.

**The experimental hydrocarbon-phase composition (solvent-free basis) is also the basis, or starting point, for the estimation.

C. Cyclohexane-Cetane-Furfural

The experimental equilibria for the system cyclohexane-hexadecane (cetane)-furfural were obtained at the three temperature levels of 30, 60, and 90°C. These are compared with the estimated equilibria as follows:

1. Equilibria at 30°C.--The experimental equilibria for cyclohexane-cetane-furfural at 30°C. are compared with estimated equilibria based both on van Laar and Scatchard-Hamer activity coefficients as shown in Figure 33 and Table 7.

The calculations using the van Laar activity coefficients were initiated first with the hydrocarbon phase and then with the solvent phase. Since an equal order of precision was indicated, and the solvent-phase-initiated calculations converge more rapidly to a solution, the calculations with Scatchard-Hamer activity coefficients were initiated only with the solvent phase.

Figure 33 shows that the estimated X-Y equilibria are displaced somewhat from the experimental for both van Laar and Scatchard-Hamer calculations. However, the van Laar based calculations show better agreement at low cyclohexane concentrations, and the Scatchard-Hamer based calculations show better agreement at high cyclohexane concentrations. Calculations based on van Laar activity coefficients for one component and Scatchard-Hamer activity coefficients for the other obviously fall between the two sets of calculated values.

2. Equilibria at 60°C.--The experimental equilibria for cyclohexane-cetane-furfural at 60°C. are compared with estimated equilibria based on van Laar activity coefficient data as shown in Figure 34 and Table 8.

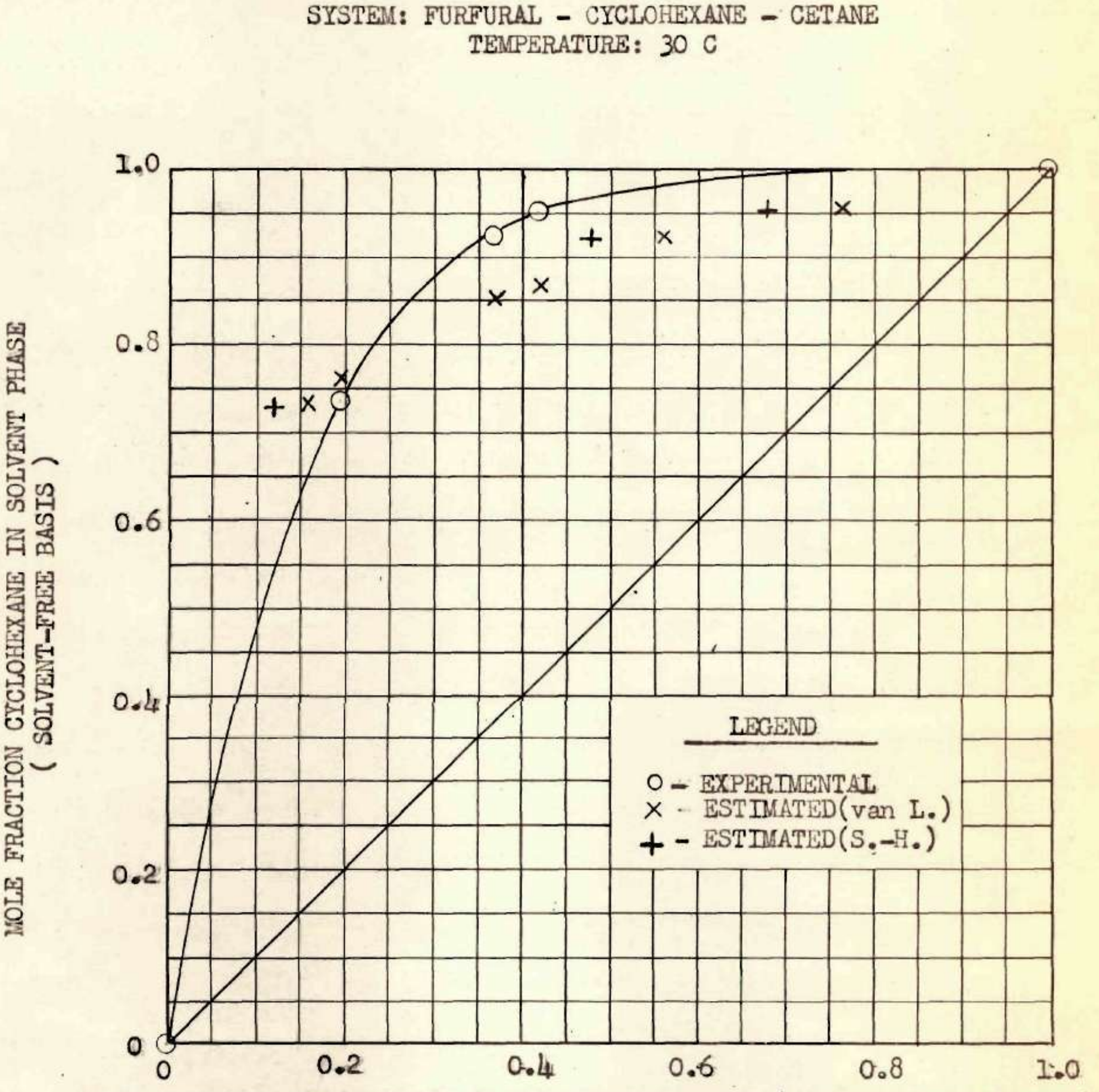

FIG. 33. X-Y EQUILIBRIA IN CYCLOHEXANE - CETANE - FURFURAL AT 30 C

Table 7. Comparison of Experimental and Estimated Equilibria for Cyclohexane-Cetane-Furfural at 30°C.

A. Based on van Laar Activity Coefficients

Composition	Run 33		Run 35		Run 36	
	Exp.	Est.	Exp.	Est.	Exp.	Est.
(1. Calculations Initiated with the Solvent-Free Hydrocarbon-Phase Composition.)						
$(\frac{X_N}{1-X_F})_{Hc}$	0.193		0.399		0.456	
$(\frac{X_N}{1-X_F})_{Sol.}$	0.733	0.763	0.924	0.860	0.956	0.880
$(X_F)_{Hc}$	0.074	0.077	0.076	0.073	0.085	0.072
$(X_F)_{Sol.}$	0.985	0.976	0.965	0.952	0.936	0.945
(2. Calculations Initiated with the Solvent-Free Solvent-Phase Composition.)						
$(\frac{X_N}{1-X_F})_{Sol.}$	0.733		0.924		0.956	
$(\frac{X_N}{1-X_F})_{Hc}$	0.193	0.155	0.399	0.561	0.456	0.767
$(X_F)_{Hc}$	0.074	0.077	0.076	0.071	0.085	0.067
$(X_F)_{Sol.}$	0.985	0.982	0.965	0.951	0.936	0.930

Table 7. Comparison of Experimental and Estimated Equilibria for Cyclohexane-Cetane-Furfural at 30°C. (Continued)

B. Based on Scatchard-Hamer Activity Coefficients

Composition	Run 33		Run 35		Run 36	
	Exp.	Est.	Exp.	Est.	Exp.	Est.
$(\frac{X_N}{1-X_F})_{Sol.}$	0.733*		0.924*		0.957*	
$(\frac{X_N}{1-X_F})_{Hc}$	0.193	0.1200	0.399	0.4800	0.456	0.680
$(X_F)_{Hc}$	0.074	0.078	0.076	0.071	0.085	0.068
$(X_F)_{Sol.}$	0.985	0.982	0.965	0.951	0.936	0.930

*Calculations initiated with the solvent-free solvent-phase composition.

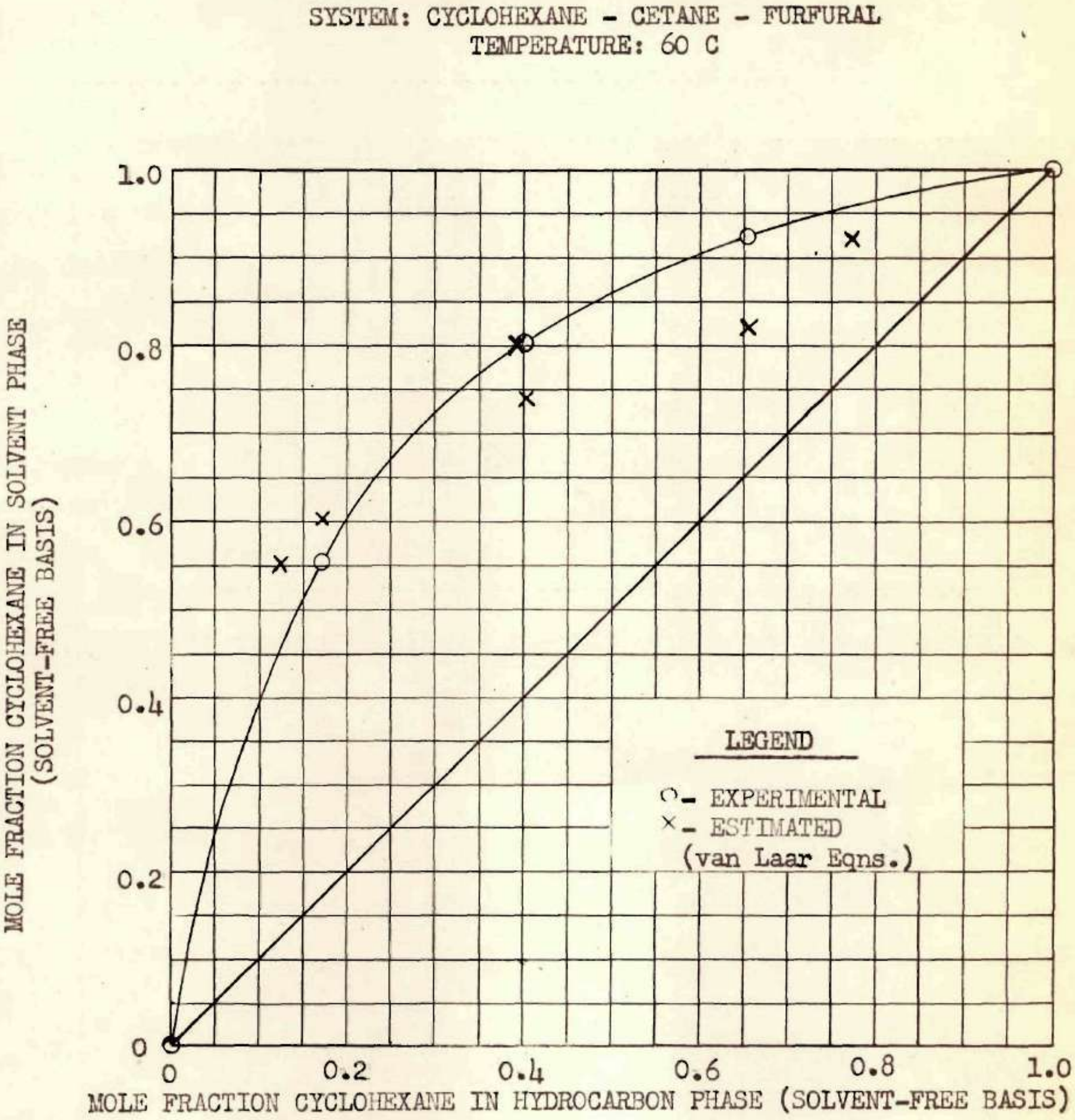

FIG. 34. X-Y EQUILIBRIA IN CYCLOHEXANE - CETANE - FURFURAL AT 60 C

Table 8. Comparison of Experimental and Estimated* Equilibria for Cyclohexane-Cetane-Furfural at 60°C.

A. Estimations Based on the Experimental Hydrocarbon-Phase Composition (Solvent-Free Basis)

Composition	Run 30		Run 31		Run 32	
	Exp.	Est.	Exp.	Est.	Exp.	Est.
$(\frac{X_N}{1-X_F})_{Hc}$	0.171		0.401		0.657	
$(\frac{X_N}{1-X_F})_{Sol.}$	0.556	0.608	0.805	0.747	0.924	0.825
$(X_F)_{Hc}$	0.141	0.163	0.129	0.176	0.126	0.189
$(X_F)_{Sol.}$	0.973	0.960	0.947	0.911	0.897	0.836

B. Estimations Based on the Experimental Solvent-Phase Composition (Solvent-Free Basis)

Composition	Run 30		Run 31		Run 32	
	Exp.	Est.	Exp.	Est.	Exp.	Est.
$(\frac{X_N}{1-X_F})_{Sol.}$	0.556		0.805		0.924	
$(\frac{X_N}{1-X_F})_{Hc}$	0.171	0.124	0.401	0.393	0.657	0.774
$(X_F)_{Hc}$	0.141	0.161	0.129	0.176	0.126	0.194
$(X_F)_{Sol.}$	0.973	0.973	0.947	0.944	0.897	0.888

*Based on van Laar activity coefficient data.

The estimations were based first on the hydrocarbon-phase compositions and then on the solvent-phase compositions.

Inspection of the figure and table shows that the estimations initiated with the solvent phase are in much closer agreement with the experimental equilibria than those initiated with the hydrocarbon phase. This phenomenon is demonstrated further in Sample Calculation E, illustrating the convergence of the successive approximation technique. In this unusual case the solvent-phase-initiated calculations converge rapidly to a solution, and the hydrocarbon-phase-initiated calculations do not. However, since rapid convergence has been obtained in all other cases, regardless of the starting phase, the lack of convergence in this special case indicated that the hydrocarbon-phase-initiated estimations were in error. Fortunately, this was verified by the experimental data. Inspection of Table 8 also shows the estimated and experimental solvent contents in the solvent phase $(X_F)_{Sol.}$ to be in much better agreement with calculations based on the solvent phase than those based on the hydrocarbon phase.

The more reliable solvent-phase-estimated equilibria at 60°C. are seen in Figure 34 to deviate from the experimental data in the same manner as the estimated equilibria at 30°C. (Figure 33). It is to be noted, however, that the deviations at 60°C. are not as pronounced as those at 30°C.

3. Equilibria at 90°C.--The experimental equilibria for cyclohexane-cetane-furfural at 90°C. are compared with estimated equilibria based on van Laar activity coefficient curves and extrapolations therefrom as shown in Figure 35 and Table 9.

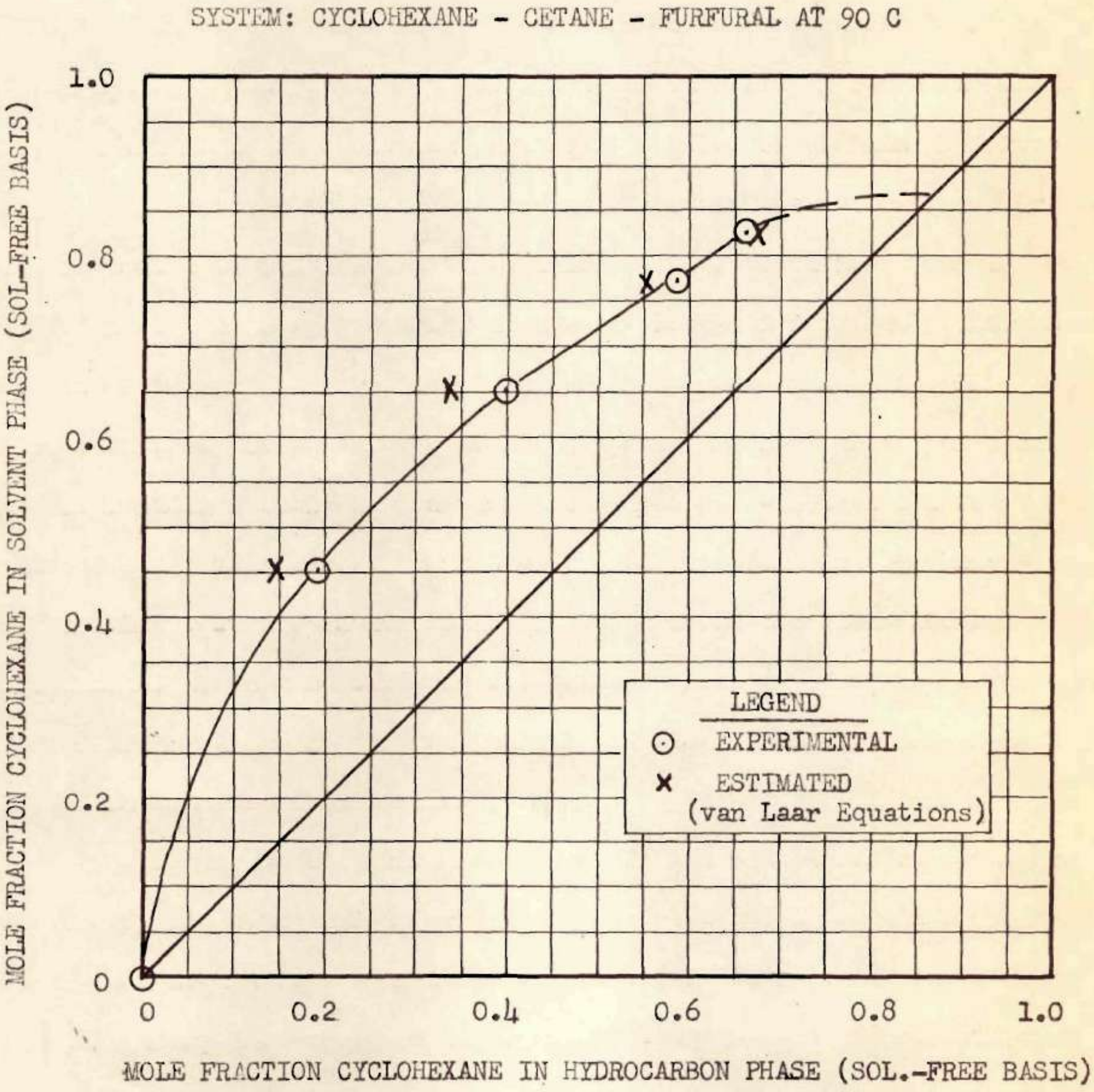

FIG. 35. X-Y EQUILIBRIA IN CYCLOHEXANE-CETANE-FURFURAL AT 90 C

Table 9. Comparison of Experimental and Estimated* Equilibria for Cyclohexane-Cetane-Furfural at 90°C.

