

A CORRELATION OF ACTIVITY COEFFICIENTS
FOR THE FURFURAL-WATER SYSTEM

BY

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ABSTRACT

The increasing importance of furfural as a selective solvent for use in liquid-liquid extraction and extractive distillation has deemed it advisable to correlate available equilibria for the furfural-water system.

Considerable data are available in the literature on the furfural-water system. Unfortunately some of these data are of questionable accuracy and general correlations are unsatisfactory. The correlation reported herein, relating activity coefficients and concentrations for isothermal conditions, is in simultaneous agreement with the Duhem relationship, liquid-liquid solubility, and the original equilibria.

An exponential-type equation is introduced as an improvement over the Margules and Van Laar equations for correlating activity coefficients in binary systems from liquid-liquid solubility data.

A fugacity coefficient correlation, deduced by graphical integration of thermodynamic properties, is shown by which the f/p ratios may be determined for water, furfural, and a number of hydrocarbons at the saturated conditions from the temperature or the reduced pressure.

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A CORRELATION OF ACTIVITY COEFFICIENTS
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CHAPTER I
INTRODUCTION

Furfural has become an important tool in the petroleum industry as a selective solvent for liquid-liquid extraction and extractive distillation. It is used extensively today in the preparation of lubricating oils, the purification of butadiene for synthetic rubber manufacture, and the concentration of olefins and aromatics for chemicals manufacture.

Considerable data are available in the literature on equilibrium in furfural-hydrocarbon and furfural-water systems. Unfortunately some of these data are of questionable accuracy, and general correlations are unsatisfactory. Some correlations, conveniently expressed in graphs of activity coefficients versus concentration for binary systems and isothermal conditions, consider only simultaneous agreement of vapor pressure data and the Duhem relationship. Other correlations consider only simultaneous agreement of liquid-liquid solubility and the Duhem relationship. A general correlation of the data should agree simultaneously with all three.

There has been a pressing need for a general correlation of all furfural data to aid in more accurate design of future extraction and extractive distillation units. It is the purpose of this Thesis to review such a correlation of the data for the furfural-water system.

CHAPTER II
EXPERIMENTAL DATA

All available experimental data for the furfural-water system have been classified and are tabulated below. This tabulation represents the results of a great number of investigators and various techniques. Some discrepancies in the data are to be expected. When discrepancies occurred in properties such as liquid-liquid solubility or vapor pressure the values chosen were those which showed the most consistent agreement with the other data. Where it was deemed necessary, additional experimental data were obtained in the laboratory to confirm the correct value for a given property.

TABLE I
EXPERIMENTAL DATA FOR THE FURFURAL-WATER SYSTEM

<u>Originator</u>	<u>Type Data</u>	<u>Temperature, F</u>	<u>Pressure psia</u>	<u>Reference</u>
Gerster-Pearce	Vapor Pressures*	100,150,200(a) 68-250(b)	0.3-12.3(a) 0.02-4.1(b)	4
Mains	Vapor-Liquid Equilibria	208-212	14.7	9
Mains	Liquid-Liquid Solubility	46-205	14.7	9
Quaker Oats	Vapor Pressure of Furfural	60-450	0.04-77.0	12
Griswold	Liquid-Liquid Solubility	100-200	14.7	5
Evans and Aylesworth	Liquid-Liquid Solubility	82-250	14.7	3
Phillips Petroleum Co.	Vapor-Liquid Equilibria	292-359	64.2	11
Phillips Petroleum Co.	Liquid-Liquid Solubility	75-186	14.7	11
Keenan & Keyes	Vapor Pressure of Water	100-500	1.0-680.0	8

*Includes vapor pressure of furfural-water solutions (a) and vapor pressures of pure furfural. (b)

A. Vapor Pressures

1. Furfural: Table I lists two sets of vapor pressure data for furfural: (a) the Quaker Oats Company data (12), and (b) the Gerster-Pearce data (4). Gerster and Pearce report that their low temperature vapor pressure data are an improvement over that of the Quaker Oats Company. This writer confirmed that report when it became evident that at temperatures in the range of 100-200 F a better correlation of activity coefficients was possible with the Gerster-Pearce than the Quaker Oats data.

Figure 1 is a temperature-vapor pressure curve of furfural covering the temperature range of 60 to 400 F as was used in this correlation. The data shown are those of Gerster-Pearce except for the extrapolation from the Gerster-Pearce value at 250 F to the Quaker Oats value at 400 F.

2. Water: Vapor pressures for water were taken from the steam tables of Keenan and Keyes (8).

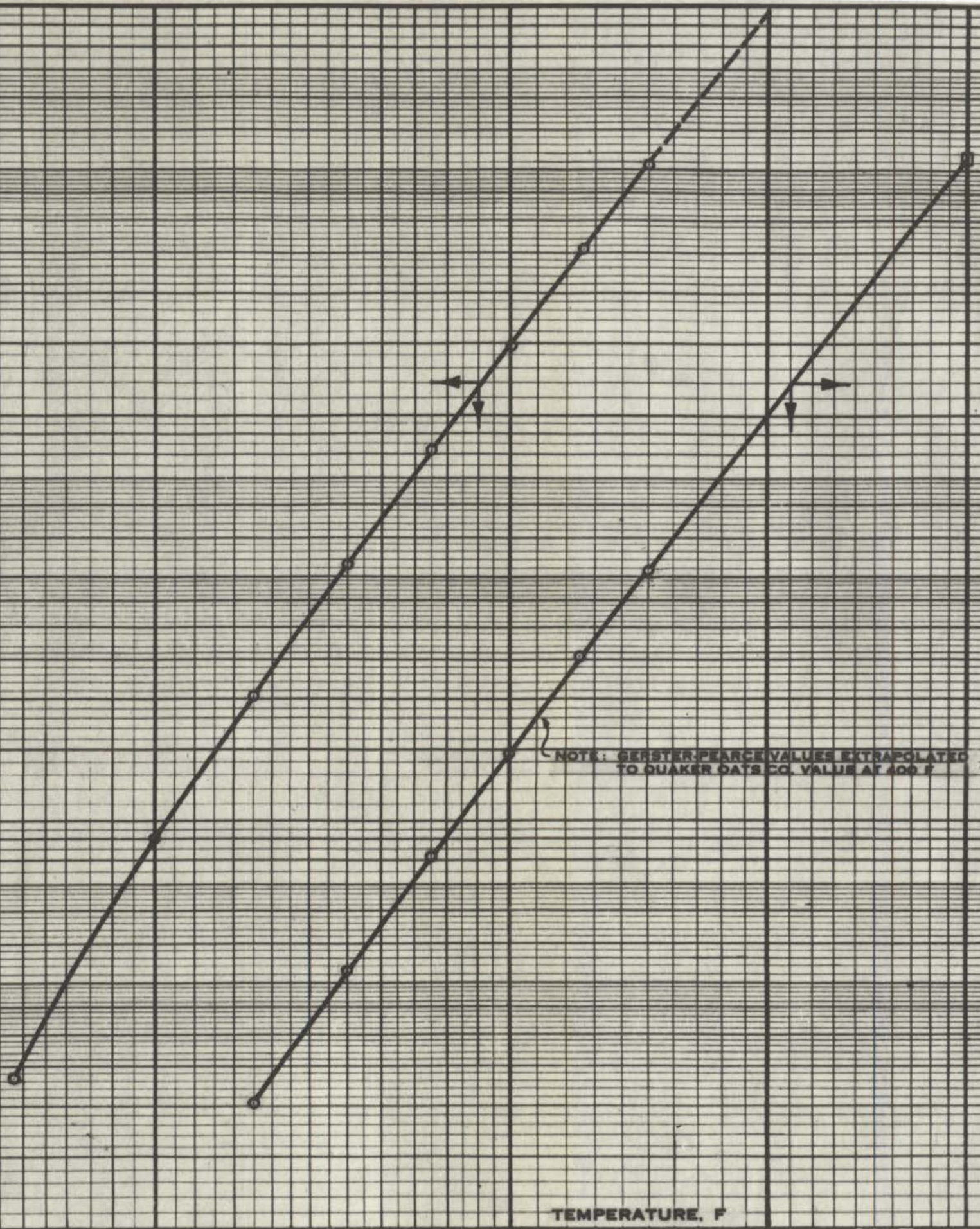
B. Liquid-Liquid Solubilities

Table I lists four sets of liquid-liquid solubility for the furfural-water system. Three of these sets of data were available before this correlation was undertaken, but none were of sufficient accuracy to include as a basis in this correlation. Consequently, additional data were determined in

(12) Quaker Oats Technical Bulletin No. 2 (1940).

(4) Gerster, J. A., and Pearce, E. J., "Experimental and Theoretical Vapor-Liquid Relationships in the Furfural-Water System", Thesis, University of Delaware, 1949.

(8) Keenan, J. H., and Keyes, F. G., "Thermodynamic Properties of Steam", First Edition, New York, New York, John Wiley & Sons, Inc., Eighteenth Printing, September 1948.



TEMPERATURE, F

100

200

300

400

500

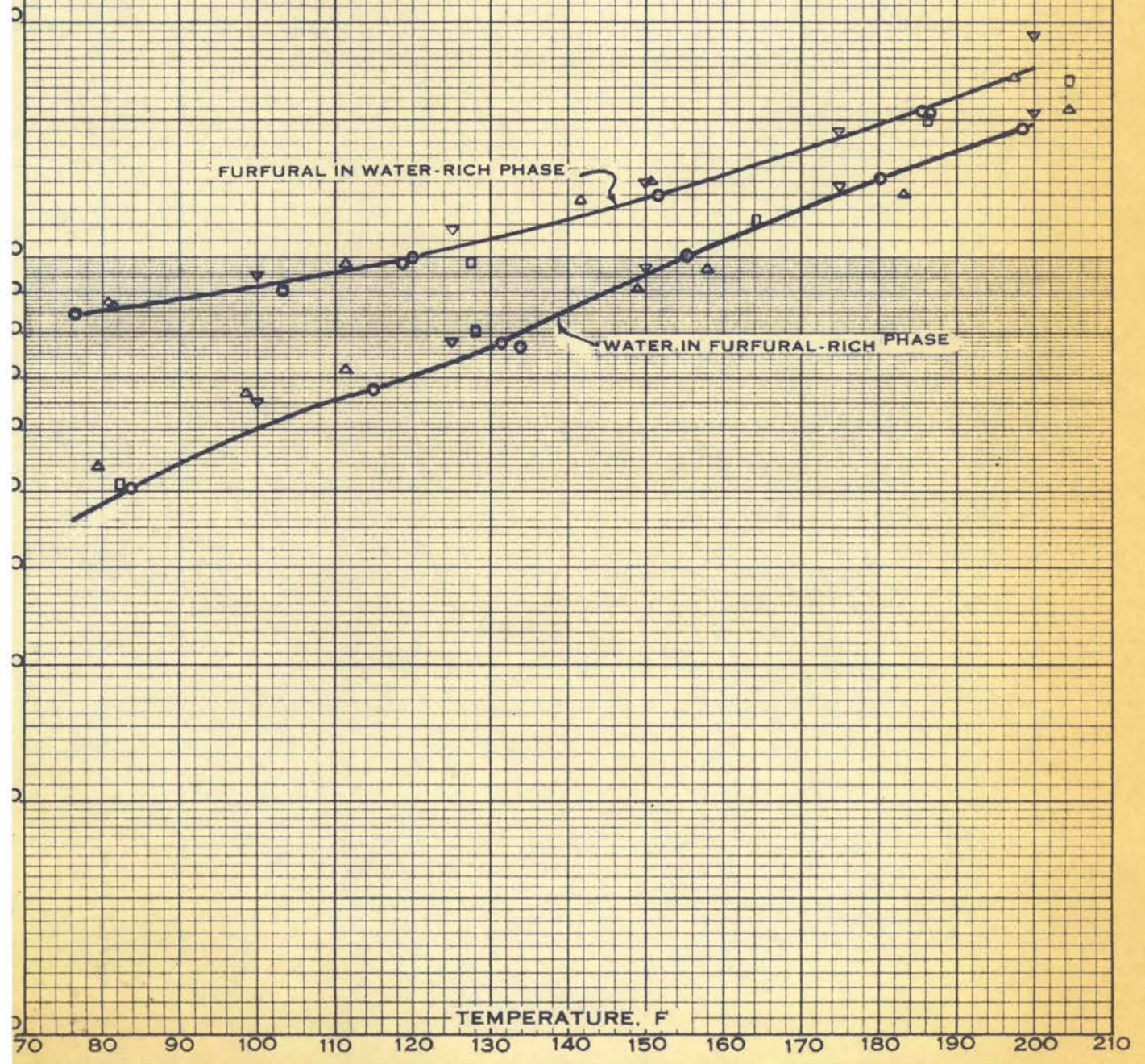
the laboratory by the writer, Marwil, and Pennington (11) to establish the correct mutual solubility for the system. These data are shown in Figure 2 with a smoothed curve drawn to represent the values used in these correlations.