	Run 23		Run 24		Run 25		Run 26	
Composition	Exp.	Est.	Exp.	Est.	Exp.	Est.	Exp.	Est.
$(\frac{X_N}{1-X_F})_{Sol.}$	0.454**		0.652**		0.770**		0.827**	
$(\frac{X_N}{1-X_F})_{Hc}$	0.191	0.149	0.401	0.339	0.586	0.557	0.663	0.725
$(X_F)_{Hc}$	0.287	0.272	0.282	0.283	0.300	0.298	0.302	0.328
$(X_F)_{Sol.}$	0.948**		0.919**		0.879**		0.826**	

*Activity coefficient data are based on the van Laar equations.

**Estimations are initiated with the experimental solvent-phase compositions.

Here, as with the system cyclohexane-n-heptane-furfural, the temperature of 90°C. is above the critical solution temperature for the binary pair, furfural-cyclohexane, and it is necessary to assume knowledge of the binodal curve. Then, to obtain rapid convergence on the tie-line extremities, the calculations were initiated with the experimental solvent phase composition only.

Inspection of Figure 35 shows good agreement between the estimated and experimental X-Y equilibria for this system at this temperature level. This is particularly encouraging because of the deviations noted in the equilibria for this system at the two lower temperatures, and the extrapolations necessary to obtain activity coefficient data at this temperature.

Apparently a molecular weight or shape effect has produced the low temperature deviations of experimental and estimated equilibria in this system, since the other paraffin-naphthene systems have correlated well (see Figure 29 and 32). Further, the noted molecular weight or shape effect must decrease with increased temperature, and become insignificant at about 90°C.

D. Octene-1-n-Heptane-Furfural

Experimental equilibria for the system octene-1-n-heptane-furfural were obtained at the two temperature levels of 30°C. and 60°C. These are compared with estimated equilibria as follows:

1. Equilibria at 30°C.--The experimental equilibria for octene-1-n-heptane-furfural at 30°C. are compared with estimated equilibria based on van Laar activity coefficient data as shown in Figure 36 and Table 10. The estimations were calculated both ways, with each phase alternately

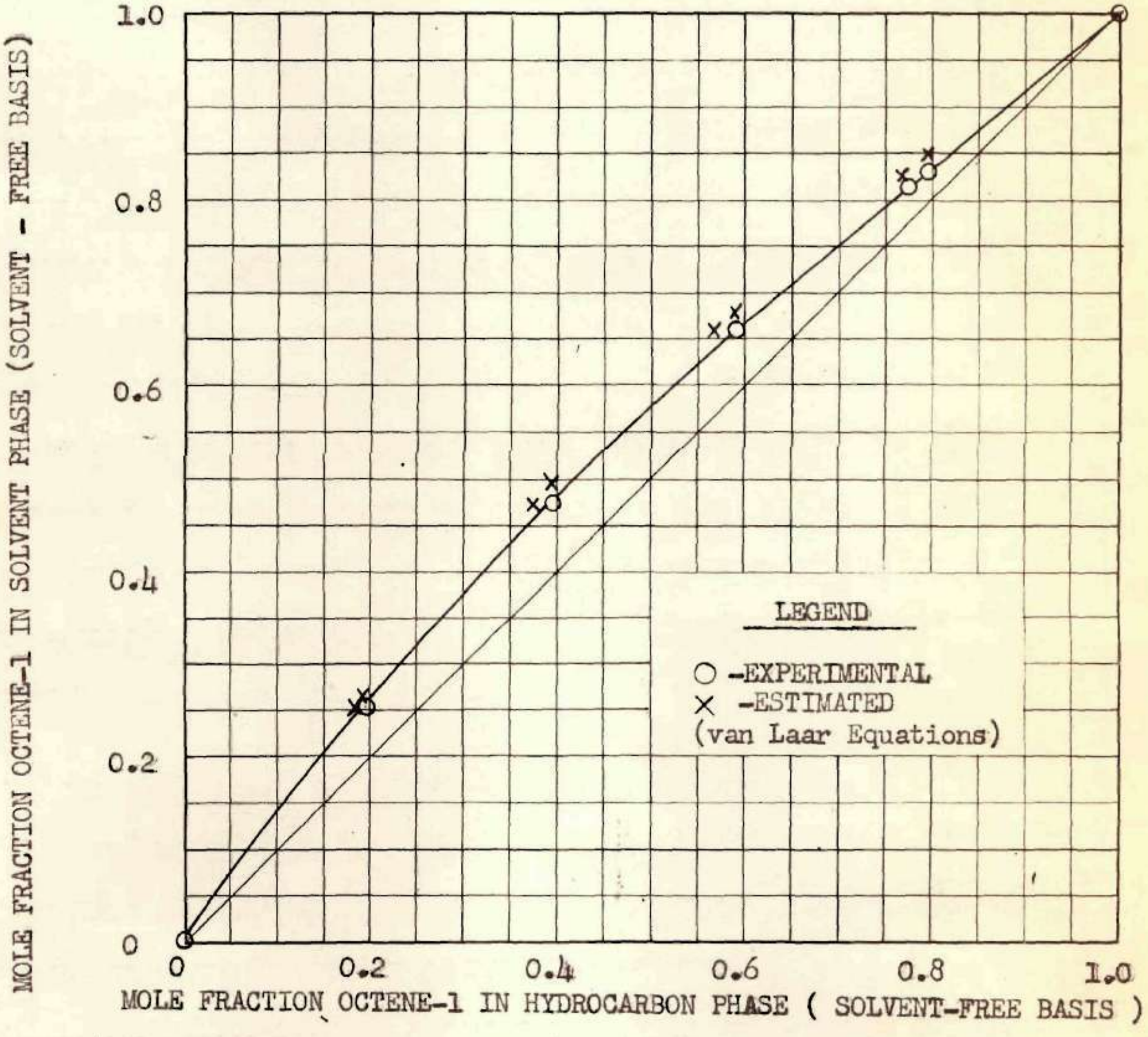
SYSTEM: n-HEPTANE - OCTENE -1 - FURFURAL
TEMPERATURE: 30 C

FIG. 36. X-Y EQUILIBRIA IN n-HEPTANE - OCTENE-1 - FURFURAL AT 30 C

Table 10. Comparison of Experimental and Estimated* Equilibria for Octene-1-n-Heptane-Furfural at 30°C.

	Run 41		Run 40		Run 39		Run 38	
Composition	Exp.	Est.	Exp.	Est.	Exp.	Est.	Exp.	Est.
A. Estimations Based on the Experimental Hydrocarbon-Phase Composition (Solvent-Free Basis)								
$(\frac{X_o}{1-X_F})_{Hc}$	0.197		0.398		0.591		0.794	
$(\frac{X_o}{1-X_F})_{Sol.}$	0.251	0.268	0.474	0.500	0.661	0.681	0.830	0.851
$(X_F)_{Hc}$	0.074	0.075	0.086	0.091	0.100	0.106	0.116	0.122
$(X_F)_{Sol.}$	0.934	0.934	0.926	0.925	0.911	0.915	0.901	0.905
B. Estimations Based on the Experimental Solvent-Phase Composition (Solvent-Free Basis)								
$(\frac{X_o}{1-X_F})_{Sol.}$	0.251		0.474		0.661		0.830	
$(\frac{X_o}{1-X_F})_{Hc}$	0.197	0.180	0.398	0.373	0.591	0.564	0.794	0.765
$(X_F)_{Hc}$	0.074	0.075	0.086	0.089	0.100	0.104	0.116	0.119
$(X_F)_{Sol.}$	0.934	0.934	0.926	0.924	0.911	0.915	0.901	0.904

where
X_o = Mole fraction olefin (octene-1)
X_F = Mole fraction furfural
$\frac{X_o}{1-X_F}$ = Mole fraction octene-1 (solvent-free basis) in indicated phase

Subscripts: Hc, Sol. refer to hydrocarbon and solvent phase respectively.

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*Based on van Laar activity coefficient data.

being the starting point and end point. Again however, the convergence was rapid and the same order of precision was indicated independent of the starting phase.

Figure 36 shows excellent agreement of the experimental and estimated X-Y equilibria. Table 10 shows excellent agreement of experimental and estimated solvent contents for both the hydrocarbon and solvent phase.

2. Equilibria at 60°C.--The experimental equilibria for octene-1-n-heptane-furfural at 60°C. are compared with the estimated equilibria based on van Laar activity coefficient data as shown in Figure 37 and Table 11.

Figure 37 shows that the estimated equilibria are slightly higher than experimental over the entire concentration range. This indicates a greater selectivity than actually exists. The estimated equilibria show a slight decrease in selectivity between 30°C. and 60°C., but not in the same order of magnitude as the decrease shown by the experimental equilibria. Nevertheless, these estimated X-Y equilibria are in quite good agreement with the experimental data, and are sufficiently accurate for most engineering work.

Table 11 shows good agreement between the estimated and experimental data for the mole fraction furfural in the solvent phase. This quantity deviates somewhat in the hydrocarbon phase, but not sufficiently to impair the general correlation.

E. Cyclohexane-Octene-1-Furfural

Experimental equilibria for the system cyclohexane-octene-1-furfural were obtained only at 30°C. These data are compared with estimated

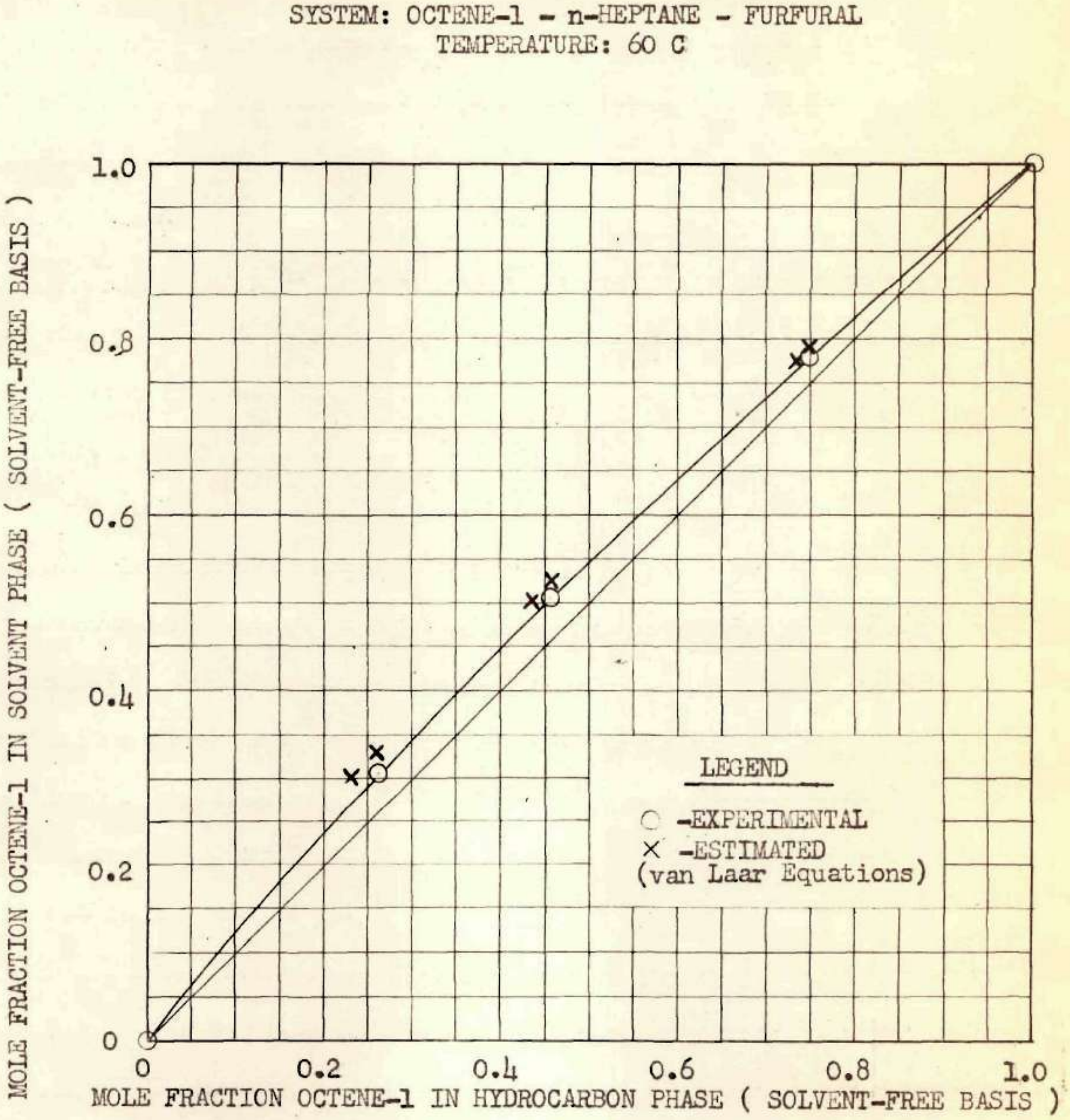

FIG. 37. X-Y EQUILIBRIA IN n-HEPTANE - OCTENE-1 - FURFURAL AT 60 C

Table 11. Comparison of Experimental and Estimated*
Equilibria for Octene-1-n-Heptane-Furfural at 60°C.

A. Based on Hydrocarbon Phase

Composition	Run 46		Run 45		Run 47	
	Exp.	Est.	Exp.	Est.	Exp.	Est.
$(\frac{X_O}{1-X_F})_{Hc}$	0.261		0.454		0.749	
$(\frac{X_O}{1-X_F})_{Sol.}$	0.302	0.334	0.509	0.531	0.779	0.792
$(X_F)_{Hc}$	0.178	0.222	0.211	0.278	0.284	0.349
$(X_F)_{Sol.}$	0.871	0.864	0.855	0.838	0.798	0.792

B. Based on Solvent Phase

Composition	Run 46		Run 45		Run 47	
	Exp.	Est.	Exp.	Est.	Exp.	Est.
$(\frac{X_O}{1-X_F})_{Sol.}$	0.302		0.509		0.779	
$(\frac{X_O}{1-X_F})_{Hc}$	0.261	0.230	0.454	0.426	0.749	0.731
$(X_F)_{Hc}$	0.178	0.212	0.211	0.270	0.284	0.346
$(X_F)_{Sol.}$	0.871	0.864	0.855	0.839	0.798	0.790

*Based on van Laar activity coefficient data.

X-Y equilibria based on van Laar activity coefficient data as shown in Figure 38 and Table 12. The calculations were initiated first from the hydrocarbon phase, and as the convergence was rapid, the solvent phase calculations were not made.

Figure 38 shows that the estimated solvent-phase compositions are smaller over the entire concentration range than that given by experiment. This indicates a poorer selectivity for the separation than is actually the case.

The use of the estimated equilibria in design calculations would result in an "over design" of equipment that could be reflected in higher-purity products than were anticipated. That is certainly more desirable than an equivalent "under design," but both should be avoided.

The numerical values for the estimated solvent-phase compositions shown in Table 12 show a maximum deviation from the experimental data of only 2.3 mole per cent cyclohexane. This is in Run 54 where the estimated solvent-phase compositions is 74.4 mole per cent cyclohexane (on a solvent-free basis). Nevertheless, the author considers this correlation one of the poorest in the study with regard to accuracy in design. This comes about because the difficulty of separation, which reflects directly on the equilibrium stage requirements and hence on the accuracy of design calculations, is indicated by the ratio of the logarithms of the selectivity factors. Thus, small errors are considerably more important in systems with low selectivity than in those with high.

The selectivity in this system is expressed mathematically as

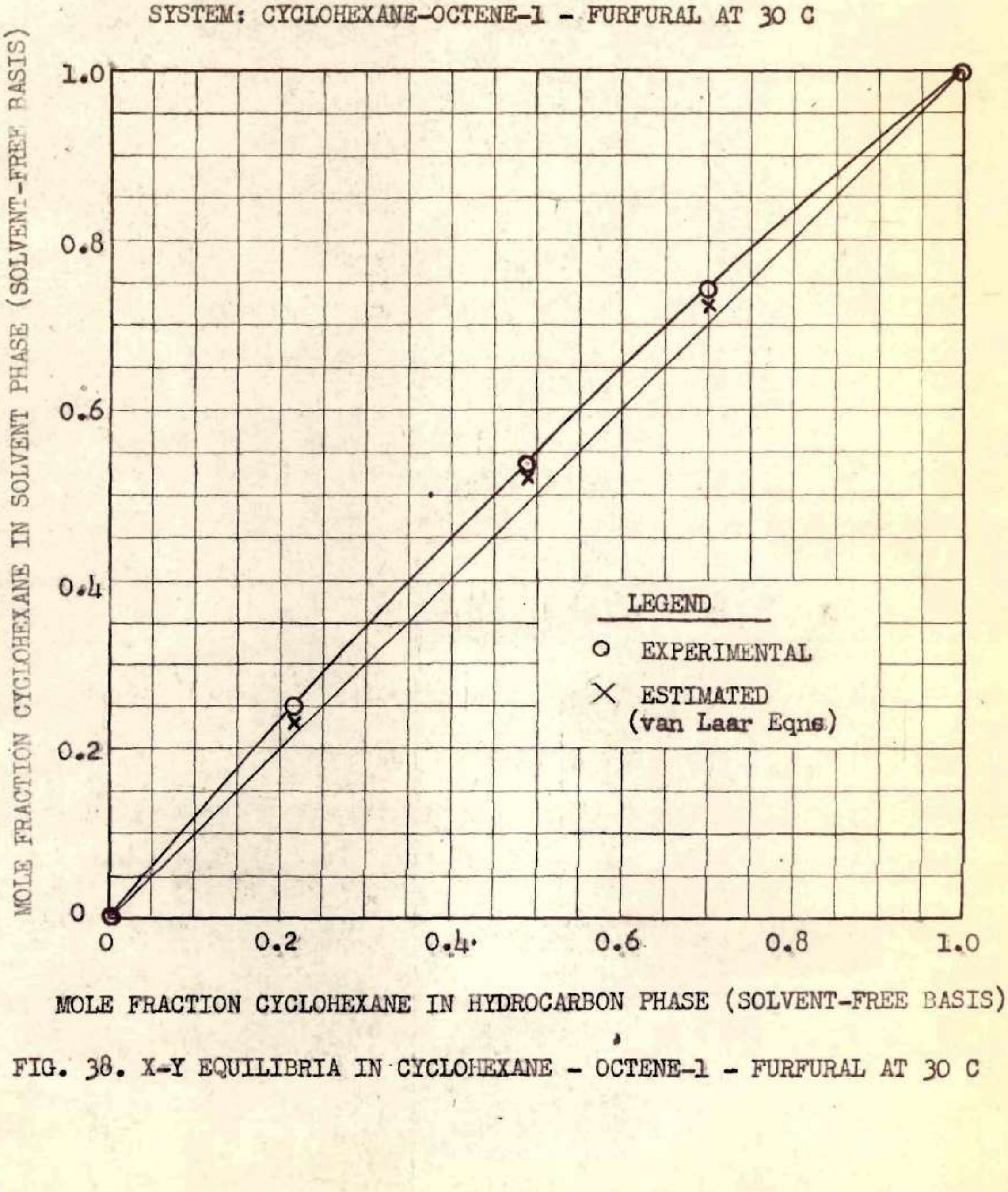

FIG. 38. X-Y EQUILIBRIA IN CYCLOHEXANE - OCTENE-1 - FURFURAL AT 30 C

$$\beta = \frac{\left(\frac{X_N}{X_O}\right)_{Sol.}}{\left(\frac{X_N}{X_O}\right)_{Hc.}}$$

where β is the selectivity factor, X_N the mole fraction naphthene (cyclohexane), X_O the mole fraction olefin (octene-1), and the subscripts Sol. and Hc refer to the solvent- and hydrocarbon-rich phases respectively.

For Run 54 the experimental selectivity is only 1.38 and the estimated selectivity 1.23. The ratio of the difficulty of separation, estimated to experimental, is then

$$\frac{\log 1.38}{\log 1.23} = \frac{0.140}{0.090} = \frac{1.555}{1}$$

In other words, for this low-selectivity system the small numerical error in the estimated solvent-phase composition reflects an approximate 50 per cent error in the difficulty of separation.

It was noted in the naphthene-paraffin separations that changing from van Laar to Scatchard-Hamer activity coefficients had the effect of raising the estimated X-Y equilibrium curves. It is therefore possible that a better correlation might be obtained in this case with another basis for activity coefficients. However, no theoretical justification could be found for the change, so the case was not investigated.

Table 12. Comparison of Experimental and Estimated* Equilibria for Cyclohexane-Octene-1-Furfural at 30°C.

Composition	Run 53 Exp.	 Est.	Run 52 Exp.	 Est.	Run 54 Exp.	 Est.
$(\frac{X_N}{1-X_F})_{Hc}$	0.211		0.489		0.700	
$(\frac{X_N}{1-X_F})_{Sol.}$	0.250	0.233	0.539	0.521	0.744	0.721
$(X_F)_{Hc}$	0.129	0.122	0.111	0.102	0.093	0.087
$(X_F)_{Sol.}$	0.880	0.880	0.867	0.870	0.861	0.862

*Based on van Laar activity coefficient data.

Table 12 shows good agreement between estimated and experimental solvent contents, even though the solvent-free hydrocarbon compositions reflect a considerable error in selectivity.

CHAPTER VIII

SUMMARY AND CONCLUSIONS

The conclusions drawn from this research project, entitled "Phase Equilibria in Complex Non-Ideal Systems" are as follows:

1. Experimental liquid-liquid equilibria have been determined for ten different ternary systems involving the five different hydrocarbon separations, cyclohexane-n-heptane, cyclohexane-isooctane, cyclohexane-cetane, cyclohexane-octene-1, and octene-1-n-heptane. Each of the separations was chosen to illustrate certain hydrocarbon types or molecular weights. Each was studied at one or more of the three temperature levels of 30, 60, and 90°C. with furfural as the selective solvent.

2. Experimental liquid-liquid solubility measurements were made for the seven binary pairs, furfural-cyclohexane, furfural-n-heptane, furfural-isooctane, furfural-cetane, furfural-octene-1, furfural-benzene, and furfural-toluene, over the temperature range of 10-15°C. to 125°C.

3. Activity coefficient calculations based on van Laar equations and the experimental mutual solubility were made for the hydrocarbons in the five binary systems, furfural-cyclohexane, furfural-n-heptane, furfural-isooctane, furfural-cetane, and furfural-octene-1, at one or more of the three temperature levels 30, 60, and 90°C.

4. Activity coefficient calculations based on Scatchard-Hamer

equations and the experimental mutual solubility were made for the hydrocarbons in the three binary systems, furfural-cetane, furfural-cyclohexane, and furfural-n-heptane at 30°C.

5. Activity coefficients for cyclohexane in furfural based on the van Laar equation and the mutual solubility have been extrapolated to 90°C., which is considerably above the critical solution temperature for the binary pair. This interpolation utilized a graph of the logarithm of the activity coefficients versus $\frac{1}{T}$, $(°K)^{-1}$, and was based on the assumption that the differential heats of solution were constant. Since the constancy of those heats of solution have been demonstrated for the temperature range of 15 to 60°C., the extrapolation to 90°C. is in order.

6. An estimation method is developed similar to the methods used previously by Bethea (18), Hachmuth (20), and Pennington-Marwil (23) for estimating equilibria in ternary systems from binary solubility or binodal curves and an activity coefficient equation.

7. Application was made of the van Laar and Scatchard-Hamer activity coefficient equations in the estimation method for the systems cyclohexane-n-heptane-furfural and cyclohexane-cetane-furfural at 30°C. The correlation based on the van Laar equations showed better agreement with experimental data for cyclohexane-n-heptane-furfural than that

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(18) Bethea, C. F., Unpublished Memorandum, Phillips Petroleum Co., 1949.

(20) Hachmuth, K. H., p. 83, Unpublished Fraction Symposium, Phillips Petroleum Co., 1949.

(23) Pennington, E. M., and Marwil, S. J., Ind. Eng. Chem., 45, 1371 (1953).

utilizing the Scatchard-Hamer equations. However, with the system cyclohexane-cetane-furfural estimations based on the Scatchard-Hamer correlation showed better agreement with experimental data in the cyclohexane-rich region and estimations based on van Laar correlations showed better agreement in the cetane-rich region.

8. The correlations utilizing the van Laar activity coefficient equations showed a precision of an equal order of magnitude regardless of whether the calculations were initiated from the solvent phase or from the hydrocarbon phase - provided both the estimation methods converged rapidly on a solution. Where rapid convergence was not obtained, the calculations initiated with the solvent phase converged more rapidly than those initiated with the hydrocarbon phase and agreed more closely with experimental data.

9. The estimation method utilizing van Laar activity coefficient equations showed excellent agreement with experimental data for the system cyclohexane-n-heptane-furfural at the three temperature levels of 30, 60, and 90°C.

The agreement of the estimated equilibria with the experimental data at 90°C. is of special interest because an extrapolation of the activity coefficient data was necessary since this temperature is approximately 23°C. above the critical solution temperature for the cyclohexane-furfural system. Further, the phase diagram at this temperature reduced to that of a single pair of non-consolute components, and a modification of method requiring knowledge of the binodal curve was needed.

10. The estimation method utilizing van Laar activity coefficient correlations showed excellent agreement with experimental data for the

system cyclohexane-isooctane-furfural at 30°C.

11. The agreement between experimental and van Laar estimated equilibria for cyclohexane-cetane-furfural showed progressive improvement with increased temperature at the levels of 30, 60, and 90°C. The discrepancy at low temperature was apparently a molecular weight or shape effect that was not alleviated by use of Scatchard-Hamer activity coefficients or combinations of van Laar and Scatchard-Hamer coefficients. The good agreement of the estimated and experimental data at 90°C. shows that the apparent molecular weight effect had a temperature coefficient. Again, particular attention was called to the 90°C. comparison because of the extrapolations and modification of method necessary in the estimation procedure.

12. The agreement between experimental and van Laar estimated equilibria for octene-1-n-heptane-furfural was excellent at the temperature level of 30°C. and good at 60°C. The estimated equilibria did not show the same magnitude of selectivity decrease between 30°C. and 60°C. as the experimental equilibria, but still displayed close agreement.

13. The experimental and van Laar estimated equilibria for the system cyclohexane-octene-1-furfural were not in as good agreement with regard to the difficulty of separation as the other systems considered in this study. However, the estimations were on the side of conservatism, and would be of considerable value in design work if experimental data were lacking. It was noted, however, that this system exhibited the smallest separation factor (poorest selectivity) encountered in the study. Data on additional low-selectivity systems would be needed to establish whether this trend were general.

APPENDIX

APPENDIX I

CALIBRATION DATA

A. Refractive Index - Composition Data

Refractive index - composition curves were determined at 30°C. for the four hydrocarbon systems, cyclohexane-n-heptane, cyclohexane-2,2,4-trimethylpentane (isooctane), cyclohexane-octene-1, and n-heptane-octene. The data for these systems are shown in Tables 13-16 inclusive and are plotted in Figures 39-42 inclusive. These follow:

Table 13. Refractive Index - Composition Data for Cyclohexane and n-Heptane at 30°C.

Wt. % Cyclohexane	30°C. n_D	Wt. % Cyclohexane	30°C. n_D
0.0	1.38281	58.7	1.40228
8.2	1.38529	65.0	1.40484
15.5	1.38742	70.0	1.40691
23.2	1.38999	81.4	1.41159
30.2	1.39233	85.9	1.41367
44.5	1.39725	93.0	1.41687
50.0	1.39910	100.0	1.42045

Table 14. Refractive Index - Composition Data for Cyclohexane-2,2,4-Trimethylpentane at 30°C.

Wt. % Cyclohexane	Refractive Index 30°C. n_D	Wt. % Cyclohexane	Refractive Index 30°C. n_D
0.0	1.38680	59.95	1.40599
9.87	1.38985	59.64	1.40937
20.03	1.39301	80.24	1.41315
29.77	1.39603	90.22	1.41678
40.51	1.39947	100.00	1.42041
50.02	1.40232		

Table 15. Refractive Index - Composition Data for Cyclohexane-Octene-1 at 30°C.

Wt. % Cyclohexane	Refractive Index 30°C. n_D	Wt. % Cyclohexane	Refractive Index 30°C. n_D
0.0	1.40392	50.00	1.41070
9.98	1.40524	60.03	1.41231
20.18	1.40643	69.85	1.41401
29.88	1.40769	80.05	1.41600
35.60	1.40846	89.82	1.41795
39.89	1.40907	100.00	1.42041

Table 16. Refractive Index - Composition Data for n-Heptane-Octene-1 at 30°C.

Wt. % Octene-1	Refractive Index 30°C. n_D	Wt. % Octene-1	Refractive Index 30°C. n_D
0.0	1.38291		
11.7	1.38539	62.6	1.39580
22.0	1.38742	72.6	1.39798
32.7	1.38962	82.2	1.40005
43.1	1.39177	89.5	1.40161
53.1	1.39384	100.00	1.40396