(11) Phillips Petroleum Company, Unpublished Data

MUTUAL SOLUBILITY OF FURFURAL-WATER SYSTEM

LEGEND:

SYMBOL	ORIGINATOR
○	MARWIL & PENNINGTON (8)(11)
□	EVANS & AYLESWORTH (3)
△	MAINS (7)
▽	GRISWOLD (5)



CHAPTER III

THEORY

A. Simple Correlations

Numerous methods and equations have been derived to correlate activity coefficients and composition in binary systems for isothermal conditions. The best known of these are the Van Laar (2) and Margules (2) equations. These equations are quite suited for vapor pressure data and vapor-liquid equilibria, but are quite bulky when applied to liquid-liquid solubility. Moreover, the above equations fail to correlate some of the more simple of the binary systems.

Another type of equation which often matches data better than either the Van Laar or Margules equations, and which is conveniently applied in the case of liquid-liquid data, is the exponential equation developed by K. H. Hachmuth (6). This is shown as follows:

$$(III-1) \log \gamma_i = (1 - X_i)^Z A$$

$$(III-2) \log \gamma_j = \sqrt{1 + (Z - 1)(1 - X_i)^Z - Z(1 - X_i)^{Z-1}} B$$

$$\text{Where: } Z = \frac{A+B}{B}, Z > 1.0$$

$$\log \gamma_i = A \text{ when } X_i = 0$$

$$\log \gamma_j = B \text{ when } X_j = 0$$

and

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

(2) Ibid

(6) Hachmuth, K. H., "Fractionation", Unpublished Lecture, Notes Distributed Within Phillips Petroleum Company in April 1949.

γ_i = activity coefficient of component i

γ_j = activity coefficient of component j

X_i = mole fraction of component i

X_j = mole fraction of component j

Hachmuth, in his introduction of the exponential equation, made several comparisons between the exponential, Van Laar, and Margules equations. All three sets of equations obey the Duhem relationship for slopes at isothermal conditions as follows:

$$(III-3) \quad \frac{\frac{\partial \log \gamma_i}{\partial X_i}}{\frac{\partial \log \gamma_j}{\partial X_i}} = - \left(\frac{1 - X_i}{X_i} \right)$$

Moreover, all three sets of equations reduce to the same form when $A = B$, that is,

$$\log \gamma_i = (1 - X_i)^2 A$$

and,

$$\log \gamma_j = X_i^2 B$$

One typical difference between the Margules, Van Laar, and exponential equations is that one can not substitute A for B and i for j in equation III-2 and get equation III-1 as can be done with the other sets of equations. The exponential equations offer two choices regarding the shape of the curves to apply to any binary system depending upon which component is selected as the ith component. Usually values of Z between 1 and 2 seem to represent data best.

The exponential equation is conveniently applied in the case of liquid-liquid solubility because of the ease with which the constants are evaluated. The equations follow:

$$(III-4) Z = \frac{\log \left(\frac{X_{i1}}{X_{ih}} \right)}{\log \left(\frac{1-X_{ih}}{1-X_{i1}} \right)} + 1$$

and,

$$(III-5) A = \frac{\log \left(\frac{X_{i1}}{X_{ih}} \right)}{(1-X_{ih})^Z - (1-X_{i1})^Z}$$

Where: X_{i1} = mole fraction of i in the light phase

X_{ih} = mole fraction of i in the heavy phase

None of these simple equations was adequate for a correlation of the furfural-water data. The exponential equation was useful, however, in estimating ratios of activity coefficients for substitution into the more complicated equations following, and for estimating activity coefficients for the component in major concentration where the activity coefficient for that component was near 1.0. These values were then substituted in an equation for calculating the activity coefficient for the component in minor concentration.

A correlation of activity coefficients based on the mutual solubility data for the furfural-water system, as smoothed from the mains data (9) and presented in the International Critical Tables (7), and the exponential equation are shown on Figure 3. The values shown on this figure do not agree with the final correlation.