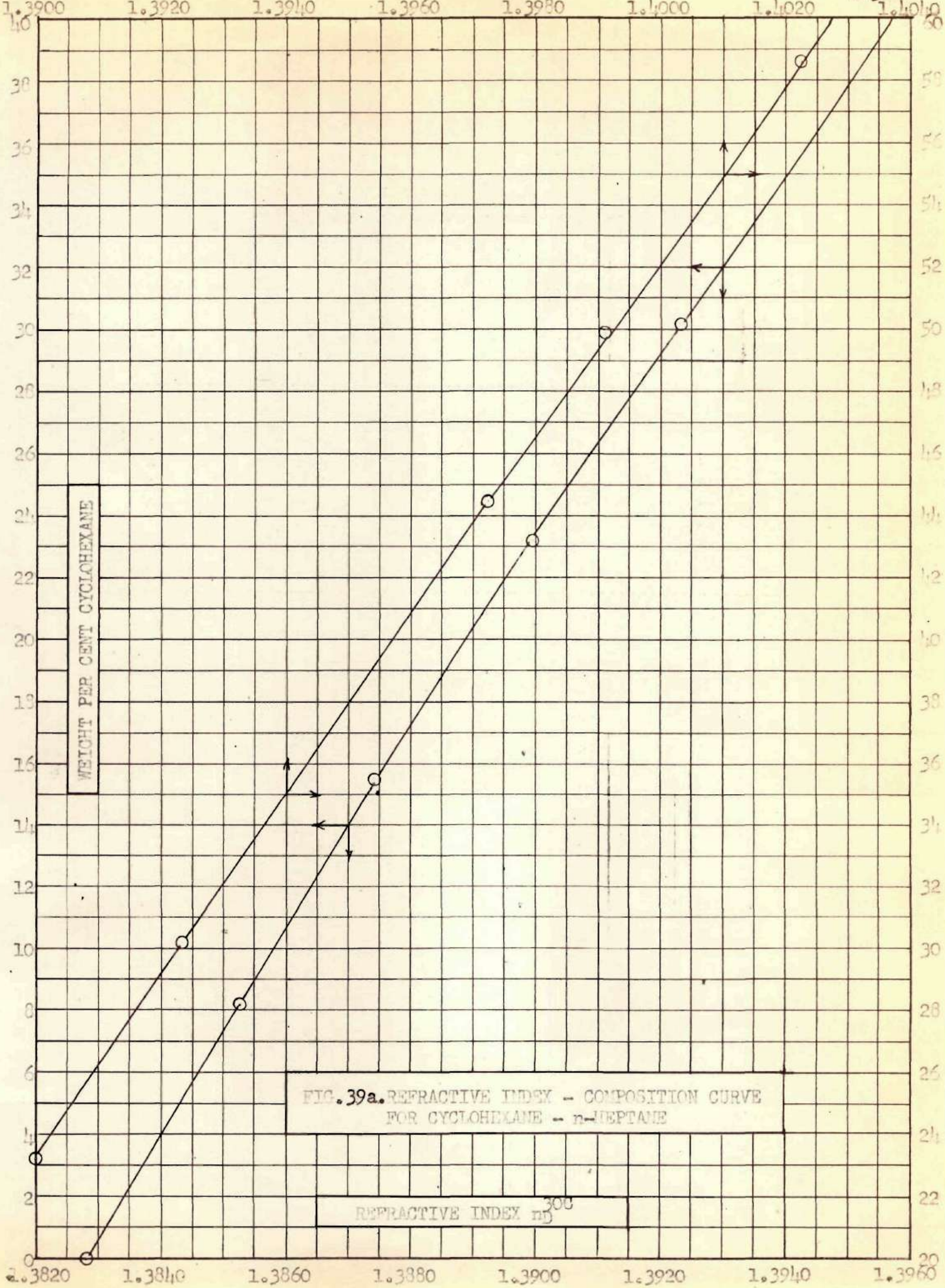

FIG. 39a. REFRACTIVE INDEX - COMPOSITION CURVE FOR CYCLOHEXANE - n-HEPTANE

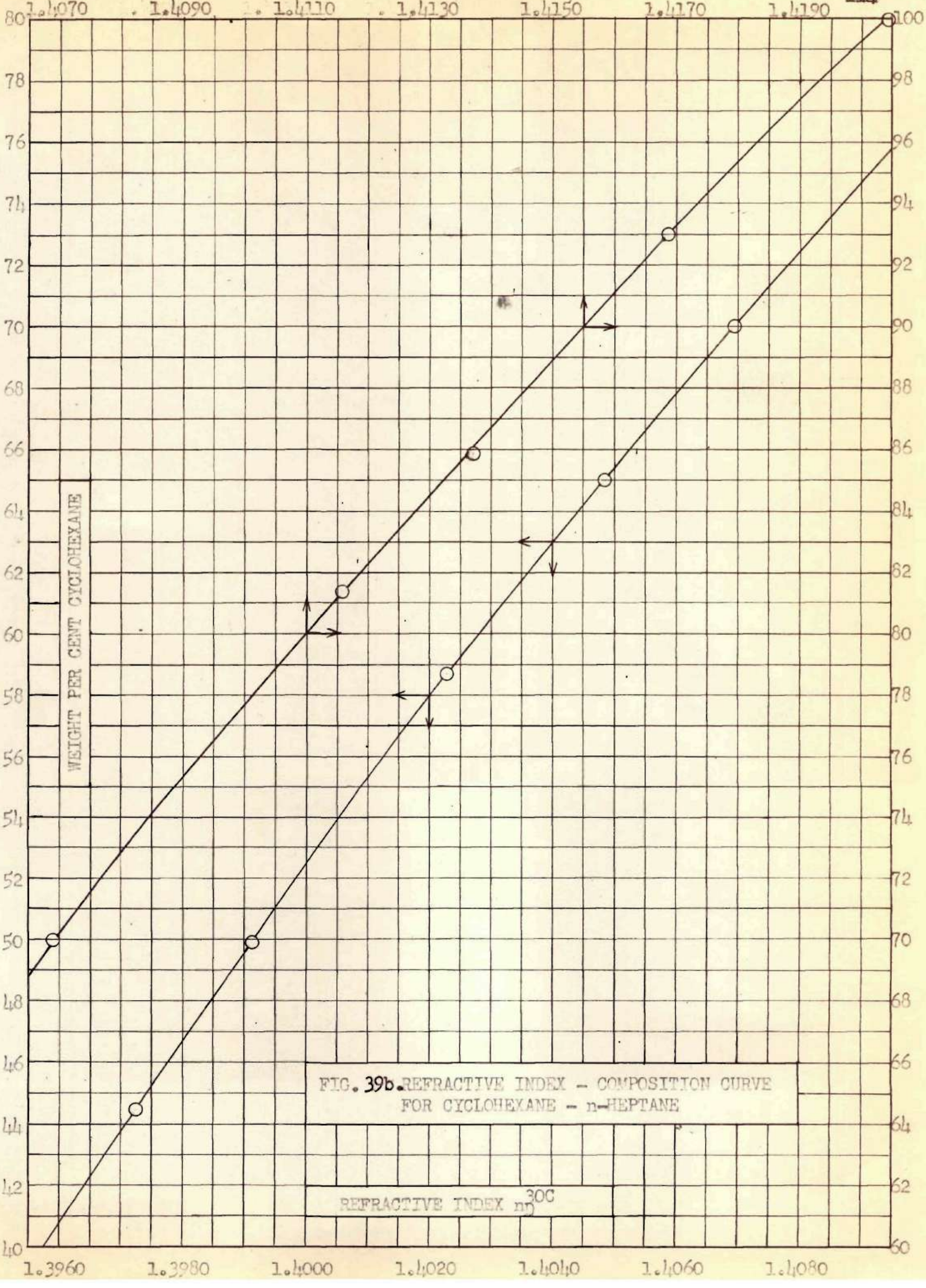
FIG. 39b. REFRACTIVE INDEX - COMPOSITION CURVE FOR CYCLOHEXANE - n-HEPTANE

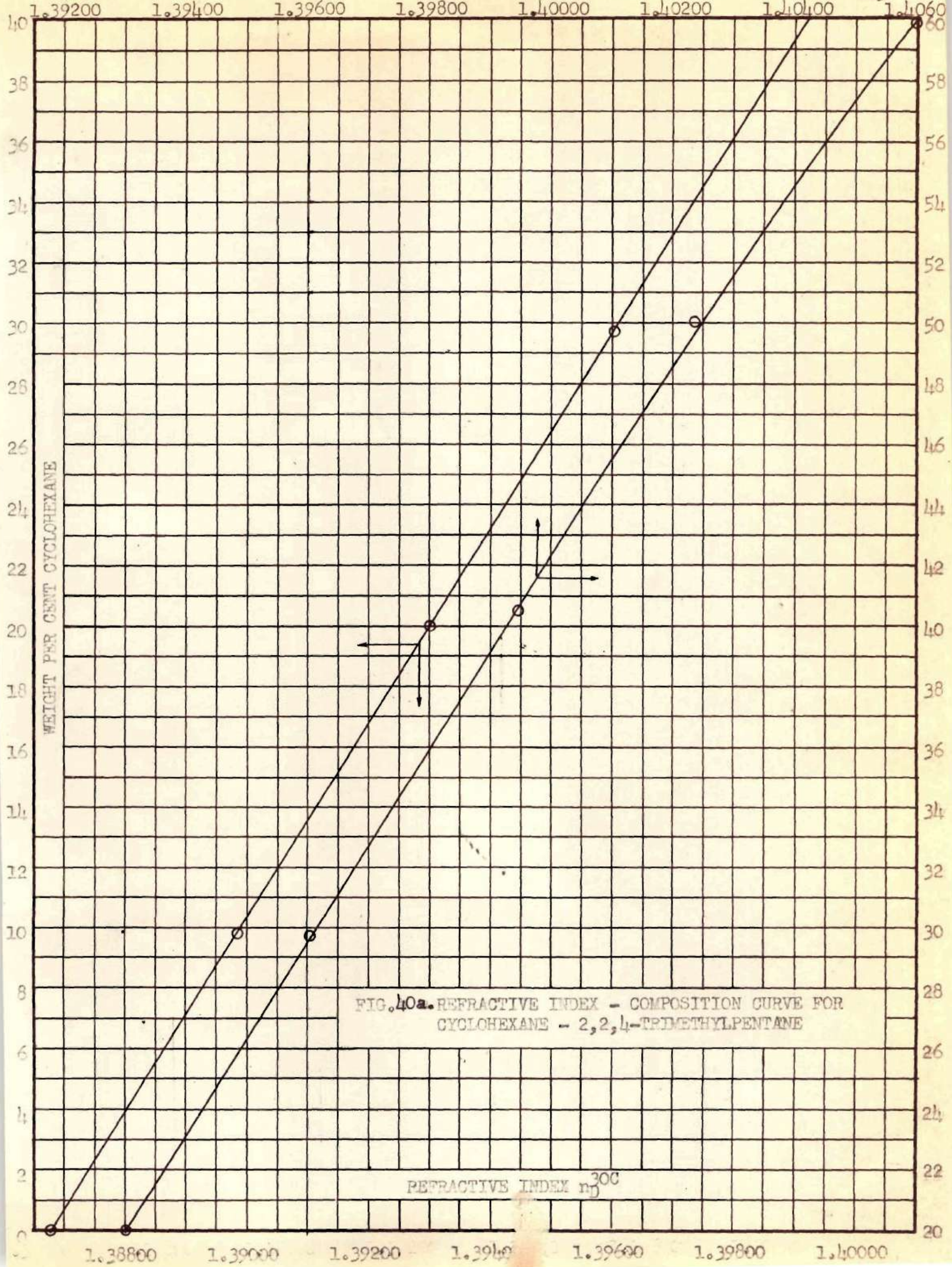

FIG. 40a. REFRACTIVE INDEX - COMPOSITION CURVE FOR CYCLOHEXANE - 2,2,4-TRIMETHYLPENTANE

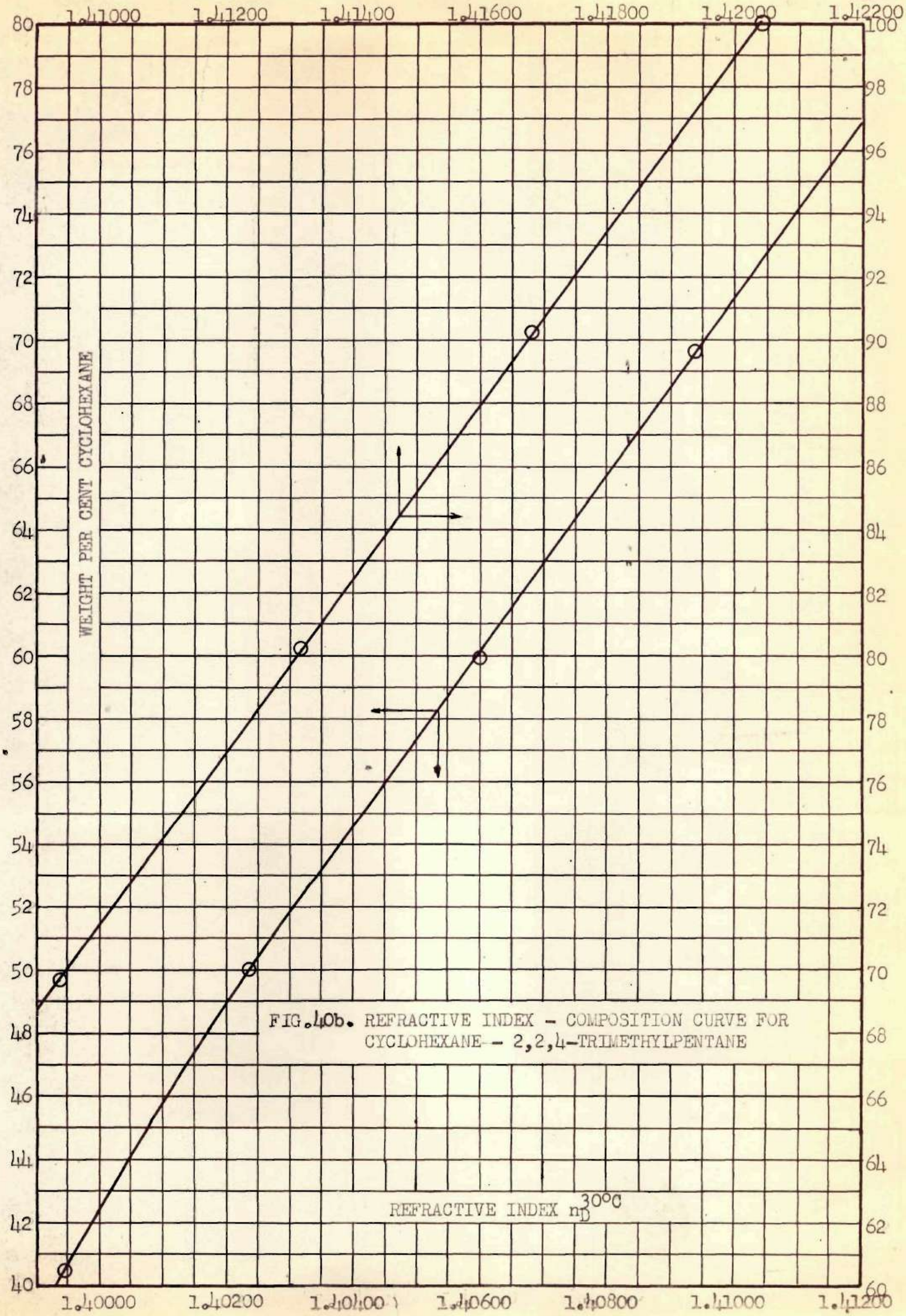

FIG. 40b. REFRACTIVE INDEX - COMPOSITION CURVE FOR CYCLOHEXANE - 2,2,4-TRIMETHYLPENTANE

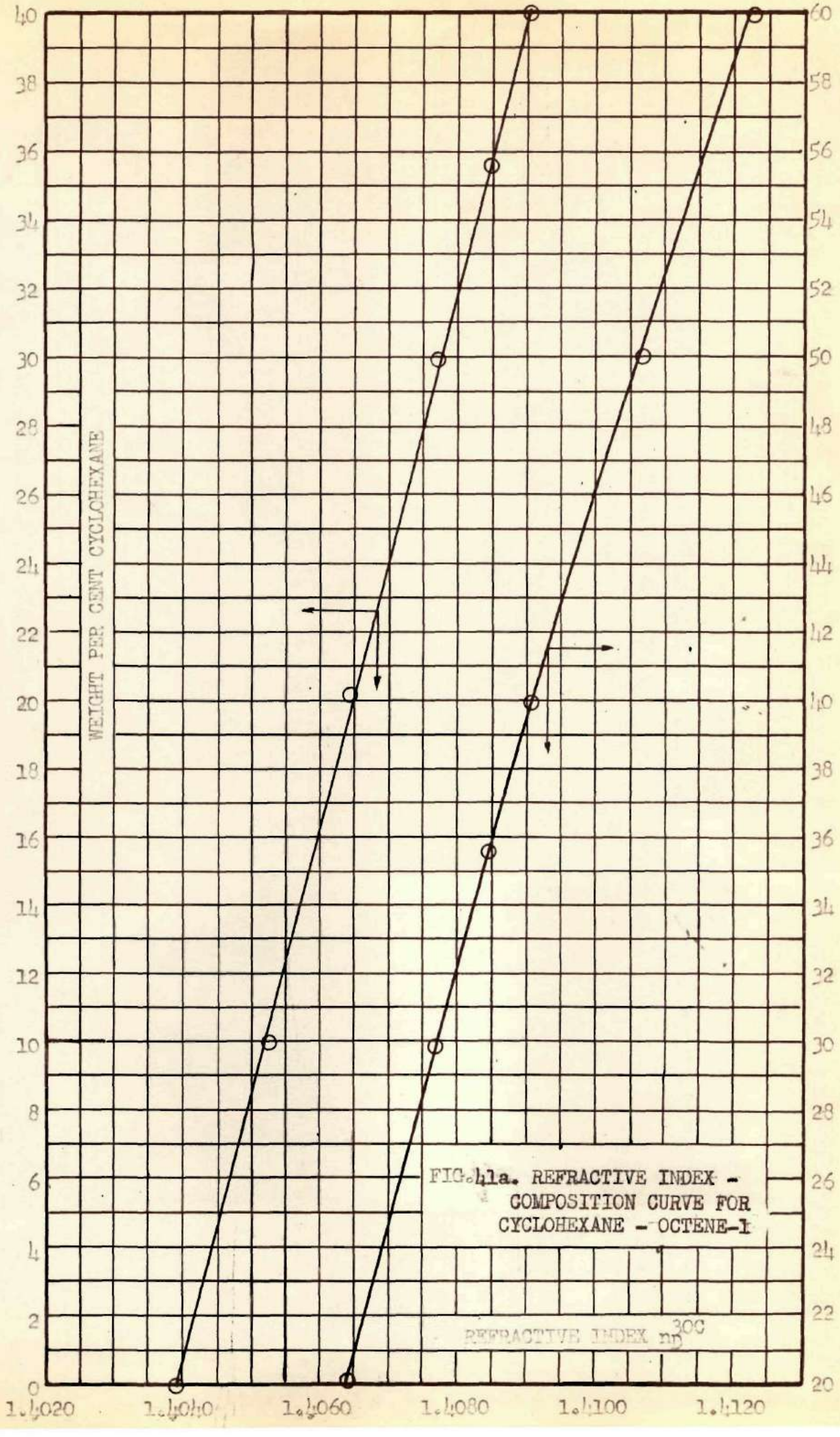

FIG. 41a. REFRACTIVE INDEX - COMPOSITION CURVE FOR CYCLOHEXANE - OCTENE-1

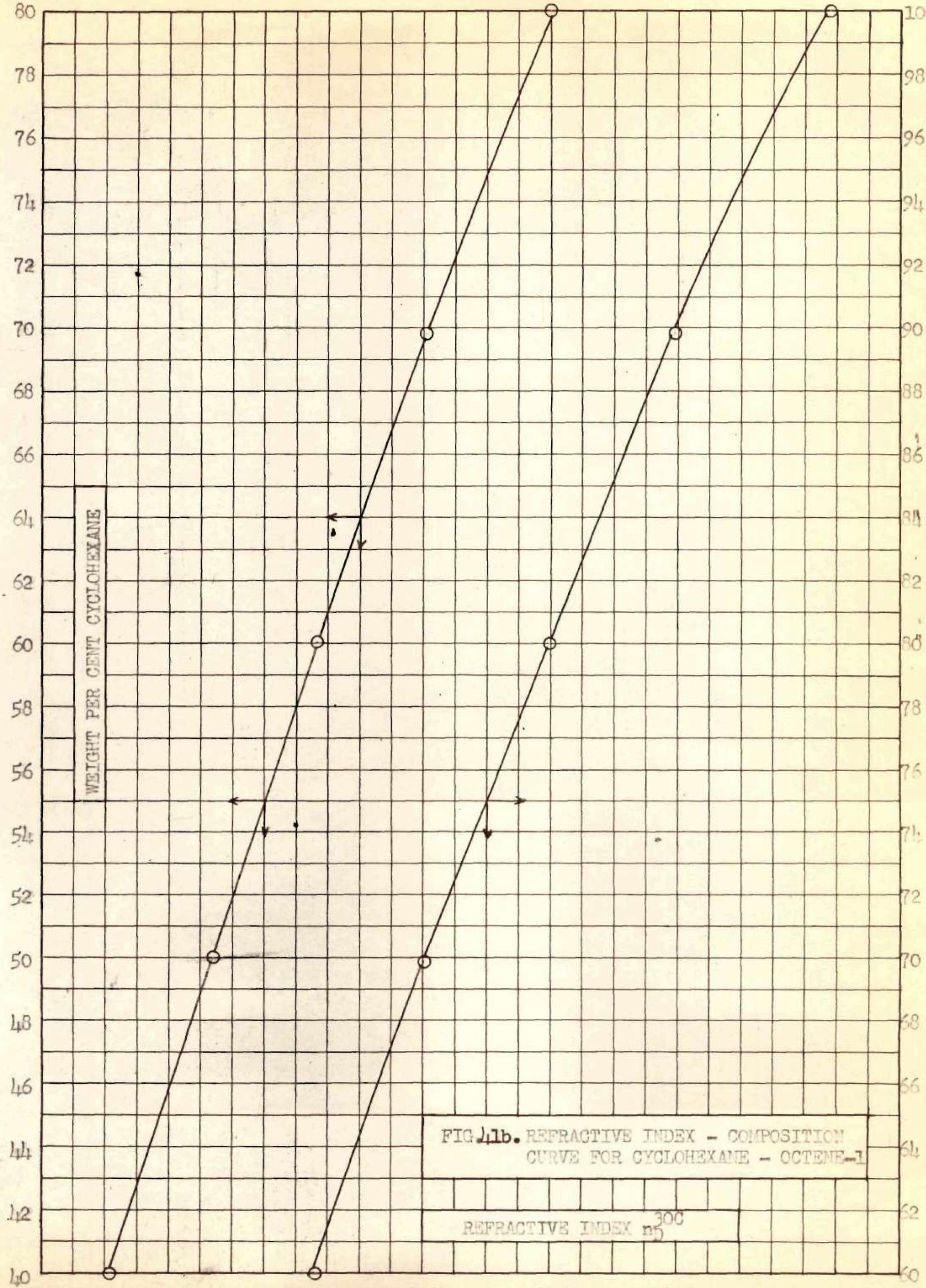

FIG. 41b. REFRACTIVE INDEX - COMPOSITION CURVE FOR CYCLOHEXANE - OCTENE-1

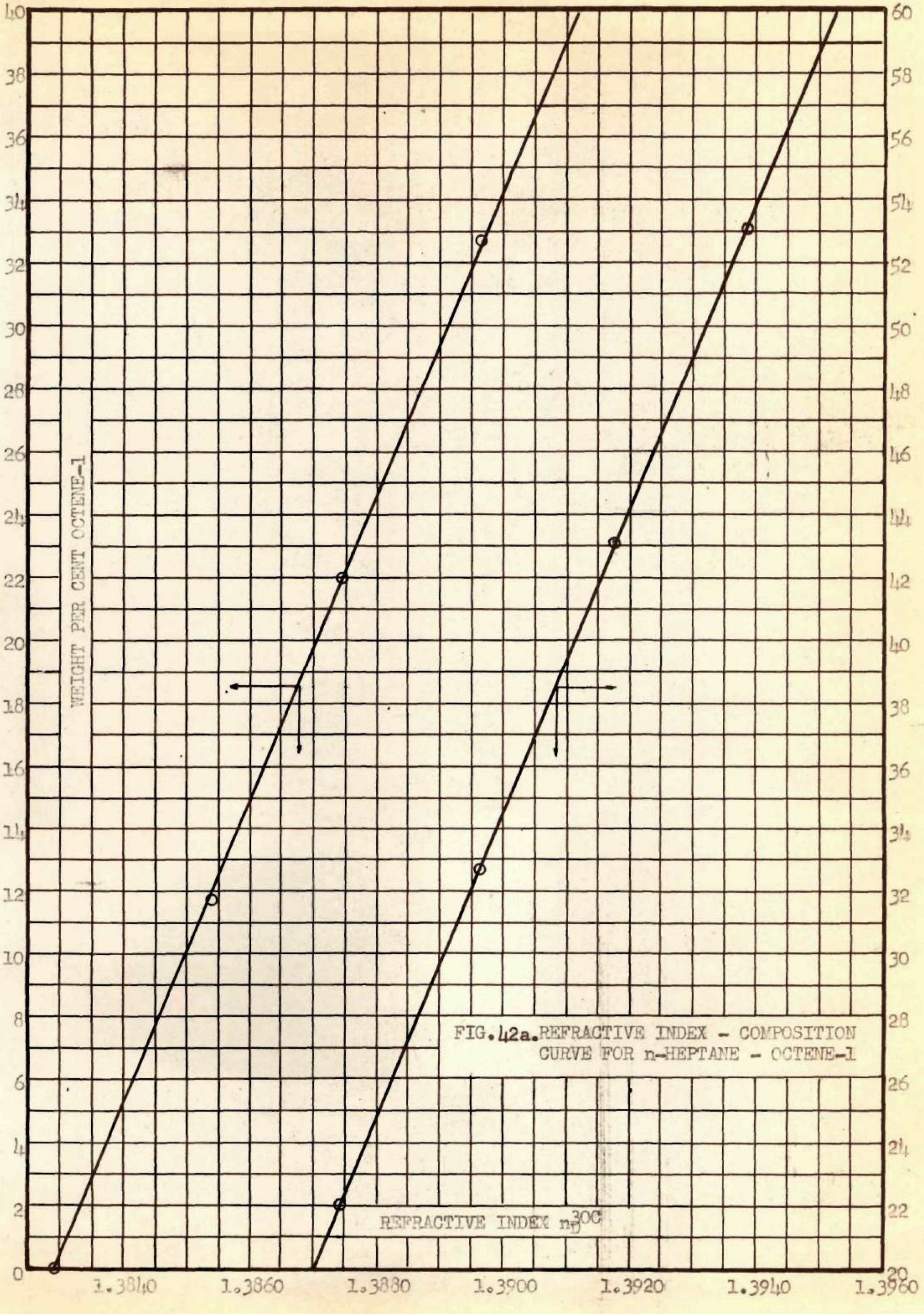

FIG. 42a. REFRACTIVE INDEX - COMPOSITION CURVE FOR n-HEPTANE - OCTENE-1

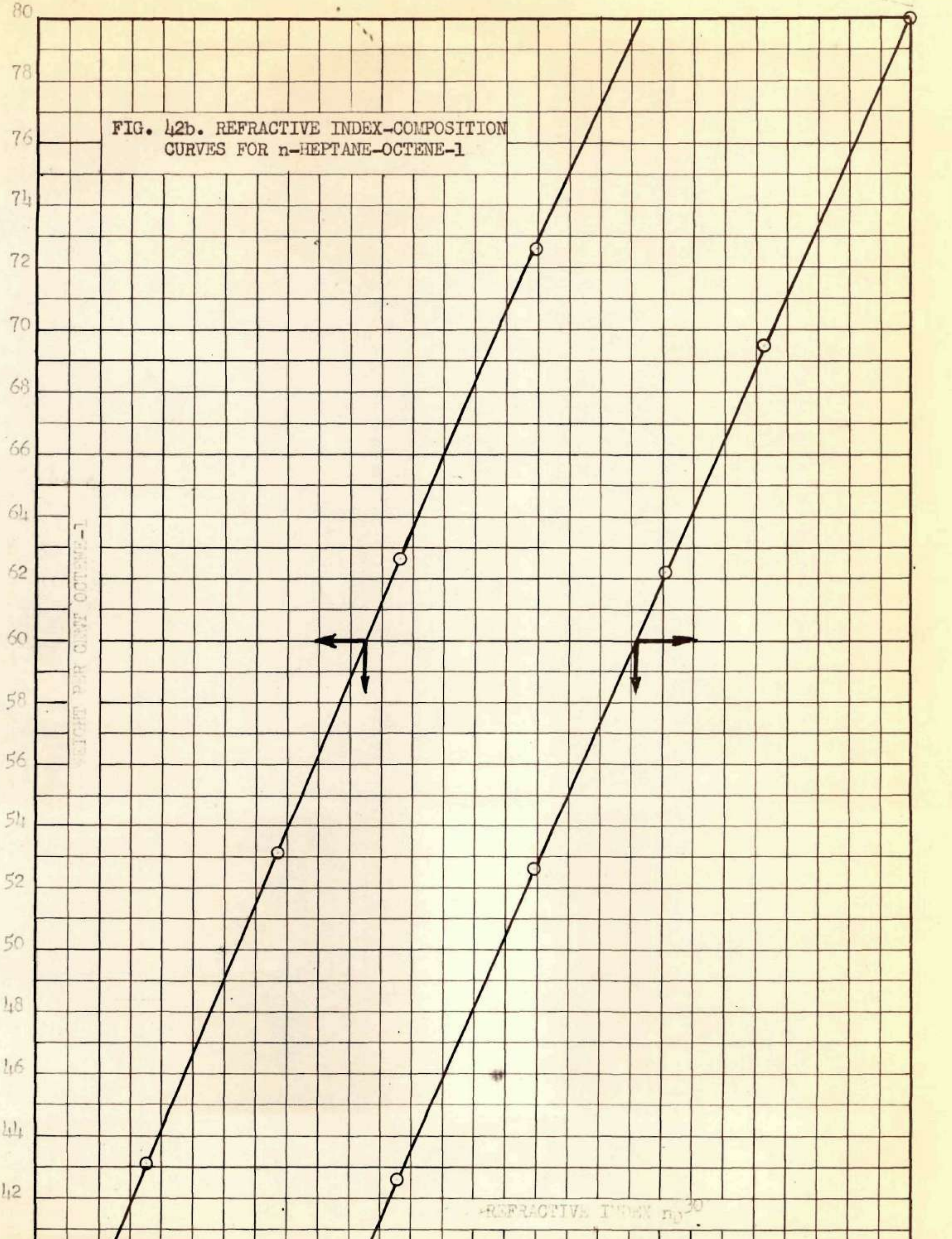

FIG. 42b. REFRACTIVE INDEX-COMPOSITION CURVES FOR n-HEPTANE-OCTENE-1

B. Equilibrium Cell Calibrations

The calibration data on the 500 ml Pyrex glass equilibrium cell at temperatures of 30, 60, and 90°C. are tabulated in Tables 17, 18, and 19 as follows:

Table 17. Calibration* of Equilibrium Cell at 30°C.

Cell Reading ml	True Volume ml	Cell Reading ml	True Volume ml
100	101.13	400	401.04
"	101.24	"	401.54
"	101.24	"	401.24
"	101.13	"	401.34
200	201.67	500	500.67
"	201.57	"	500.48
"	201.27	"	500.67
"	201.57	"	500.48
300	301.21		
"	300.70		
"	301.00		
"	301.21		

*Calibrated with freshly distilled water.

Table 18. Calibration* of Equilibrium Cell at 60°C.

Cell Reading ml	True Volume ml	Cell Reading ml	True Volume ml
100	102.03	400	402.13
"	101.94	"	402.22
200	202.32	500	501.29
"	201.95	"	501.48
300	301.85		
"	301.85		

*Calibrated with Ethylene Glycol Solution ($\rho^{60^\circ\text{C.}} = 1.080$)

Table 19. Calibration* of Equilibrium Cell at 90°C.

Cell Reading ml	True Volume ml	Cell Reading ml	True Volume ml
100	101.43	400	402.06
"	101.77	"	402.40
"	101.89	"	402.36
200	201.95	500	501.89
"	202.40	"	502.34
"	202.17	"	502.01
300	301.54		
"	302.00		
"	301.66		

*Calibrated with Kraft cooking oil ($\rho^{90°C.} = 0.8745$)

APPENDIX II

EXPERIMENTAL DATA

A. Cloud Point and Activity Coefficient Data

A summary of the mutual solubility for furfural-cyclohexane, furfural-n-heptane, furfural-isooctane, furfural-cetane, and furfural-octene-1 is shown in Tables 20 through 24. These data have been interpolated to determine the mutual solubility at one or more of the temperatures of 15, 30, 45, 60, and 90°C. for use in activity coefficient calculations. A summary of these data and calculations appears in Tables 25 through 30. A summary of critical constants, densities, and molal volumes for the four components (furfural, cyclohexane, n-heptane, and cetane) that were studied with the Scatchard-Hamer equations is made in Table 31. These follow:

Table 20. Summary of Cloud Point Measurements for Furfural-Cyclohexane

Mole Per Cent Furfural	Mole Per Cent Cyclohexane	Temperature °C.
0.0619	0.9381	29.4
0.0660	0.9340	31.7
0.0570	0.9430	26.9
0.0727	0.9273	33.9
0.1290	0.8710	49.7
0.1895	0.8005	58.5
0.2035	0.7965	59.9
0.2190	0.7810	60.8
0.2750	0.7250	64.7
0.6640	0.3360	61.7
0.7080	0.2920	57.8
0.7510	0.2490	51.7
0.8132	0.1862	40.8
0.8199	0.1801	37.9
0.8648	0.1352	25.0
0.8671	0.1329	24.4

Table 21. Summary of Cloud Point Measurements for Furfural-n-Heptane

Mole Per Cent Furfural	Mole Per Cent n-Heptane	Cloud Point Temperature °C.
0.1250	0.8750	57.5
0.0977	0.9023	48.6
0.0714	0.9286	37.7
0.0492	0.9508	25.0
0.0579	0.9421	29.9
0.0629	0.9371	33.8
0.0578	0.9422	30.7
0.1995	0.8005	74.4
0.2940	0.7060	85.7
0.3220	0.6780	88.4
0.6940	0.3060	92.6
0.8315	0.1685	77.5
0.9046	0.0954	52.7
0.9479	0.0521	23.9
0.2450	0.7550	81.5
0.1656	0.8344	69.5
0.8676	0.1324	67.8

Table 22. Summary of Cloud Point Measurements for Furfural-Isooctane (2,2,4-Trimethylpentane)

Mole Fraction Furfural	Mole Fraction Isooctane	Temperature °C.
0.0501	0.9499	23.7
0.0663	0.9337	34.0
0.1181	0.8819	55.7
0.1835	0.8165	72.6
0.289	0.711	88.5
0.309	0.691	90.6
0.408	0.592	97.2
0.7525	0.2475	96.5
0.8579	0.1421	80.5
0.9210	0.0790	54.0
0.9394	0.0606	41.1
0.9481	0.0519	32.0
0.9502	0.0498	31.4
0.9552	0.0448	26.7

Table 23. Summary of Cloud Point Measurements for Furfural-Cetane