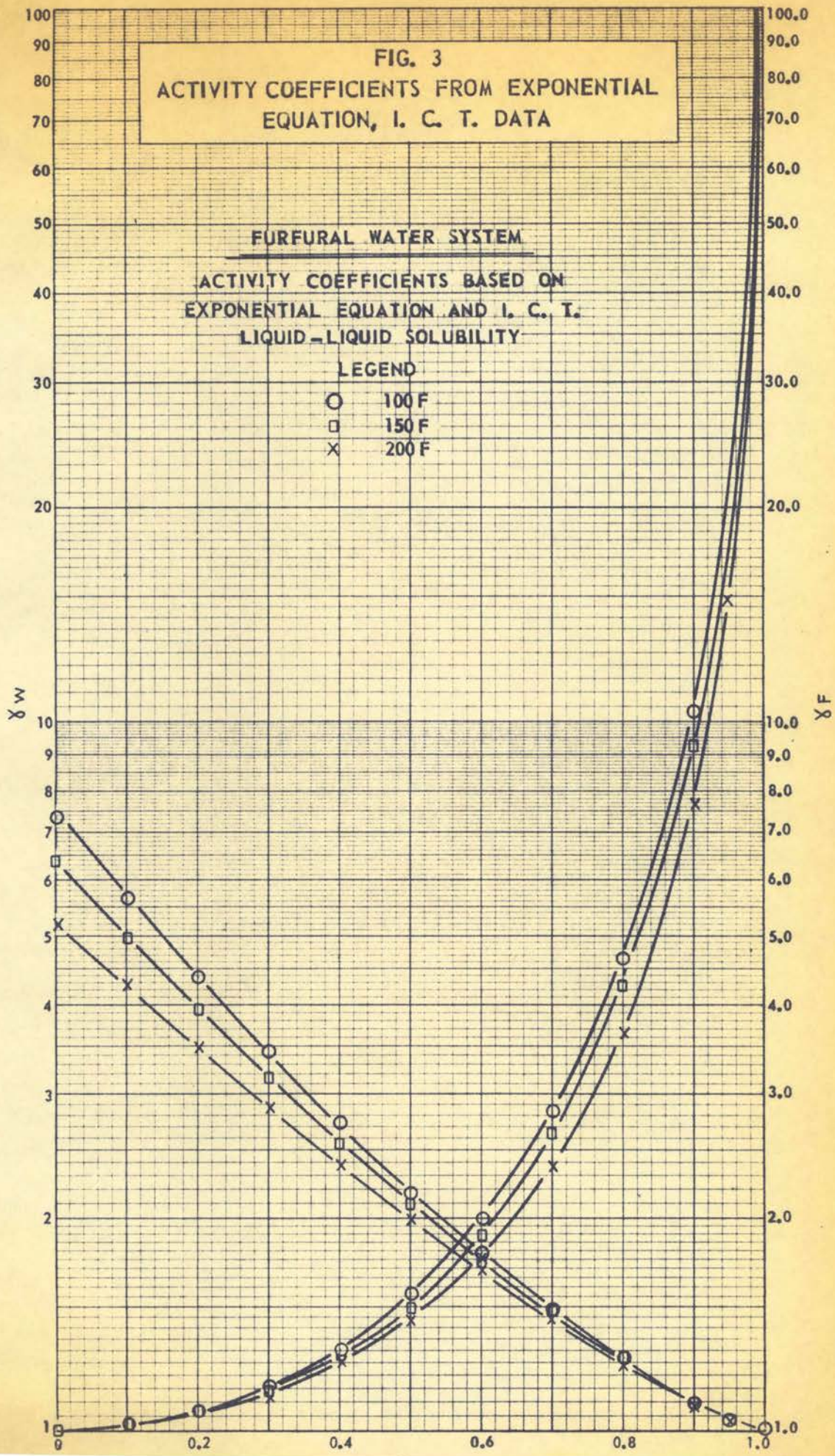
B. Relative Volatility Correlation

A correlation was developed by K. H. Hachmuth in an unpublished report showing that the use of α , the relative volatility, in activity coefficient equations could eliminate the effect of small errors in temperature and pressure determinations.

(9) Mains, G. H., Chem. & Met. Engr. 26, No. 17, 779 (1922).

(7) International Critical Tables, Vol. III, 388.

FIG. 3
ACTIVITY COEFFICIENTS FROM EXPONENTIAL
EQUATION, I. C. T. DATA



Thus -

$$(III-6) \quad \frac{\gamma_i}{\gamma_j} = \frac{\frac{K_i \text{ (experimental)}}{K_i \text{ (ideal)}}}{\frac{K_j \text{ (experimental)}}{K_j \text{ (ideal)}}} = \alpha \frac{K_j \text{ (ideal)}}{K_i \text{ (ideal)}}$$

$$= \alpha \left(\frac{\bar{T}_i f_j^0}{\bar{T}_j f_i^0} \right) = \frac{\alpha}{\left(\frac{\bar{T}_j f_i^0}{\bar{T}_i f_j^0} \right)}$$

Where: $K \text{ (experimental)} = \text{experimental } K = \frac{y}{x}$

\bar{T} = Partial fugacity, assumed to be equal to the fugacity which the pure component would have as a vapor at temperature and pressure obtaining

f^0 = Standard fugacity of the liquid. Defined as the fugacity the pure component would have at the temperature and pressure obtaining.

α = Relative volatility = $\frac{K_i \text{ (exp.)}}{K_j \text{ (exp.)}}$

Subscript i, j = Components i, j respectively

The substitution of phase equilibria and fugacities in the above equation permits the calculation of γ_i/γ_j for given concentration of i. The ratios can then be adjusted, if necessary, to constant temperature, and the values for the given concentration can then be substituted into a Benedict-type equation to form a general equation for $\log (\gamma_i/\gamma_j)$ versus X_i . For example, the values of $\log (\gamma_i/\gamma_j)$ at concentrations of $X_i = 0.2, 0.4, 0.6,$ and 0.8 have been denoted as $f(0.2), f(0.4), f(0.6),$ and $f(0.8)$ respectively and substituted into the general Benedict-type equation shown as III-11 on page 14 to produce the following equations:

$$\begin{aligned}
 \text{(III-7)} \quad \log \left(\frac{\gamma_i}{\gamma_j} \right) = & - \frac{3750}{456} \sqrt{11} f(0.2) + f(0.4) + f(0.6) + f(0.8) \sqrt{x_1}^4 \\
 & + \frac{1000}{456} \sqrt{73} f(0.2) + 36 f(0.4) - 21 f(0.6) + 92 f(0.8) \sqrt{x_1}^3 \\
 & - \frac{150}{456} \sqrt{271} f(0.2) + 339 f(0.4) - 231 f(0.6) + 461 f(0.8) \sqrt{x_1}^2 \\
 & + \frac{20}{456} \sqrt{331} f(0.2) + 1158 f(0.4) - 723 f(0.6) + 1034 f(0.8) \sqrt{x_1} \\
 & + \frac{1}{456} \sqrt{240} f(0.2) - 2880 f(0.4) + 1680 f(0.6) - 2040 f(0.8) \sqrt{x_1}
 \end{aligned}$$

And,

$$\begin{aligned}
 \text{(III-8)} \quad \log \gamma_j = & \frac{3000}{456} \sqrt{11} f(0.2) + f(0.4) + f(0.6) + f(0.8) \sqrt{x_1}^5 \\
 & - \frac{750}{456} \sqrt{73} f(0.2) + 36 f(0.4) - 21 f(0.6) + 92 f(0.8) \sqrt{x_1}^4 \\
 & + \frac{100}{456} \sqrt{271} f(0.2) + 339 f(0.4) - 231 f(0.6) + 461 f(0.8) \sqrt{x_1}^3 \\
 & - \frac{10}{456} \sqrt{331} f(0.2) + 1158 f(0.4) - 723 f(0.6) + 1034 f(0.8) \sqrt{x_1}^2 \\
 \text{and } \log \gamma_i = & \log \left(\frac{\gamma_i}{\gamma_j} \right) + \log \gamma_j
 \end{aligned}$$

Hachmuth, in his presentation of the relative volatility correlation in an unpublished report, showed an excellent correlation for the normal heptane-toluene system.

C. Benedict-Type Correlation

The Benedict-type equations (1) are equations similar to the exponential, Margules, and Van Laar equations for relating activity coefficients and concentrations while simultaneously agreeing with the Duhem relationship (Equation III-3). The Benedict-type equations are shown as follows:

(1) Benedict, M., Johnson, C. A., Solomon, E., and Rubin, L. C., Trans. Am. Inst. Chem. Engrs. 41, 371 (1945).

$$(III-9) \log \gamma_i = (X_i^3 X_j - X_i^3 X_j)4D + (6X_i^2 X_j^2 - 8X_i^3 X_j^2)E + \\ (4X_i X_j^3 - 8X_i^2 X_j^3)F + (X_j^4 - 4X_i X_j^4)G$$

$$(III-10) \log \gamma_j = (X_i^4 - 4X_i^4 X_j)D + (4X_i^3 X_j - 8X_i^3 X_j^2)E + \\ (6X_i^2 X_j^2 - 8X_i^2 X_j^3)F + (X_i X_j^3 - X_i X_j^4) 4G$$

Where: X_i, X_j = mole fraction of i and j respectively

D,E,F,G = coefficients which must be determined from four actual or assumed values of $\log \gamma_i$, $\log \gamma_j$, or $\log (\gamma_i/\gamma_j)$.