Mole Fraction Furfural	Mole Fraction Cetane	Cloud Point Temperature °C.
0.0771	0.9229	28.8
0.0860	0.9140	34.7
0.0870	0.9130	34.0
0.1038	0.8862	40.6
0.1590	0.8410	60.7
0.1600	0.8400	60.5
0.2475	0.7525	81.3
0.2865	0.7135	88.0
0.388	0.612	103.7
0.9648	0.0352	96.0
0.9723	0.0277	88.6
0.9833	0.0167	70.8
0.9903	0.0097	49.6
0.9946	0.0054	29.9
0.7335	0.2665	128.2
0.7510	0.2490	129.0
0.698	0.302	127.3
0.8400	0.1600	127.5
0.6370	0.3630	126.0
0.471	0.529	115.5
0.502	0.498	117.5
0.9277	0.0723	116.5
0.7710	0.2290	129.0
0.8865	0.1135	125.0

Table 24. Summary of Cloud Point Measurements for Furfural-Octene-1

Mole Fraction Furfural	Mole Fraction Octene-1	Cloud Point Temperature °C.
0.1325	0.8675	29.0
0.1489	0.8511	32.3
0.2155	0.7845	44.8
0.288	0.712	53.4
0.357	0.643	58.1
0.394	0.606	59.7
0.7030	0.2970	60.7
0.7410	0.2590	58.7
0.8180	0.1820	49.8
0.8835	0.1165	32.8
0.9000	0.1000	25.8

Table 25. Mutual Solubility, van Laar Constants, and van Laar Activity Coefficient Data for Furfural-Cyclohexane System

	Temperature				
Data	15°C.	30°C.	45°C.	60°C.	90°C.
1. Mutual Solubility					
Mole fraction furfural in cyclohexane-rich phase.	0.0390	0.063	0.1075	0.206	Completely Miscible
Mole fraction cyclohexane in furfural-rich phase.	0.110	0.149	0.2095	0.318	Completely Miscible
2. van Laar Constants					
A	1.521	1.360	1.200	1.031	-
B	1.127	1.031	0.942	0.854	0.705
3. Activity Coefficient of Cyclohexane at Indicated Mole Fraction Cyclohexane in Solution.					
0.0	13.42	10.75	8.77	7.15	5.08
0.1	9.21	7.55	6.29	5.21	3.82
0.2	6.34	5.37	4.56	3.86	2.95
0.4	3.205	2.855	2.55	2.27	1.89
0.6	1.790	1.681	1.582	1.482	1.34
0.8	1.81	1.159	1.135	1.113	1.095
0.9	1.048	1.041	1.035	1.030	1.018
1.0	1.000	1.000	1.000	1.000	1.000
$\frac{10^3}{T}$, $(°K)^{-1}$	3.471	3.299	3.144	3.002	2.754

Table 26. Mutual Solubility, van Laar Constants, and van Laar Activity Coefficient Data for Furfural-n-Heptane System

	Temperature		
Data	30°C.	60°C.	90°C.
1. Mutual Solubility			
Mole fraction furfural in n-heptane-rich phase.	0.058	0.131	0.352
Mole fraction n-heptane in furfural-rich phase.	0.059	0.111	0.269
2. van Laar Constants			
A	1.370	1.103	0.845
B	1.366	1.167	0.976
3. Activity Coefficient of n-Heptane at Indicated Mole Fraction n-Heptane in Solution.			
0.0	23.25	14.71	9.49
0.1	12.92	8.61	5.86
0.2	7.62	5.36	3.89
0.4	3.13	2.53	2.05
0.6	1.665	1.498	1.351
0.8	1.138	1.105	1.075
0.9	1.031	1.028	1.019
1.0	1.000	1.000	1.000

Table 27. Mutual Solubility van Laar Constants, and van Laar Activity Coefficient Data for Furfural-2,2,4-Trimethylpentane (Isooctane)

Data	Temperature 30°C.
1. Mutual Solubility	
Mole fraction furfural in isooctane-rich phase.	0.060
Mole fraction isooctane in furfural-rich phase.	0.048
2. van Laar Constants	
A	1.352
B	1.442
3. Activity Coefficient of Isooctane at Indicated Mole Fraction Isooctane in Solution.	
0.0	27.7
0.1	14.25
0.2	7.92
0.4	3.12
0.6	1.635
0.8	1.128
0.9	1.031
1.0	1.000

Table 28. Mutual Solubility, van Laar Constants, and van Laar Activity Coefficient Data for Furfural-Cetane System

	Temperature		
Data	30°C.	60°C.	90°C.
1. Mutual Solubility			
Mole fraction furfural in cetane-rich phase.	0.080	0.156	0.295
Mole fraction cetane in furfural-rich phase.	0.0054	0.0126	0.029
2. van Laar Constants			
A	1.192	0.9549	0.7370
B	2.290	1.9360	1.6208
3. Activity Coefficient of Cetane at Indicated Mole Fraction Cetane in Solution.			
0.0	195.0	86.50	41.90
0.1	35.6	19.50	11.12
0.2	11.05	7.12	4.73
0.4	2.765	2.239	1.847
0.6	1.420	1.314	1.224
0.8	1.075	1.055	1.040
1.0	1.000	1.000	1.000

Table 29. Mutual Solubility, van Laar Constants, and van Laar Activity Coefficient Data for Furfural-Octene-1 System

Data	Temperature 30°C.	 60°C.
1. Mutual Solubility		
Mole fraction furfural in octene-1-rich phase.	0.137	0.400
Mole fraction octene-1 in furfural-rich phase.	0.110	0.281
2. van Laar Constants		
A	1.089	0.822
B	1.079	0.975
3. Activity Coefficient of Octene-1 at Indicated Mole Fraction Octene-1 in Solution.		
0.0	14.89	9.45
0.1	8.65	5.79
0.2	5.34	3.81
0.4	2.50	1.651
0.6	1.485	1.340
0.8	1.102	1.071
0.9	1.025	1.018
1.0	1.000	1.000

Table 30. Mutual Solubility, Scatchard-Hamer Constants and Activity Coefficient Data for Cyclohexane, n-Heptane, and Cetane in Furfural at 30°C.