The writer prefers to combine the above two equations in the form of the ratio to facilitate the use of liquid-liquid solubility to solve for one of the coefficients. The ratio form becomes -

$$(III-11) \log \frac{\gamma_i}{\gamma_j} = X_i^3 D (4X_j - X_i) + 4X_i^2 X_j E(6X_j - 4X_i) \\ + X_i X_j^2 F(4X_j - 6X_i) + X_j^3 G(X_j - 4X_i)$$

The equations involving liquid-liquid solubility are based on the condition that when the two phases reach equilibrium the activity of each component is the same in the light phase as in the heavy phase. Expressed algebraically,

$$a_{il} = a_{ih}$$

$$a_{jl} = a_{jh}$$

Where: a = activity

Subscript l = light phase

h = heavy phase

i, j = components i and j respectively.

Therefore, since $\gamma = \frac{a}{X}$ or $a = \gamma X$,

$$\gamma_{il} X_{il} = \gamma_{ih} X_{ih}$$

and,

$$\gamma_{j1} X_{j1} = \gamma_{jh} X_{jh}$$

Rewriting,

$$\frac{\gamma_{ih}}{\gamma_{il}} = \frac{X_{il}}{X_{ih}}$$

$$\frac{\gamma_{jh}}{\gamma_{j1}} = \frac{X_{j1}}{X_{jh}}$$

Taking logarithms,

$$(III-12) \log \gamma_{ih} - \log \gamma_{il} = \log \frac{X_{il}}{X_{ih}}$$

$$(III-13) \log \gamma_{jh} - \log \gamma_{j1} = \log \frac{X_{j1}}{X_{jh}}$$

Subtracting (III-13 from (III-12) -

$$(III-14) \log \left(\frac{\gamma_{ih}}{\gamma_{jh}} \right) - \log \left(\frac{\gamma_{il}}{\gamma_{j1}} \right) = \log \left(\frac{X_{il}}{X_{ih}} \cdot \frac{X_{jh}}{X_{j1}} \right)$$

Equation III-14 may be substituted into the Benedict equations to yield the following equation as one of the four for determining the coefficients D, E, F, and G.

$$(III-15) \log \left(\frac{X_{il}}{X_{ih}} \frac{X_{jh}}{X_{j1}} \right) = D \sqrt{X_{ih}^3 (4X_{jh} - X_{ih}) - X_{il}^3 (4X_{j1} - X_{il})} \\ + E \sqrt{X_{ih}^2 X_{jh} (6X_{jh} - 4X_{ih}) - X_{il}^2 X_{j1} (6X_{j1} - 4X_{il})} \\ + F \sqrt{X_{ih} X_{jh}^2 (4X_{jh} - 6X_{ih}) - X_{il} X_{j1}^2 (4X_{j1} - 6X_{il})} \\ + G \sqrt{X_{jh}^3 (X_{jh} - 4X_{ih}) - X_{j1}^3 (X_{j1} - 4X_{il})}$$

The values for X_{il} , X_{ih} , X_{jh} , and X_{j1} are the liquid-liquid solubility data.

The other three coefficients in the Benedict-type equation may be evaluated by estimating the value of $\log (\gamma_i / \gamma_j)$ for three given compositions and calculating the general equation. The writer preferred to use one ratio near each terminal of concentration and one near the middle because such selection would facilitate estimating smooth curves. In addition, actual data are more often available near the terminals of

concentration, and better estimates of the ratios may be made. Smooth curves of $\log (\gamma_i/\gamma_j)$ versus X should be obtained in most binary systems, although the calculated curves may be displaced slightly from that which would be estimated from the data.

D. Fugacity Correlations

1. Hydrocarbons: The values for \bar{f} and f^0 for hydrocarbons and other essentially non-polar substances may be obtained from the following relationships:

For pure components and saturated conditions (vapor pressure)

$$(III-16) \quad C = 1 - 0.517 P_r^{0.683}$$

$$(III-17) \quad \left(\frac{f}{p}\right) = C + \frac{3}{4} (1-C)^2$$

Where: C = compressibility factor

$$P_r = \text{reduced pressure} = \frac{\text{vapor pressure}}{\text{critical pressure}}$$

f = fugacity of the saturated liquid

p = vapor pressure of the saturated liquid

Hachmuth reports that equation (III-16) for C is quite accurate for reduced pressures between zero and 0.5, but is not good at higher pressures. Equation (III-17) for f/p is reasonably accurate for all pressures up to and including the critical. The f/p values for the vapor at other pressures, π , may be calculated by the use of the following equation:

$$(III-18) \quad \left(\frac{f}{p}\right)_{\text{vapor at } \pi} = 1 - \frac{\pi}{p} \left(1 - \left(\frac{f}{p}\right)_{\text{sat. liq.}}\right)$$

Where: p = vapor pressure

Equation (III-18) should not be used at pressures too far from the vapor pressure of the component in question.

Values for f° and \bar{f} may be obtained by multiplying $\left(\frac{f}{P}\right)_{\text{sat. liq.}}$ and

$\frac{f}{P}$ vapor at π by the vapor pressure and total pressure (π) respectively.

The f° is the standard fugacity of the liquid, defined as the fugacity the pure component would have as a liquid at the temperature and pressure obtaining. Therefore, it may be necessary to make a pressure correction to

f° vapor pressure to $\left(f^{\circ}\right)_{\pi}$. This is as follows:

$$(III-19) \ln \frac{f_{\pi}^{\circ}}{f_p^{\circ}} = \frac{v_m(\pi - P)}{RT}$$

Where: f_{π}° = fugacity of liquid under total pressure

f_p° = fugacity of liquid under vapor pressure p

v_m = average molal volume

π = total pressure

R = gas constant

T = absolute temperature

The \bar{f} of equation (III-18) is the partial fugacity, assumed to be equal to the fugacity the pure component would have as a vapor at the temperature and pressure obtaining.

Graphs have been constructed relating P_r and C, and f/p and C. These are shown on Figures 4 and 5 respectively. It is apparent that Fig. 4 would be more useful if rearranged to relate temperature and C. This is shown on Figure 6. These figures represent an accurate and rapid method for determining fugacities. It is necessary only to read two graphs and make a few simple computations in order to evaluate a fugacity.