	System: Furfural-Hydrocarbon		
Data	Cyclohexane	n-Heptane	Cetane
1. Mutual Solubility, 30°C.			
Mole fraction furfural in hydrocarbon-rich phase.	0.063	0.058	0.0800
Mole fraction hydrocarbon in furfural-rich phase.	0.149	0.059	0.0054
2. Scatchard-Hamer Constants			
A	1.321	1.340	1.177
B	0.876	1.265	2.255
V_1(Furfural), cc./gm. mole	83.7	83.7	83.7
V_2(Hydrocarbon) cc./gm. mole	109.9	147.8	297
3. Activity Coefficient of Hydrocarbon at Indicated Mole Fraction Hydrocarbon in Solution.			
0.0	7.53	18.45	180
0.1	6.84	13.62	51.0
0.2	5.47	8.59	13.70
0.4	3.00	3.29	2.735
0.6	1.698	1.643	1.375
0.8	1.149	1.121	1.060
1.0	1.000	1.000	1.000

Table 31. Critical Constant, Densities and Molal Volumes for Furfural, Cyclohexane, n-Heptane, and Cetane

	Component			
Data	Furfural	Cyclohexane	n-Heptane	Cetane
Molecular Weight	96.08	84.16	100.20	226.44
Critical Temperature, °K	645.6	554.1	540.0	722.2
Critical Pressure, PSIA	710	593.4	396.8	221
Density 20C., gms./cc.	1.159	0.779	0.684	0.774
Estimated Density 30C., gms./cc.	1.148	0.766	0.679	0.763
Molecular Volume, cc./gms. mole	83.7	109.9	147.8	297.0

B. Equilibrium Cell Measurements

A summary of the binary and ternary equilibria obtained in the equilibrium cell apparatus is made in Tables 32 through 36. The ternary data are for the five systems, cyclohexane-n-heptane-furfural, cyclohexane-isooctane-furfural, cyclohexane-cetane-furfural, octene-1-n-heptane-furfural, and cyclohexane-octene-1-furfural. These follow:

Table 32. Phase Equilibria for Cyclohexane-n-Heptane-Furfural

		Extract Phase				Raffinate Phase			
Run No.	Temp. °C.	Mole Per Cent Cyclohexane	Mole Per Cent n-Heptane	Mole Per Cent Furfural	Mole Per Cent Cyclohexane: Sol.-Free Basis	Mole Per Cent Cyclohexane	Mole Per Cent n-Heptane	Mole Per Cent Furfural	Mole Per Cent Cyclohexane: Sol.-Free Basis
3	30	14.40	0.00	85.60	100.0	93.50	0.00	6.50	100.00
4	30	2.82	4.98	92.20	36.2	22.94	71.06	6.00	24.4
5	30	6.17	3.53	90.30	63.6	46.33	47.27	6.40	49.5
6	30	10.75	1.55	87.70	87.4	74.49	19.21	6.30	79.5
7	30	0.00	6.00	94.00	0.0	0.00	94.00	6.00	0.0
8	30	4.09	4.41	91.50	48.1	31.86	61.84	6.30	34.4
9	30	6.06	3.54	90.40	63.1	45.02	48.38	6.60	48.2
43	30	0.00	5.70	94.30	0.0	0.0	94.0	6.00	0.0
55	30	14.90	0.00	85.10	100.0	93.58	0.00	6.42	100.00
10	60	0.00	10.90	89.10	0.0	0.00	88.20	12.80	0.0
12	60	30.90	0.00	69.10	100.0	80.50	0.0	19.50	100.00
13	60	10.10	7.10	82.80	58.8	41.60	43.40	15.00	48.9
14	60	8.62	7.68	83.70	52.9	35.60	49.90	14.50	41.6

Table 32 Phase Equilibria for Cyclohexane-n-Heptane-Furfural
(Continued)

		Extract Phase				Raffinate Phase			
Run No.	Temp. °C.	Mole Per Cent Cyclohexane	Mole Per Cent n-Heptane	Mole Per Cent Furfural	Mole Per Cent Cyclohexane: Sol.-Free Basis	Mole Per Cent Cyclohexane	Mole Per Cent n-Heptane	Mole Per Cent Furfural	Mole Per Cent Cyclohexane Sol.-Free Basis
15	60	5.04	8.76	86.20	36.5	24.15	62.05	13.8	28.0
16	60	18.20	4.80	77.00	79.1	61.40	21.90	16.70	73.7
17	90	25.40	0.00	74.60	100.0	66.60	0.00	33.40	100.0
18	90	3.34	26.16	70.50	11.3	5.21	54.69	40.10	8.7
19	90	2.17	25.33	72.50	7.9	3.94	57.56	38.50	6.4
20	90	4.36	26.34	69.30	14.2	6.95	51.45	41.60	11.9
21a	90	12.2	38.8	49.0	23.9	-	-	-	-
21b	90	11.89	36.63	54.48	26.2	-	-	-	-

Table 33. Phase Equilibria for Cyclohexane-2,2,4-Trimethylpentane (Isooctane)-Furfural

		Extract Phase				Raffinate Phase			
Run No.	Temp. °C.	Mole Per Cent Cyclohexane	Mole Per Cent Isooctane	Mole Per Cent Furfural	Mole Per Cent Cyclohexane: Sol.-Free Basis	Mole Per Cent Cyclohexane	Mole Per Cent Isooctane	Mole Per Cent Furfural	Mole Per Cent Cyclohexane: Sol.-Free Basis
48	30	0.00	4.60	95.40	0.00	0.00	93.88	6.12	0.00
49	30	6.19	2.94	90.86	67.79	47.79	45.74	6.47	51.10
50	30	2.66	3.97	93.37	40.19	22.29	71.40	6.31	23.79
51	30	9.63	1.85	88.52	83.90	68.25	25.10	6.64	73.11
3	30	14.40	0.00	85.60	100.00	93.50	0.00	6.50	100.00
55	30	14.90	0.00	85.10	100.00	93.58	0.00	6.42	100.00

Table 34. Phase Equilibria for Cyclohexane-Cetane-Furfural

		Extract Phase				Raffinate Phase			
Run No.	Temp. °C.	Mole Per Cent Cyclohexane	Mole Per Cent Cetane	Mole Per Cent Furfural	Mole Per Cent Cyclohexane Sol.-Free Basis	Mole Per Cent Cyclohexane	Mole Per Cent Cetane	Mole Per Cent Furfural	Mole Per Cent Cyclohexane Sol.-Free Basis
34	30	0.00	0.50	99.50	0.0	0.00	91.80	8.20	0.0
35	30	3.244	0.268	96.488	92.36	36.90	55.53	7.57	39.92
36	30	6.13	0.28	93.59	95.64	41.73	49.75	8.52	45.62
33	30	1.119	0.406	98.475	73.30	17.90	74.90	7.40	19.30
3	30	14.40	0.00	85.60	100.00	93.50	0.00	6.50	100.00
55	30	14.90	0.00	85.10	100.00	93.58	0.00	6.42	100.00
32	60	9.450	0.775	89.775	92.42	57.40	30.00	12.60	65.70
31	60	4.30	1.04	94.66	80.54	34.90	52.20	12.90	40.10
30	60	1.505	1.202	97.293	55.60	14.71	71.19	14.10	17.10
29	60	0.00	1.23	98.77	0.00	0.00	84.80	15.20	0.00
12	60	30.90	0.00	69.10	100.00	80.50	0.00	19.50	100.00

Table 34. Phase Equilibria for Cyclohexane-Cetane-Furfural
(Continued)

		Extract Phase				Raffinate Phase			
Run No.	Temp. °C.	Mole Per Cent Cyclohexane	Mole Per Cent Cetane	Mole Per Cent Furfural	Mole Per Cent Cyclohexane Sol.-Free Basis	Mole Per Cent Cyclohexane	Mole Per Cent Cetane	Mole Per Cent Furfural	Mole Per Cent Cyclohexane Sol.-Free Basis
28	90	45.02	9.15	45.83	83.11	-	-	-	-
27	90	32.61	5.21	62.18	86.22	-	-	-	-
26	90	14.40	3.00	82.60	82.70	46.30	23.50	30.20	66.30
25	90	9.32	2.78	87.90	77.03	41.00	28.96	30.04	58.60
24	90	5.26	2.82	91.92	65.15	28.80	43.00	28.20	40.10
23	90	2.36	2.84	94.80	45.38	13.60	57.70	28.70	19.10
22	90	0.00	2.70	97.80	0.00	0.00	71.10	28.90	0.00

Table 35. Phase Equilibria for Octene-1-n-Heptane-Furfural

		Extract Phase				Raffinate Phase			
Run No.	Temp. °C.	Mole Per Cent Octene-1	Mole Per Cent n-Heptane	Mole Per Cent Furfural	Mole Per Cent Octene-1 Sol.-Free Basis	Mole Per Cent Octene-1	Mole Per Cent n-Heptane	Mole Per Cent Furfural	Mole Per Cent Octene-1 Sol.-Free Basis
37	30	11.59	0.00	88.41	100.00	86.26	0.00	13.24	100.00
38	30	8.20	1.68	90.12	83.0	70.17	18.22	11.61	79.4
39	30	5.88	3.02	91.10	66.1	53.10	36.90	10.00	59.1
40	30	3.50	3.87	92.63	47.36	36.30	55.08	8.62	39.76
41	30	1.69	4.94	93.37	25.14	18.70	74.44	7.36	19.65
42	30	8.49	1.90	89.61	81.72	67.92	19.89	12.19	77.34
43	30	0.00	5.69	94.31	0.00	0.00	6.07	93.93	0.00
44	60	27.83	0.00	72.17	100.00	61.70	0.00	38.30	100.00
45	60	7.37	7.11	85.52	50.9	35.80	43.10	21.10	45.4
46	60	3.92	9.05	87.05	30.2	21.40	60.80	17.80	26.1
47	60	15.69	4.49	79.82	77.9	53.60	18.00	28.40	74.9
10	60	0.00	70.90	89.10	0.00	0.00	88.20	12.80	0.00

Table 36. Phase Equilibria for Cyclohexane-Octene-1-Furfural

		Extract Phase				Raffinate Phase			
Run No.	Temp. °C.	Mole Per Cent Cyclohexane	Mole Per Cent Octene-1	Mole Per Cent Furfural	Mole Per Cent Cyclohexane Sol.-Free Basis	Mole Per Cent Cyclohexane	Mole Per Cent Octene-1	Mole Per Cent Furfural	Mole Per Cent Cyclohexane Sol.-Free Basis
52	30	7.19	6.14	86.67	53.94	43.46	45.40	11.14	48.91
53	30	3.00	9.03	87.97	24.96	18.37	68.74	12.89	21.09
54	30	10.36	3.56	86.08	74.43	63.47	27.25	9.28	69.96
55	30	14.90	0.00	85.10	100.00	93.58	0.00	6.42	100.00
56	30	0.00	11.70	88.30	0.00	0.00	85.90	14.10	0.00

APPENDIX III

SAMPLE CALCULATIONS

Sample calculations have been made to illustrate five points: (A) the calculation of activity coefficients using the van Laar equations and the mutual solubility data shown in Table II, (B) the detailed "general case" calculation of equilibria starting with an assumed composition in the hydrocarbon phase, (C) the calculation of equilibria in a system for which the calculations converge rapidly to a solution regardless of which phase is used as a starting point, (D) the calculation of equilibria in a system with only one pair of non-consolute components, and (E) the calculation of equilibria in a system for which rapid convergence is obtained only if calculations are initiated from the solvent phase. These follow:

A. Activity Coefficients for Cyclohexane in Furfural at 30°C.

The calculation of activity coefficients using the van Laar equations (equation 22) and the mutual solubility data shown in Table II is illustrated for cyclohexane in furfural at 30°C.

The mutual solubility data for cyclohexane and furfural at 30°C. have been taken from Table II and are shown here for convenience. These are:

$$\begin{array}{lll} X_1' = 0.851 & \quad & X_1'' = 0.063 \\ X_2' = \underline{0.149} & & X_2'' = \underline{0.937} \\ \quad\;\; 1.000 & & \quad\;\; 1.000 \end{array}$$

where X_1' is the mole fraction furfural in the furfural-rich phase

X_2' is the mole fraction cyclohexane in the furfural-rich phase

X_1'' is the mole fraction furfural in the cyclohexane-rich phase

X_2'' is mole fraction cyclohexane in the cyclohexane-rich phase.

The above data are substituted into equations 25, which were derived in Chapter II from the van Laar equations. Thus,

$$\frac{A}{B} = \frac{\left(\frac{X_1'}{X_2'} + \frac{X_1''}{X_2''}\right)\left(\frac{\log X_1''/X_1'}{\log X_2'/X_2''}\right) - 2}{\frac{X_1'}{X_2'} + \frac{X_1''}{X_2''} - \frac{2X_1'X_1'' \log X_1''/X_1'}{X_2'X_2'' \log X_2'/X_2''}}$$

and (25)

$$A = \frac{\log X_1''/X_1'}{\frac{1}{\left(1 + \frac{A\ X_1'}{B\ X_2'}\right)^2} - \frac{1}{\left(1 + \frac{A\ X_1''}{B\ X_2''}\right)^2}}$$

Here it is convenient to solve for the ratios of the compositions before substituting into equation 25. Thus,

$$\frac{X_1'}{X_2'} = \frac{0.851}{0.149} = 5.71 \qquad \frac{X_1''}{X_2''} = \frac{0.063}{0.937} = 0.0672$$

$$\log \frac{X_1''}{X_1'} = -\log \frac{0.851}{0.063} = -1.130 \quad \log \frac{X_2'}{X_2''} = -\log \frac{0.937}{0.149} = -0.798$$

and

$$\frac{A}{B} = \frac{(5.71 + 0.0672)\left(\frac{1.130}{0.798}\right) - 2}{(5.71 + 0.0672) - \frac{(2)(5.71)(0.0672)(1.130)}{0.798}} = \frac{6.18}{4.689} = 1.319$$

$$A = \frac{-1.130}{\frac{1}{1 + (1.319)(5.71)^{2}} - \frac{1}{1 + (1.319)(0.0672)^{2}}} = \frac{-1.130}{-0.8312} = 1.360$$

The values for B/**A** and B are then obtained as follows:

$$\frac{B}{A} = \frac{1}{1.319} = 0.758$$

and

$$B = \frac{1.360}{1.319} = 1.031$$

The above values for B/A and B are then substituted into the appropriate form of equation 22 to obtain the activity coefficients of cyclohexane in furfural at any desired composition. This is as follows:

$$\log \gamma_2 = \frac{B\,X_1^{2}}{(X_1 + \frac{B}{A}X_2)^2} \qquad (22)$$

where γ_2 is the activity coefficient for cyclohexane
A and B are the constants obtained above
X is mole fraction
Subscripts 1, 2 refer to furfural and cyclohexane respectively.

For X_2 = 0.0 (mole fraction cyclohexane), X_1 = 1.0, and

$$\log \gamma_2 = 1.031 \text{ and } \gamma_2 = 10.75$$

For $X_2 = 0.1$, $X_1 = 0.9$, and

$$\log \gamma_2 = \frac{(1.031)(0.81)}{0.9 + (0.758)(0.1)^2} = \frac{0.835}{0.952} = 0.877$$

$$\text{and } \gamma_2 = 7.55$$

For $X_2 = 0.6$, $X_1 = 0.4$, and

$$\log \gamma_2 = \frac{(1.031)(0.16)}{0.4 + (0.758)(0.6)^2} = \frac{0.1650}{0.731} = 0.2255$$

$$\text{and } \gamma_2 = 1.681$$

For $X_2 = 1.0$, $X_1 = 0.0$, and

$$\log \gamma_2 = 0.0 \text{ and } \gamma_2 = 1.0$$

The complete table of activity coefficients for cyclohexane in furfural, calculated as above with the van Laar equations, is shown in Table 25. These data are plotted in Figure 23.

B. Equilibria in Cyclohexane-n-Heptane-Furfural at 30°C.

The system cyclohexane-n-heptane-furfural at 30°C. was chosen to illustrate the detailed "general case" calculation of equilibria when starting from an assumed composition in the hydrocarbon-rich phase. This is demonstrated for Run 5 shown in Table 3, where the experimental ternary-system data were taken from Table 32, Appendix II.

It is explained in Chapter VII that any assumed hydrocarbon-phase composition, on a solvent-free basis, may be used as a starting point for the calculation of the equilibrium solvent phase. Here, however, the experimental hydrocarbon-rich-phase composition of Run 5, expressed as mole fraction cyclohexane on a solvent-free basis, is used as a starting point for the calculations. This is done to provide a direct comparison of the estimated and experimental data for the solvent phase in that run.

The estimation procedure provides for the calculation of ternary equilibria from the solubilities of two binary pairs. Therefore, the mutual solubility data for furfural-cyclohexane and furfural-n-heptane at 30°C., as taken from Table 2, are shown below.

30°C. Solubilities for Binary Pairs
in Cyclohexane-n-Heptane-Furfural System

Furfural-n-Heptane	Hydrocarbon Phase	Solvent Phase
X_F	0.058	0.941
X_{Hc}	0.942	0.059
X_F/X_{Hc}	0.0616	15.95
Furfural-Cyclohexane		
X_F	0.063	0.851
X_{Hc}	0.937	0.149
X_F/X_{Hc}	0.0672	5.71

where:

X is mole fraction.
Subscripts F, Hc refer to furfural and hydrocarbon respectively.
X_F/X_{Hc} is a ratio expressed as mols of solvent per mol of hydrocarbon.

Maloney and Schubert (34) have demonstrated the utility of a graph, representing moles of solvent per mole of hydrocarbon as ordinate and mole fraction hydrocarbon A (on a solvent-free basis) as abscissa, in design calculations for liquid-liquid extraction. This type graph is a modification of the Ponchon type (42, 43) used in distillation, where the ordinate represents enthalpy rather than solvent content.

In this work it is necessary to make an assumption regarding the solvent content of the phase that is used to initiate the calculations. This is only an assumption, and it cannot be verified except by comparison with experimental data. A first approximation is also necessary for the solvent content in the phase to be calculated, but this can be verified by the successive-approximation technique employed.

A study of several systems has shown that the curves, representing the solvent and hydrocarbon phases on the graph developed by Maloney and Schubert (34), do not deviate much from straight lines. Therefore, it can be assumed that the terminal points, obtained from the binary-system solubility measurements, can be joined by straight lines. This provides a basis for the estimation of the solvent content in the two phases of a ternary system at any given hydrocarbon composition, expressed on a solvent-free basis. This is illustrated for this system in Figure 43, where the experimental ternary data have been added for comparison and are joined by tie lines.

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(34) Maloney and Schubert, _op_. _cit_., p. 741.

(42) Ponchon, M., Tech. Moderne, _13_, 20 (1921).

(43) Savarit, R., Arts et Metiers, pp. 65, 142, 178 (1922).

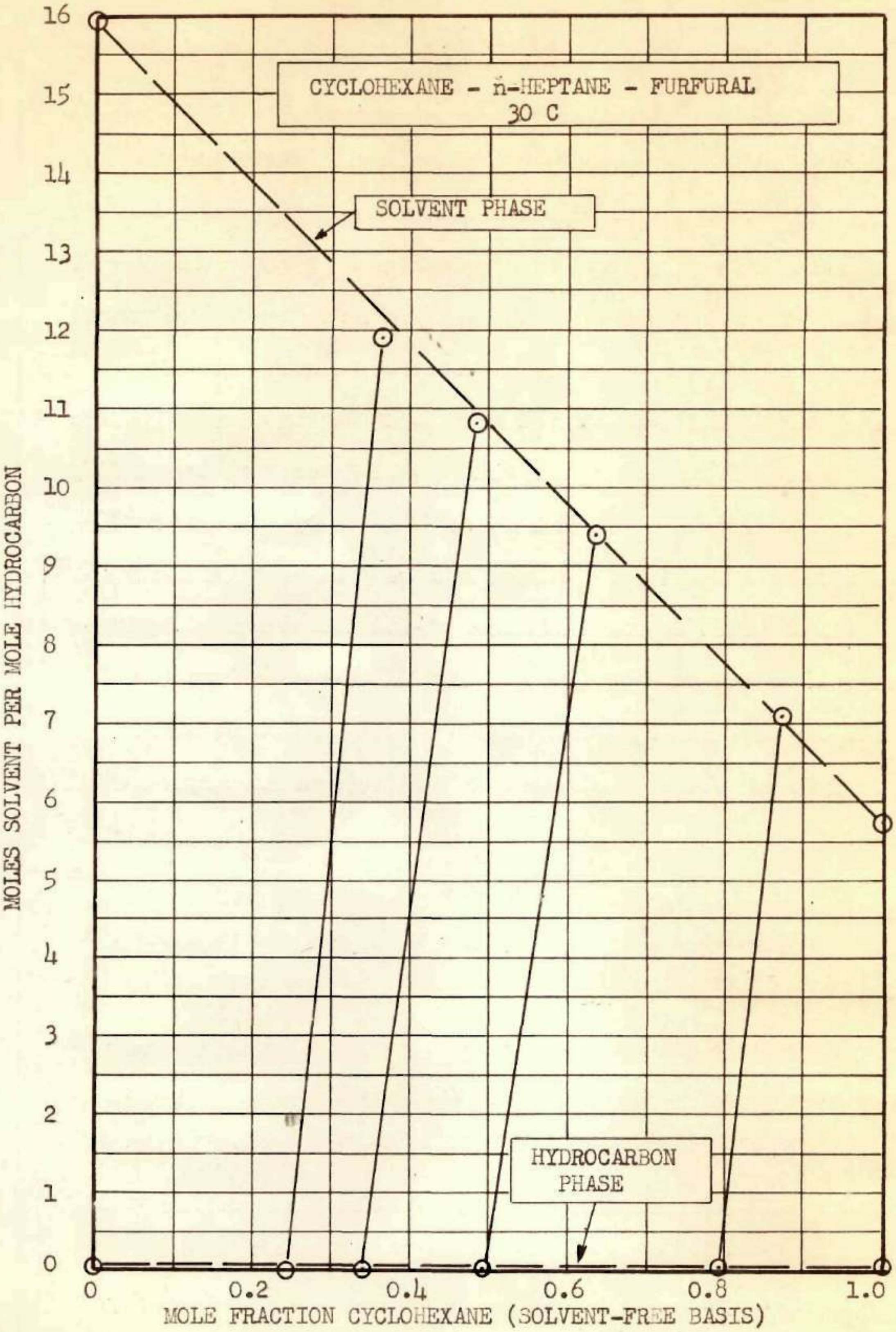

FIG. 43. ESTIMATED PHASES IN CYCLOHEXANE-n-HEPTANE-FURFURAL AT 30 C

The problem is to estimate the equilibrium solvent-phase composition when the solvent-free hydrocarbon composition is 0.495 (from Run 5). Since the hydrocarbon phase is the starting point, the fixed assumption is made that the solvent content of the phase is linear with composition on the graph of Figure 43. The numerical value is then obtained by use of the ratios listed in the above tabulation of solubilities. Thus,

$$(0.495)(0.0672) + (0.505)(0.0616) = 0.0645 \text{ mols of furfural per mole of hydrocarbon}$$

The overall hydrocarbon phase is then shown as

	Mols	Mole Fraction
Cyclohexane	0.495	0.465
n-Heptane	0.505	0.474
Furfural	0.0645	0.061
	1.0645	1.000

Now, refer to the activity coefficient curves of Figures 23 and 24, and recall the assumption in Chapter II that the activity coefficient of cyclohexane and n-heptane may be obtained from their appropriate hydrocarbon-furfural activity coefficient curves at the mole fraction hydrocarbon of 0.939 (the total hydrocarbon composition).

Thus for the hydrocarbon phase:

$$\gamma_{\text{cyclohexane}} = 1.01$$

$$\gamma_{\text{n-heptane}} = 1.01$$

Then, as a first approximation, the equilibrium solvent phase composition is estimated to be 0.64 mole fraction cyclohexane, on a solvent-free basis. The solvent phase may then be estimated if linearity of the curve on Figure 43 is assumed. Thus,

$(0.64)(5.71) + (0.36)(15.95) = 9.39$ mols of furfural per mole of hydrocarbon in the solvent phase.

The first approximation of the solvent phase is then:

	Mols	Mole Fraction
Hydrocarbon	1.00	0.0963
Furfural	9.39	0.9037
	10.39	1.0000

Again the activity coefficients for cyclohexane and n-heptane are obtained from Figures 23 and 24. This time the coefficients are evaluated at 0.0963 mole fraction hydrocarbon on the 30°C. curves. Thus

$$\gamma_{\text{cyclohexane}} = 7.65$$
$$\gamma_{\text{n-heptane}} = 13.4$$

The estimated hydrocarbon-phase composition with the corresponding activity coefficients, and the first approximation activity coefficients for the solvent phase have now been obtained. These are related by equation 23 as follows:

$$X_1' = X_1'' \left(\frac{\gamma_1''}{\gamma_1'}\right) \qquad (23)$$

Therefore, the calculated solvent-phase compositions are

$$X\ \text{cyclohexane} = (0.465)\left(\frac{1.01}{7.65}\right) = 0.0615$$

$$X \text{ n-heptane} = (0.474)\left(\frac{1.01}{13.4}\right) = 0.0357$$

$$X \text{ furfural} = 1.0 - X'\text{s} = \underline{0.9028}$$

$$1.0000$$

The calculation may be repeated using the calculated mole fraction hydrocarbon of 0.0972 for the second approximation of activity coefficients, rather than the initial value of 0.0963. However, from Figures 23 and 24, no change in activity coefficients is evident.

The above compositions may be expressed as mole fraction cyclohexane on a solvent-free basis for representation on the conventional X-Y diagrams. Thus,

$$\frac{0.0615}{0.0972} = 0.634 \text{ mole fraction cyclohexane on a solvent-free basis.}$$

This value is compared with the experimental value of 0.636 in Table 3 and Figure 29. The estimated solvent-phase furfural content of 0.9028 mole fraction furfural agrees with the experimental data to three decimal places. The estimated hydrocarbon-phase furfural content of 0.061 mole fraction furfural agrees closely with the experimental value of 0.064. Actually, the same activity coefficient value is read from Figures 23 and 24 for both furfural compositions.

C. Equilibria in Cyclohexane-n-Heptane-Furfural at 60°C.

The system cyclohexane-n-heptane-furfural at 60°C. was chosen to illustrate a system with which the calculations converge rapidly to a solution regardless of the choice of phase to initiate them.

The mutual solubilities for the two non-consolute binaries in this system have been taken from Table 2. Activity coefficient data were calculated using the van Laar equations and are shown in Tables 25 and 26 and Figures 23 and 24. The mutual solubility data obtained in the cloud point apparatus are repeated here for convenience.

60°C. Solubilities for Binary Pairs
in Cyclohexane-n-Heptane-Furfural System

Furfural-n-Heptane	Hydrocarbon Phase	Solvent Phase
X_F	0.131	0.889
X_{Hc}	0.869	0.111
X_F/X_{Hc}	0.1509	8.00
Furfural-Cyclohexane		
X_F	0.206	0.682
X_{Hc}	0.794	0.318
X_F/X_{Hc}	0.2595	2.145

1. Calculations Initiated with Hydrocarbon Phase.--The problem is to calculate the solvent-phase composition when the solvent-free hydrocarbon-phase composition conforms to that in Run 15 shown in Tables 4 and 32. From these data, the mole fraction cyclohexane (solvent-free basis) in the hydrocarbon phase is 0.280. Now, since the ratio of mols solvent per mol hydrocarbon is assumed linear with composition

(on a solvent-free basis) for the initiating phase, the estimated X_F/X_{Hc} for the hydrocarbon mixture is

$(0.280)(0.2595) + (0.720)(0.1509) = 0.1810$ mols solvent per mol hydrocarbon.

The hydrocarbon-phase composition is then calculated from the above solvent-hydrocarbon ratio figure and initial solvent-free hydrocarbon phase composition as follows:

	Moles	Mole Fraction
Cyclohexane	0.280	0.237
n-Heptane	0.720	0.610
Furfural	0.181	0.153
	1.181	1.000

Reference is now made to the activity coefficient curves of Figures 23 and 24 at the total hydrocarbon content of 0.847.

For this hydrocarbon phase,

$$\gamma_{(\text{cyclohexane})} = 1.06$$
$$\gamma_{(\text{n-heptane})} = 1.05$$

Then, as a first approximation, 0.280 mole fraction cyclohexane (solvent-free basis) in the hydrocarbon phase is assumed to be in equilibrium with 0.330 mole fraction cyclohexane (solvent-free basis) in the solvent phase. The solvent-phase composition may now be calculated if linearity of the solvent-phase graph of mols solvent per mole hydrocarbon versus composition (on a solvent-free basis) is assumed. Thus for the solvent-phase solvent content -

$(0.33)(2.145) + (0.67)(8.00) = 6.059$ mols solvent per mol hydrocarbon

and the solvent phase is

	Mols	Mole Fraction
Hydrocarbon	1.000	0.1417
Furfural	6.059	0.8583
	7.059	1.0000

Again, the activity coefficients for cyclohexane and n-heptane may be obtained from Figures 23 and 24 at 0.1417 mole fraction hydrocarbon on the 60°C. curves. Thus

$$\gamma\text{(cyclohexane)} = 4.55$$
$$\gamma\text{(n-heptane)} = 7.00$$

But, $X_1' = X_1''\left(\frac{\gamma_1''}{\gamma_1'}\right)$ from equation 23.

Therefore, for the solvent phase

$$X\text{(cyclohexane)} = (0.237)\left(\frac{1.06}{4.55}\right) = 0.0552$$
$$X\text{(n-heptane)} = (0.610)\left(\frac{1.05}{7.00}\right) = \underline{0.0915}$$
$$\text{Total hydrocarbons} = 0.1467$$

Now, since the calculated total hydrocarbon content does not agree ($0.1467 \neq 0.1417$) with the first approximation, a second approximation is made that the solvent phase contains 0.150 mole fraction total hydrocarbons and the activity coefficients are re-evaluated by the same procedure as follows:

$$\gamma(\text{cyclohexane}) = 4.48$$
$$\gamma(\text{n-heptane}) = 6.75$$

The hydrocarbons in the solvent phase are then recalculated as

$$X(\text{cyclohexane}) = (0.237)\left(\frac{1.06}{4.48}\right) = 0.0561$$
$$X(\text{n-heptane}) = (0.610)\left(\frac{1.05}{6.75}\right) = \underline{0.0950}$$
$$\text{Total hydrocarbons} \quad 0.1511$$

Now, 0.1511 mole fraction total hydrocarbons is sufficiently close to the second approximation of 0.1500 that no change in activity coefficients can be read from the graphs. Therefore, the estimated solvent-free hydrocarbon composition is

$$\frac{0.0561}{0.1511} = 0.371 \text{ mole fraction cyclohexane}$$

The value of 0.371 compares favorably with the experimental value of 0.365 as shown in Table 4. The estimated furfural contents, X_F, are 0.153 and 0.849 for the hydrocarbon and solvent phases respectively as shown above. They are compared with the experimental data in Table 4.

2. Calculations Initiated with Solvent Phase.--The problem is to calculate the hydrocarbon-phase compositions when the solvent-free solvent-phase composition conforms to that of Run 15 shown in Tables 4 and 32. From these data the mole fraction cyclohexane (solvent-free basis) in the solvent phase is 0.365.

The furfural content of the starting phase is based on the linearity of the curve of mols solvent per mol hydrocarbons with composition as before.

Thus,

$(0.365)(2.145) + (0.635)(8.00) = 5.859$ mols solvent per mol hydrocarbon

in the solvent phase. The solvent composition is then

	Mols	Mole Fraction
Cyclohexane	0.365	0.0532
n-Heptane	0.635	0.0925
Furfural	5.859	0.8543
	6.859	1.0000

From Figures 23 and 24 at a hydrocarbon composition of 0.1457

$$\gamma\,(\text{cyclohexane}) - 4.50$$
$$\gamma\,(\text{n-heptane}) = 6.90$$

As a first approximation, the solvent-free hydrocarbon-phase composition is estimated to be 0.30 mole fraction cyclohexane, and the solvent content of the phase is calculated as follows:

$(0.30)(0.2595) + (0.70)(0.1509) = 0.1832$ mols solvent per mole hydrocarbon

The hydrocarbon-phase composition is then

	Mols	Mole Fraction
Hydrocarbon	1.0000	0.8452
Furfural	0.1832	0.1548
	1.1832	1.0000

From Figures 23 and 24 at a total hydrocarbon composition of 0.8452

$$\gamma\,(\text{cyclohexane}) = 1.07$$
$$\gamma\,(\text{n-heptane}) = 1.06$$

The hydrocarbon-phase composition can then be calculated from the initial solvent-phase composition and the ratio of activity coefficients from equation 23. Thus,

$$\begin{aligned} X\,(\text{cyclohexane}) &= (0.0532)\left(\frac{4.50}{1.07}\right) &&= 0.2240 \\ X\,(\text{n-heptane}) &= (0.0925)\left(\frac{6.90}{1.60}\right) &&= \underline{0.6010} \\ & && \ 0.8250 \end{aligned}$$

The initial assumption of the hydrocarbon-phase composition, 0.30 mole fraction cyclohexane on a solvent-free basis, can now be verified.

Mole fraction cyclohexane = $\frac{0.2240}{0.8250}$ = 0.272 (which is not in agreement with 0.30). Recalculation of the hydrocarbon-phase solvent content based on the new composition of 0.272 mole fraction cyclohexane gives

$(0.272)(0.2595) + (0.728)(0.1509)$ = 0.1800 mols solvent per mol hydrocarbon.

The second hydrocarbon-phase composition is then

	Mols	Mole Fraction
Hydrocarbon	1.0000	0.8475
Furfural	0.1800	0.1525
	1.1800	1.0000

However, the two hydrocarbon-phase compositions are so close that no change in activity coefficients is obtained from Figures 23 and 24. Therefore, the hydrocarbon-phase composition is, as before, 0.272 mole fraction cyclohexane (on a solvent-free basis). This is in good agreement with the experimental value of 0.280 mole fraction cyclohexane as shown in Table 4.

D. Equilibria in Cyclohexane-n-Heptane-Furfural at 90°C.

The system cyclohexane-n-heptane-furfural at 90°C. was chosen to illustrate a system with only one pair of non-consolute components. Accordingly, it is necessary to assume the location of the binodal curve in order to calculate the equilibria. The experimental equilibrium data of Run 19 have been taken from Tables 5 and 32 and are tabulated as follows:

	Solvent Phase	Hydrocarbon Phase
Cyclohexane	0.0217	0.0394
n-Heptane	0.2533	0.5756
Furfural	0.7250	0.3850
	1.0000	1.0000

Activity coefficient data were calculated from the mutual solubility (cloud point apparatus) of Table 2 and are plotted on Figures 23 and 24. The binodal curve is shown in Figure 14.

1. Calculations Initiated with Hydrocarbon Phase.--The problem is to calculate the solvent-phase composition when the hydrocarbon-phase composition conforms to the experimental value shown above for Run 19.