2. Water: Values of $\left(\frac{f}{P}\right)_{\text{sat. liquid}}$ for steam may be calculated by graph-

ical integration of the following equation at any temperature:

$$(III-20) \ln \left(\frac{f}{P}\right)_{\text{sat. liq.}} = \int_0^P \frac{C - 1}{\pi} d\pi$$

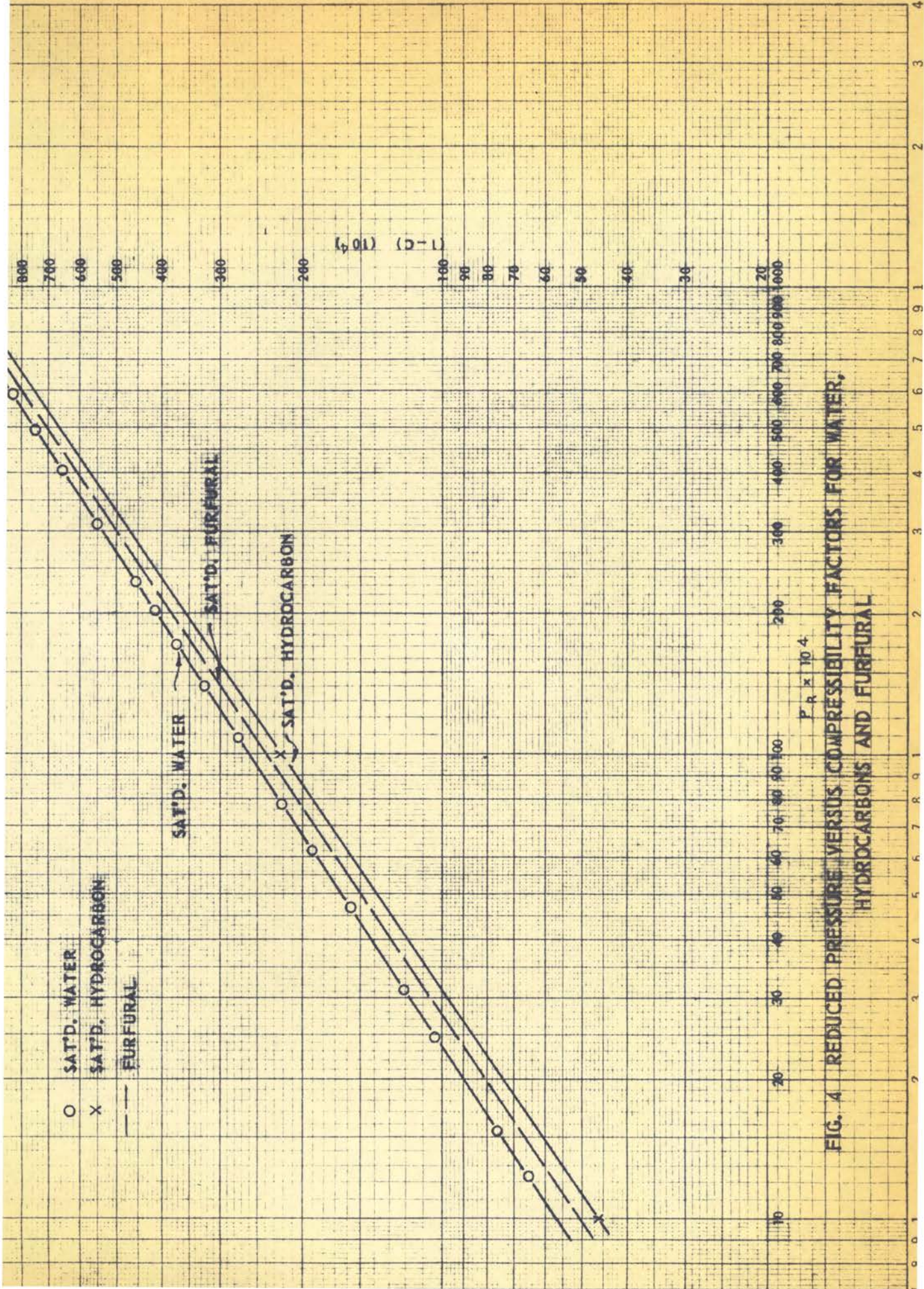


FIG. 4 REDUCED PRESSURE VERSUS COMPRESSIBILITY FACTORS FOR WATER, HYDROCARBONS AND FURFURAL

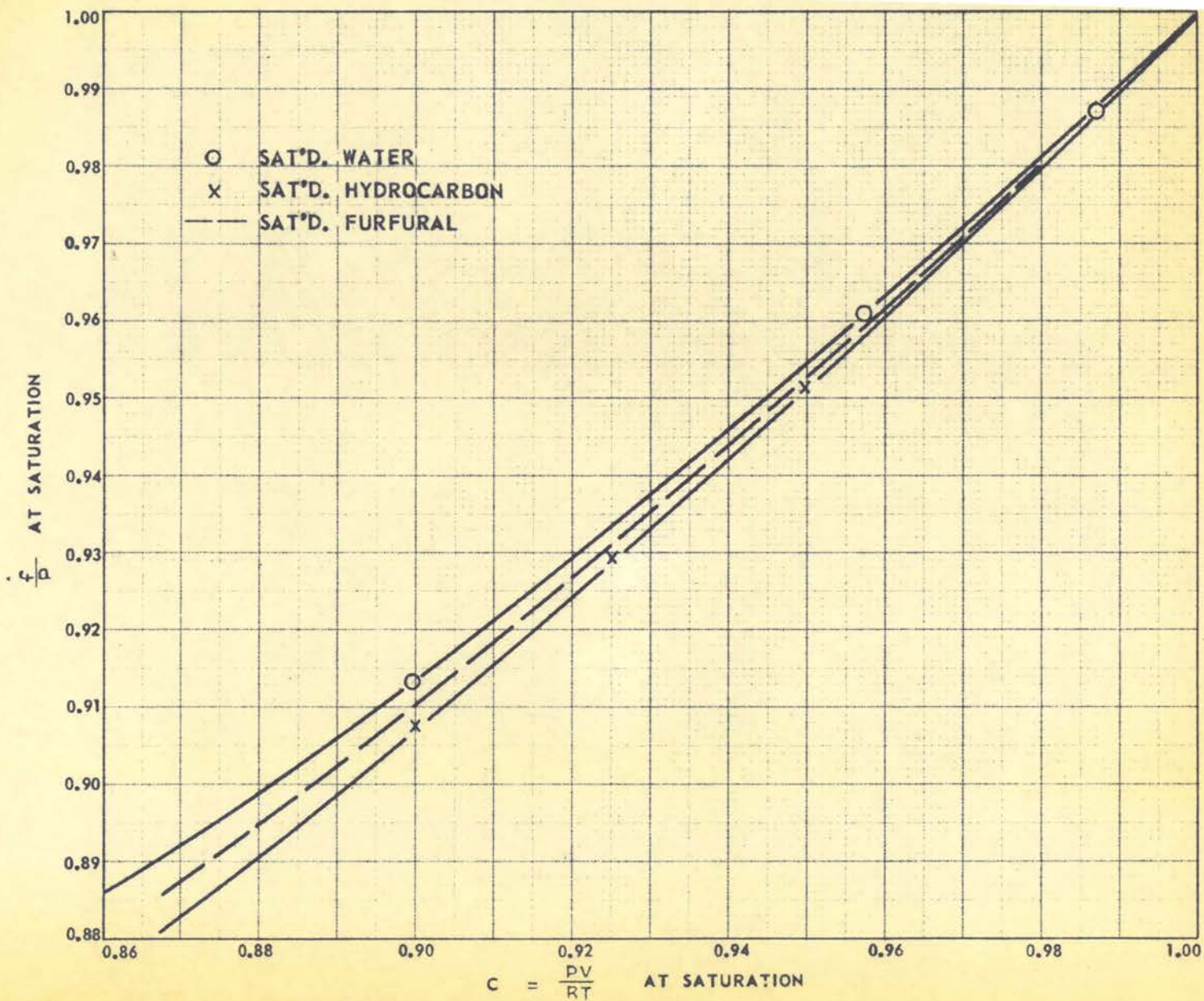


FIG. 5 COMPRESSIBILITY FACTORS VERSUS FUGACITY COEFFICIENTS FOR WATER, HYDROCARBONS, AND FURFURAL

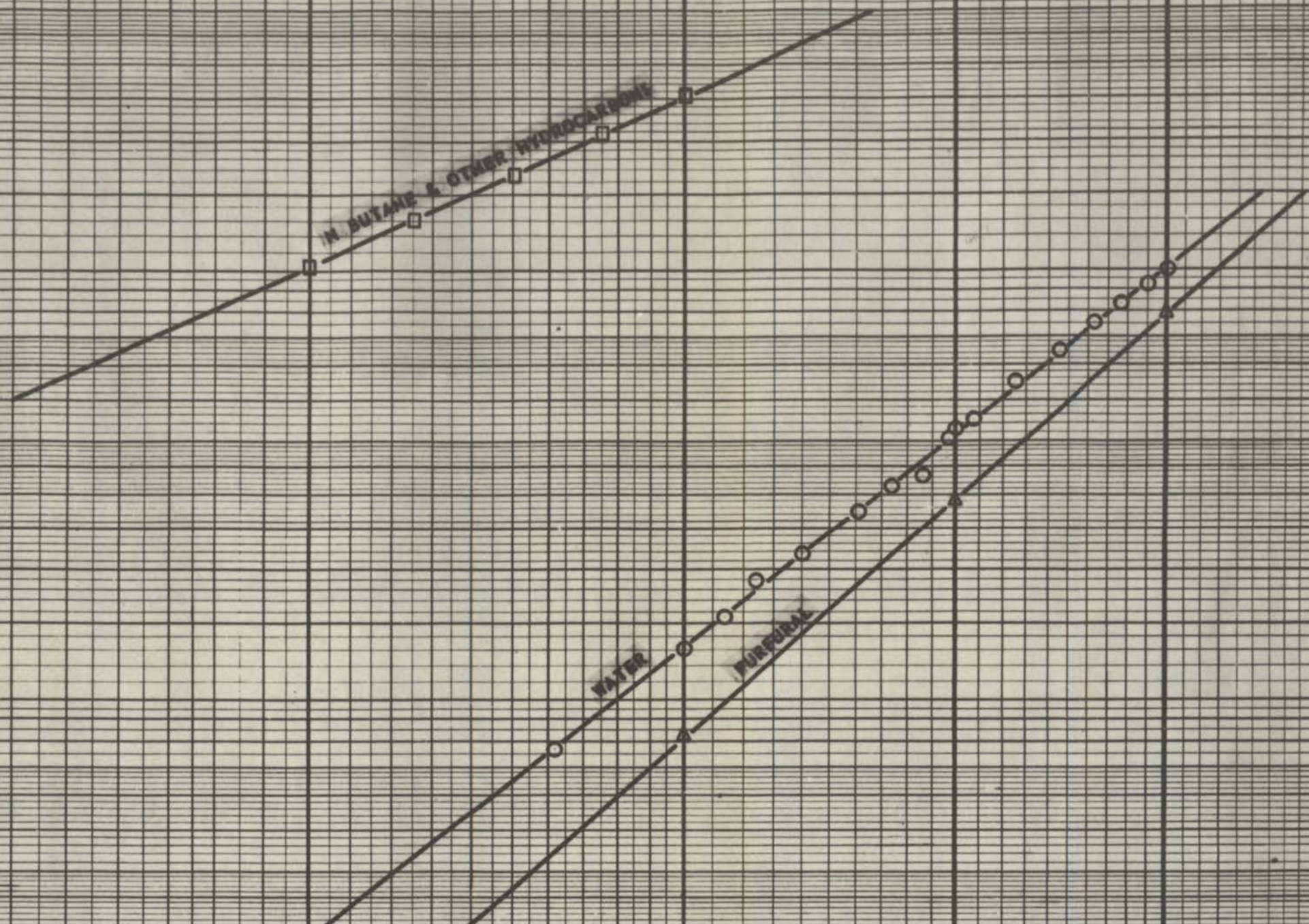


FIG. 6
TEMPERATURE VERSUS COMPRESSIBILITY
FACTOR FOR SATURATED WATER,
HYDROCARBON, AND FURFURAL

- N. BUTANE AND OTHER HYDROCARBONS AT SATURATED CONDITIONS
- SATURATED WATER (STEAM)
- △ SATURATED FURFURAL

Where: P = vapor pressure of water at the temperature obtaining

π = pressure at which the value of $C = \frac{\pi V}{RT}$ is determined

C = compressibility factor

All values of equation III-20 may be evaluated from the steam tables (8).

Graphical integrations have been made for several temperatures and curves were constructed relating P_r and C , f/p and C , and T and C . These are shown in Figures 4, 5, and 6. It is interesting to note that there is such a small difference between the water and hydrocarbon correlations.

3. Furfural: The available thermodynamic data for furfural are inadequate to permit calculation of $\left(\frac{f}{P}\right)_{\text{sat. liquid}}$ as in the cases of hydrocarbon and water. However, so little difference was obtained in the correlations for water and hydrocarbons that one could hardly expect a great deviation for furfural. Therefore, the correlations of C versus P_r and $\left(\frac{f}{P}\right)_{\text{sat. liq.}}$ versus C for furfural were represented by curves midway between those for hydrocarbons and water. These are shown on Figures 4 and 5.