From the activity coefficient curves of Figures 23 and 24 at

0.615 mole fraction total hydrocarbon:

$$\gamma\text{(cyclohexane)} = 1.31$$
$$\gamma\text{(n-heptane)} = 1.32$$

As a first approximation, the mole fraction furfural, X_F, in the solvent phase is taken to be 0.70. Then from the activity coefficient curves at 0.30 mole fraction hydrocarbon the activity coefficients are obtained. These are,

$$\gamma\text{(cyclohexane)} = 2.32$$
$$\gamma\text{(n-heptane)} = 2.75$$

The composition (first approximation) in the solvent phase is then calculated using equation 23. Thus,

$$X\text{(cyclohexane)} = (0.0394)\left(\frac{1.31}{2.22}\right) = 0.0222$$
$$X\text{(n-heptane)} = (0.5756)\left(\frac{1.32}{2.75}\right) = \underline{0.2760}$$
$$0.2982$$

The solvent-phase composition (solvent-free basis) is then $\frac{0.0222}{0.2982} = 0.0746$ mole fraction cyclohexane. This value, with the first approximation of the furfural concentration (0.70 mole fraction from above) permits calculation of the first-approximation solvent phase.

	Mole Fraction of First Solvent Phase
Cyclohexane	0.0224
n-Heptane	0.2776
Furfural	0.7000
	1.0000

However, the inspection of Figure 14 shows that the above composition does not fall on the binodal curve, and must therefore be in error.

As a second approximation the mole fraction furfural in the solvent phase is taken to be 0.74. The activity coefficient at that solvent concentration are then

$$\gamma(\text{cyclohexane}) = 2.57$$
$$\gamma(\text{n-heptane}) = 3.13$$

The second composition in the solvent phase is then calculated as follows:

$$X(\text{cyclohexane}) = (0.0394)(\tfrac{1.31}{2.57}) = 0.0205$$
$$X(\text{n-heptane}) = (0.5756)(\tfrac{1.32}{3.13}) = \underline{0.2425}$$
$$0.2630$$

The solvent-phase composition (solvent-free basis) is then $\frac{0.0205}{0.2630} = 0.0779$ mole fraction cyclohexane. This, with the assumed $X_F = 0.74$, permits the recalculation of the solvent phase as follows:

	Mole Fraction of Second Solvent Phase
Cyclohexane	0.02025
n-Heptane	0.23975
Furfural	0.74000
	1.0000

Again, however, the inspection of Figure 14 shows that the above composition is not on the binodal curve, and it must therefore be erroneous. However, the first approximation is inside of the binodal curve, and the second is without. Therefore, drawing a straight line between them will locate the proper estimated solvent content in the solvent phase.

This is 0.724 mole fraction furfural. The final estimation of the solvent-free solvent-phase hydrocarbon composition is then obtained by linear interpolation as follows:

$$\text{mole fraction cyclohexane} = 0.0746 + \left(\frac{0.024}{0.040}\right)(0.0033) = 0.0766$$

This estimated value agrees quite well with the experimental value of 0.079. The full comparison of the estimated and experimental data for this system is shown in Table 5.

2. Calculations Initiated with the Solvent Phase.--The problem is to calculate the hydrocarbon-phase composition when the solvent-phase composition conforms to the value shown above for Run 19.

From the activity coefficient curves at 0.2720 mole fraction hydrocarbon in the solvent phase at 90°C., the following values are obtained:

$$\gamma_{(\text{cyclohexane})} = 2.48$$
$$\gamma_{(\text{n-heptane})} = 2.99$$

As a first approximation the solvent content of the hydrocarbon phase is taken to be 0.38 mole fraction furfural. Then from Figures 23 and 24 at 0.62 mole fraction hydrocarbon

$$\gamma_{(\text{cyclohexane})} = 1.30$$
$$\gamma_{(\text{n-heptane})} = 1.31$$

The compositions for the hydrocarbon phase are then calculated as follows:

$$X(\text{cyclohexane}) = (0.0217)\left(\frac{2.48}{1.30}\right) = 0.0413$$

$$X(\text{n-heptane}) = (0.2533)\left(\frac{2.99}{1.31}\right) = \underline{0.5790}$$

$$0.6203$$

The hydrocarbon-phase composition (solvent-free basis) is then $\frac{0.0413}{0.6203}$ = 0.0665 mole fraction cyclohexane, and the first approximation of the hydrocarbon phase is

	Mole Fraction of First Hydrocarbon Phase
Cyclohexane	0.0412
n-Heptane	0.5788
Furfural	0.3800
	1.0000

However, from Figure 14, the above composition falls just off the binodal curve. Repeating the above with a second approximation of 0.39 mole fraction furfural gives the same solvent-free composition as before (0.0665 mole fraction cyclohexane), but gives a point on the other side of the binodal curve from the first approximation. This second value is:

	Mole Fraction of Second Hydrocarbon Phase
Cyclohexane	0.0406
n-Heptane	0.5694
Furfural	0.3900
	1.0000

The estimated solvent content is then determined by linear interpolation on Figure 14 to be 0.384 mole fraction furfural. The solvent-free composition of 0.0665 agrees closely with the experimental value of

0.064 mole fraction cyclohexane. The full comparison of these data is shown in Table 5.

E. Equilibria in Cyclohexane-Cetane-Furfural at 60°C.

The system cyclohexane-cetane-furfural at 60°C. was chosen to illustrate a system with which the calculations converge rapidly to a solution when initiated with the solvent phase, but which show poor convergence when initiated with the hydrocarbon phase.

The mutual solubilities for the two non-consolute binaries in this system have been taken from Table 2. Activity coefficient data were calculated using the van Laar equations and are shown in Tables 25 and 28 and Figures 23 and 26. The mutual solubility data, obtained in the cloud point apparatus and utilized in these calculations, are repeated here for convenience.

60°C. Solubilities for Binary Pairs
in Cyclohexane-n-Heptane-Furfural Systems

Furfural-Cetane	Hydrocarbon Phase	Solvent Phase
X_F	0.156	0.9874
X_{Hc}	0.854	0.0126
X_F/X_{Hc}	0.1828	78.3
Furfural-Cyclohexane		
X_F	0.206	0.682
X_{Hc}	0.794	0.318
X_F/X_{Hc}	0.2595	2.145

1. Calculations Initiating with the Hydrocarbon Phase.--The problem is to calculate the solvent-phase composition when the solvent-free hydrocarbon-phase composition conforms to that of Run 32 shown in Tables 8 and 34. From these data the mole fraction cyclohexane (solvent-free basis) in the hydrocarbon phase is 0.657. Now, linearity of the quantity mols of solvent per mol of hydrocarbon with composition is assumed as before for the hydrocarbon mixture, and the solvent content in the hydrocarbon phase can be calculated. Thus,

$(0.657)(0.2595) + (0.343)(0.1828) = 0.2329$ mols solvent per mol hydrocarbon in the hydrocarbon phase.

The hydrocarbon phase is then estimated as

	Mols	Mole Fraction
Cyclohexane	0.657	0.533
Cetane	0.343	0.278
Furfural	0.2329	0.189
	1.2329	1.000

The activity coefficients for cyclohexane and cetane in the hydrocarbon phase are then read from their respective Figures 23 and 26 at 0.811 mole fraction hydrocarbon. Thus,

$$\gamma_{(\text{cyclohexane})} = 1.10$$
$$\gamma_{(\text{cetane})} = 1.040$$

As a first approximation of the solvent phase, linearity of the ratio mols solvent per mol hydrocarbon with composition is assumed, and the solvent-free solvent phase composition is guessed to be 0.90 mole fraction cyclohexane. Then, (0.90)(2.145) + (0.10)(78.3) = 9.76 mols solvent per mol hydrocarbon in the solvent phase.

The first approximation of the solvent phase is then:

	Mols	Mole Fraction
Hydrocarbon	1.00	0.093
Furfural	9.76	0.907
	10.76	1.000

The activity coefficients for cyclohexane and cetane in the solvent phase are then read from Figures 23 and 26 at 0.093 mole fraction hydrocarbon as

$$\gamma(\text{cyclohexane}) = 5.30$$
$$\gamma(\text{cetane}) = 21.50$$

The solvent phase compositions are then calculated using the ratio of activity coefficients and the initial hydrocarbon-phase composition. These are:

$$X(\text{cyclohexane}) = (0.533)\left(\frac{1.10}{5.30}\right) = 0.1108$$
$$X(\text{cetane}) = (0.278)\left(\frac{1.040}{21.50}\right) = \underline{0.01344}$$
$$0.12424 \text{ (but, } 0.1242 \neq 0.093)$$

A second approximation with 0.130 mole fraction hydrocarbons gives 0.1459, which is also not in agreement. A third approximation of solvent phase is now made using the total hydrocarbon content as 0.150 mole fraction. The activity coefficients are recalculated as before:

$$\gamma(\text{cyclohexane}) = 4.45$$
$$\gamma(\text{cetane}) = 11.00$$

and

$$X(\text{cyclohexane}) = (0.533)\left(\frac{1.10}{4.45}\right) = 0.1319$$

$$X(\text{cetane}) = (0.278)\left(\frac{1.040}{11.00}\right) = \underline{0.0263}$$

$$0.1582 \text{ (but, } 0.1582 \neq 0.150)$$

The fourth approximation of 0.160 mole fraction hydrocarbon in the solvent phase shows

$$X(\text{cyclohexane}) = 0.1350$$

$$X(\text{cetane}) = \underline{0.0289}$$

$$\text{Total Hydrocarbons} = 0.1639 \quad (0.164 \cong 0.160)$$

This fourth approximation shows the total hydrocarbons to be only close to the starting value for activity coefficients, and give a solvent-free solvent-phase composition as

$$\frac{0.1350}{0.1639} = 0.825 \text{ mol fraction cyclohexane (solvent-free basis).}$$

The above value not only deviates considerably from experiment, but the value of the solvent content of 1.00 - 0.164 = 0.836 is considerably removed from the experimental value of 0.897 as shown in Table 8.

This particular case does not converge rapidly to a solution (the fourth trial is still in error) and the resulting estimations are obviously erroneous. The method could be modified as is - i.e., still starting from the hydrocarbon phase. However, the author saw advantage in recalculating these cases from the solvent phase. This is illustrated in the following section.

2. Calculations Initiating with the Solvent Phase.--The problem is to calculate the hydrocarbon-phase composition when the solvent-free solvent-phase composition conforms to that of Run 32 shown in Tables 8 and

34. From these data the mole fraction cyclohexane (on a solvent-free basis) in the solvent phase is 0.924. Assuming linearity of the solvent-phase graph of mols solvent per mol hydrocarbon versus solvent-free composition gives

$(0.924)(2.145) + (0.076)(78.3) = 7.925$ mols solvent per mol hydrocarbon in the solvent phase.

Therefore the estimated solvent phase is:

	Mols	Mole Fraction
Cyclohexane	0.924	0.10350
Cetane	0.076	0.00851
Furfural	7.925	0.88799
	8.925	1.00000

The activity coefficients for cyclohexane and cetane in the solvent phase at 0.1120 mole fraction hydrocarbon are read from Figures 23 and 26. They are:

$$\gamma\text{(cyclohexane)} = 5.0$$
$$\gamma\text{(cetane)} = 16.8$$

By approximating the hydrocarbon phase to be 0.60 mole fraction cyclohexane (solvent-free basis) and "guessing" linearity of the hydrocarbon-phase solvent-ratio curve as before:

$(0.60)(0.2595) + (0.40)(0.1828) = 0.2285$ mols solvent per mol hydrocarbon in the hydrocarbon phase.

The hydrocarbon phase is then

	Mols	Mole Fraction
Hydrocarbon	1.0000	0.8140
Furfural	0.2285	0.1860
	1.2285	1.0000

The activity coefficients for the hydrocarbon phase are then read at 0.814 mole fraction hydrocarbon from Figures 23 and 26. Thus,

$$\gamma\text{(cyclohexane)} = 1.095$$
$$\gamma\text{(cetane)} = 1.035$$

The hydrocarbon-phase compositions are then calculated as follows:

$$\begin{aligned} X\text{(cyclohexane)} &= (0.1035)\left(\frac{5.0}{1.095}\right) = 0.472 \\ X\text{(cetane)} &= (0.00851)\left(\frac{16.8}{1.035}\right) = \underline{0.1380} \\ & \qquad\qquad\qquad\qquad\qquad 0.6100 \end{aligned}$$

The first estimation of the hydrocarbon-phase composition is then $\frac{0.472}{0.6100}$ = 0.774 mole fraction cyclohexane (solvent-free basis). However, the hydrocarbon phase had been assumed to be 0.60 mole fraction cyclohexane (on a solvent-free basis). Therefore, recalculating the hydrocarbon phase based on the calculated composition of 0.774 mole fraction cyclohexane gives

$(0.774)(0.2595) + (0.226)(0.1828) = 0.2414$ mols solvent per mol hydrocarbon

The hydrocarbon phase is then:

	Mols	Mole Fraction
Hydrocarbon	1.0000	0.806
Furfural	0.2414	0.194
	1.2414	1.000

The activity coefficients at 0.806 mole fraction hydrocarbon change only slightly in Figures 23 and 26 from the previous values at 0.814 mole fraction hydrocarbon.

These are:

$$\gamma\text{(cyclohexane)} = 1.100$$
$$\gamma\text{(cetane)} = 1.035$$

These compositions are then recalculated as:

$$X\text{(cyclohexane)} = (0.1035)\left(\frac{5.0}{1.100}\right) = 0.470$$
$$X\text{(n-heptane)} = (0.00851)\left(\frac{16.8}{1.035}\right) = \underline{0.138}$$
$$0.608$$

The second estimation of hydrocarbon-phase composition is then $\frac{0.470}{0.608} = 0.774$ mole fraction cyclohexane (solvent-free basis), which is the same as the first estimation. A rapid convergence is thus obtained. In addition, the estimated solvent contents agree well with the experimental values as may be seen in Table 8.

APPENDIX IV

NOMENCLATURE

A	Constant in activity coefficient equations. Here it is equal to the logarithm of the activity coefficient for furfural at mole fraction furfural of 0.0.
B	Constant in activity coefficient equations. Here it is equal to the logarithm of the activity coefficient for hydrocarbon at mole fraction hydrocarbon of 0.0.
E	Internal energy function.
F	Free energy function.
H^*	Molal enthalpy of ideal gas.
$\bar{H}$	Partial molal enthalpy.
H°	Molal enthalpy of pure component at temperature of solution.
N	Number of moles.
P	Pressure.
R	Gas constant.
S	Entropy.
T	Absolute temperature.
V	Volume or molal volume.
X	Mole fraction.
Z	Effective volume fraction
a	Activity
$\bar{a}$	Activity of component in solution.
$\bar{f}$	Fugacity of component in solution.

f°	Fugacity of pure component at standard state of temperature, pressure, and concentration.
p	Pressure.
q_1/q_2	A constant called the ratio of effective molal volumes.
n	Refractive Index.

Greek Letters

β	Selectivity factor.
μ°	Chemical potential at standard state of temperature, pressure and concentration.
μ	Chemical potential.
γ	Activity coefficient.

Subscripts

A, B, ----N	Components A, B, C --- N.
i	Component i.
p	Pressure.
T	Absolute temperature.
N	Number of moles.
1, 2, ----N	Components 1, 2, ---- N.

Superscripts

$'$, $''$, $'''$--Z	Coexisting equilibrium phases.
$^\circ$	Standard state.

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VITA

Charles Fuller Bethea was born in the city of Latta, the township of Bethea, the state of South Carolina, on April 22, 1921. He received his elementary education in the public schools of Latta, South Carolina, and Laguna Beach, California. He attended public high schools in Laguna Beach and Atlanta, Georgia, and was graduated from the Technological High School, Atlanta, Georgia, in June 1939. He entered the Georgia Institute of Technology, then the Georgia School of Technology, in July 1939 on the cooperative plan, and remained until ordered into the United States Army in March 1943. He attended the Chemical Warfare Officer Candidate School at Edgewood Arsenal, Maryland, and was commissioned Second Lieutenant, Chemical Warfare Service in July 1944. He served in the European Theater of operations with the 89th Chemical Mortar Battalion from November 1944 to July 1945, was engaged in the Battle of the Rheinland the Battle of Central Europe, and was awarded the Purple Heart and Bronze Star medals. He was released from active duty in October 1945, reentered the Georgia Institute of Technology, and received the Bachelor of Chemical Engineering in February 1946. He entered the employment of the Phillips Petroleum Company, Bartlesville, Oklahoma, in March 1946 and, except for a 23-day recall to active duty in the United States Army, remained with Phillips until March 1952. His recall to the United States Army, during which he was assigned to the Army Chemical and Radiological Laboratories, was terminated at the request of the Phillips Petroleum

Company, and he was discharged from the Service with the rank of First Lieutenant. During his employment with the Phillips Petroleum Company he was occupied in three different positions, all of approximately the same duration. The first was as Development Engineer and Group Leader in pilot-plant studies on the development of liquid-liquid extraction, continuous adsorption, and high-temperature pyrolysis. The second was as Technical Assistant to the Technical Consultant, Mr. K. H. Hachmuth, for separation studies and thermodynamic correlations. The third was as Process Design Engineer for process design and economic evaluations. Coinciding with his Phillips employment, Mr. Bethea attended the graduate school of the Oklahoma Institute of Technology, Stillwater, Oklahoma, and over the period of September 1947 to February 1952 earned the Master of Science in Chemical Engineering. His M. S. Thesis, entitled "A Correlation of Activity Coefficients for the Furfural-Water System" was done while in Phillips employment, and while under the supervision of Mr. Hachmuth. In January 1952 Mr. Bethea was selected to attend a special course in thermodynamics given by Dr. B. F. Dodge of Yale University. He was then granted a civil leave of absence from Phillips in March 1952 to pursue the course of study leading to the Ph.D. in Chemical Engineering at the Georgia Institute of Technology. He has been engaged in this pursuit to date, and was the recipient of the Phillips Petroleum Company fellowship from April 1952 to April 1954. Mr. Bethea is a member of the American Institute of Chemical Engineers and the Pi Mu Epsilon, Mathematics Society. He was elected to full membership in the Society of the Sigma Xi in April 1954.