In order to transpose the correlation of C versus P_r on Fig. 4 for furfural to C versus T on Fig. 6, it was necessary to evaluate the critical conditions. The critical temperature and pressure of furfural were estimated to be 702 F and 710 psia respectively from a Meissner equation (10) involving parachor.

(8) Keenan, J. H., and Keyes, F. G., "Thermodynamic Properties of Steam", First Edition, New York, New York, John Wiley & Sons, Inc., Eighteenth Printing, September 1948.

(10) Meissner, H. P., and Redding, E. M., "Prediction of Critical Constants", Ind. Engr. Chem. 34, 521 (1942).

CHAPTER IV
METHOD OF CORRELATION

A. Vapor Pressure Data

The vapor pressure data of Gerster-Pearce at temperatures of 100, 150, and 200 F were all evaluated in the same manner. First, activity coefficients were calculated from the given liquid composition, temperature, and total pressure from the relationship.

$$\gamma_i = \frac{\bar{f}_i Y_i}{f_i^o X_i} = \frac{\pi - \sum_j \gamma_j X_j P_j}{P_i X_i} \quad (\text{at low pressures})$$

Where: γ = activity coefficient of component in solution

π = total pressure

\bar{f} = partial fugacity of component in vapor

f^o = fugacity of component as liquid at temperature and pressure of the system

p = vapor pressure of component at temperature of system

X, Y = mole fraction of component in liquid or vapor

Subscripts i, j = component i or j

The calculated values for γ at the three temperatures are shown in Tables II, III, and IV (Appendix). Next, the liquid-liquid solubility for each temperature was substituted into a Benedict-type equation to yield one equation involving four unknowns for each temperature. The other three unknowns for each temperature were evaluated from knowledge of the shape of $\log \gamma_i / \gamma_j$ versus X curves, and by trial and error to match the calculated activity coefficients. The resultant equations agree simultaneously with the Duhem relationship, liquid-liquid solubility, and the original vapor pressure data. For illustration, the final equations for 100 F are shown below.

Temperature = 100 F

$$\log \gamma_W = (X_W^3 X_f - 4X_W^4 X_f)(7.2680) + (6X_W^2 X_f^2 - 8X_W^3 X_f^2)(1.4936) + \\ (4X_W X_f^3 - 8X_W^2 X_f^3)(1.5321) + (X_f^4 - 4X_W X_f^4)(1.0443)$$

$$\log \gamma_f = (X_W^4 - 4X_W^4 X_f)(1.8170) + (4X_W^3 X_f - 8X_W^3 X_f^2)(1.4936) + \\ (6X_W^2 X_f^2 - 8X_W^2 X_f^3)(1.5321) + (X_W X_f^3 - X_W X_f^4)(4.1772)$$

where: X = mole fraction component in liquid

Subscript: W = water

Subscript: f = furfural

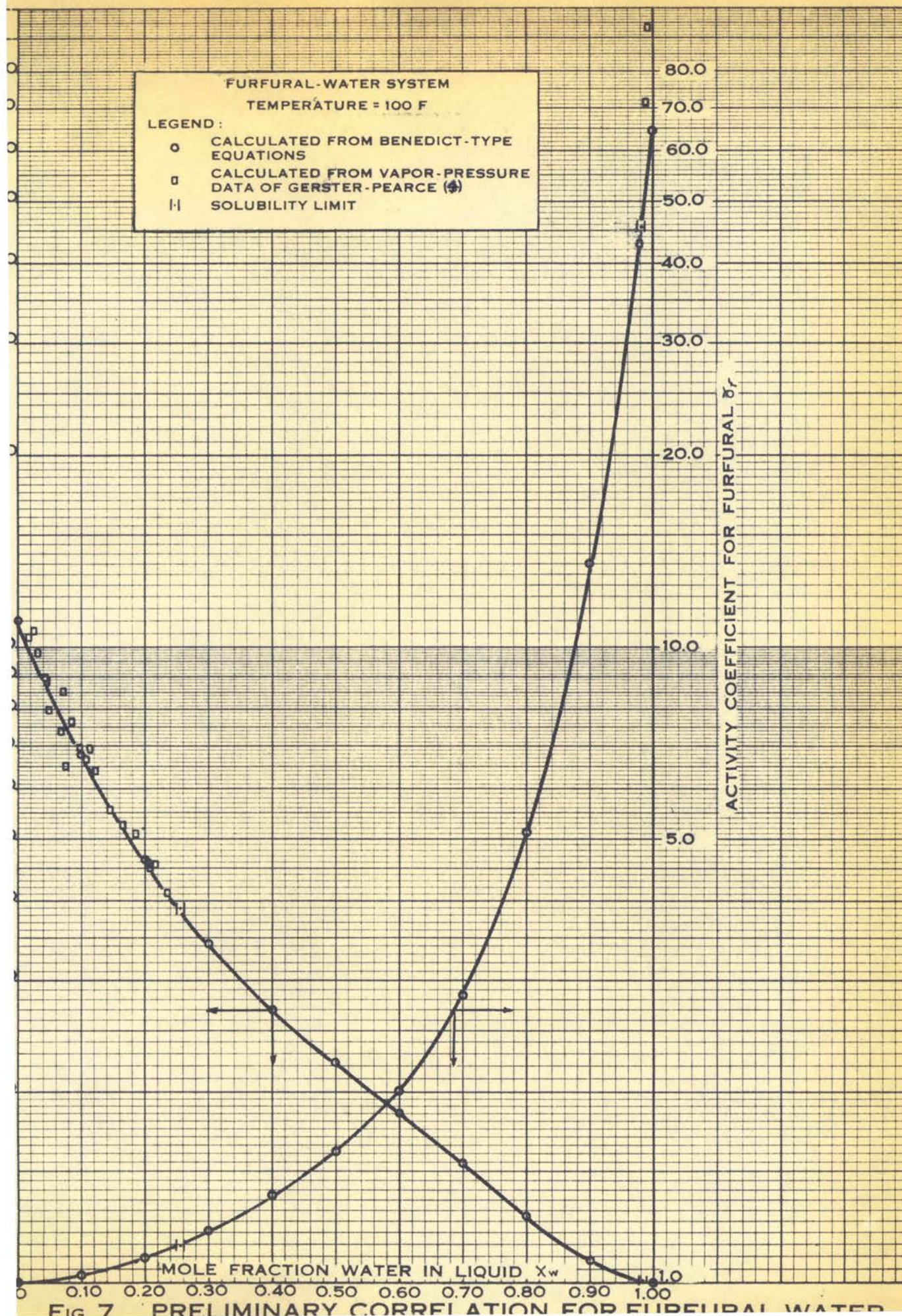
The exactness by which the equations match the experimental data may be seen by reference to Figs. 7, 8, and 9.

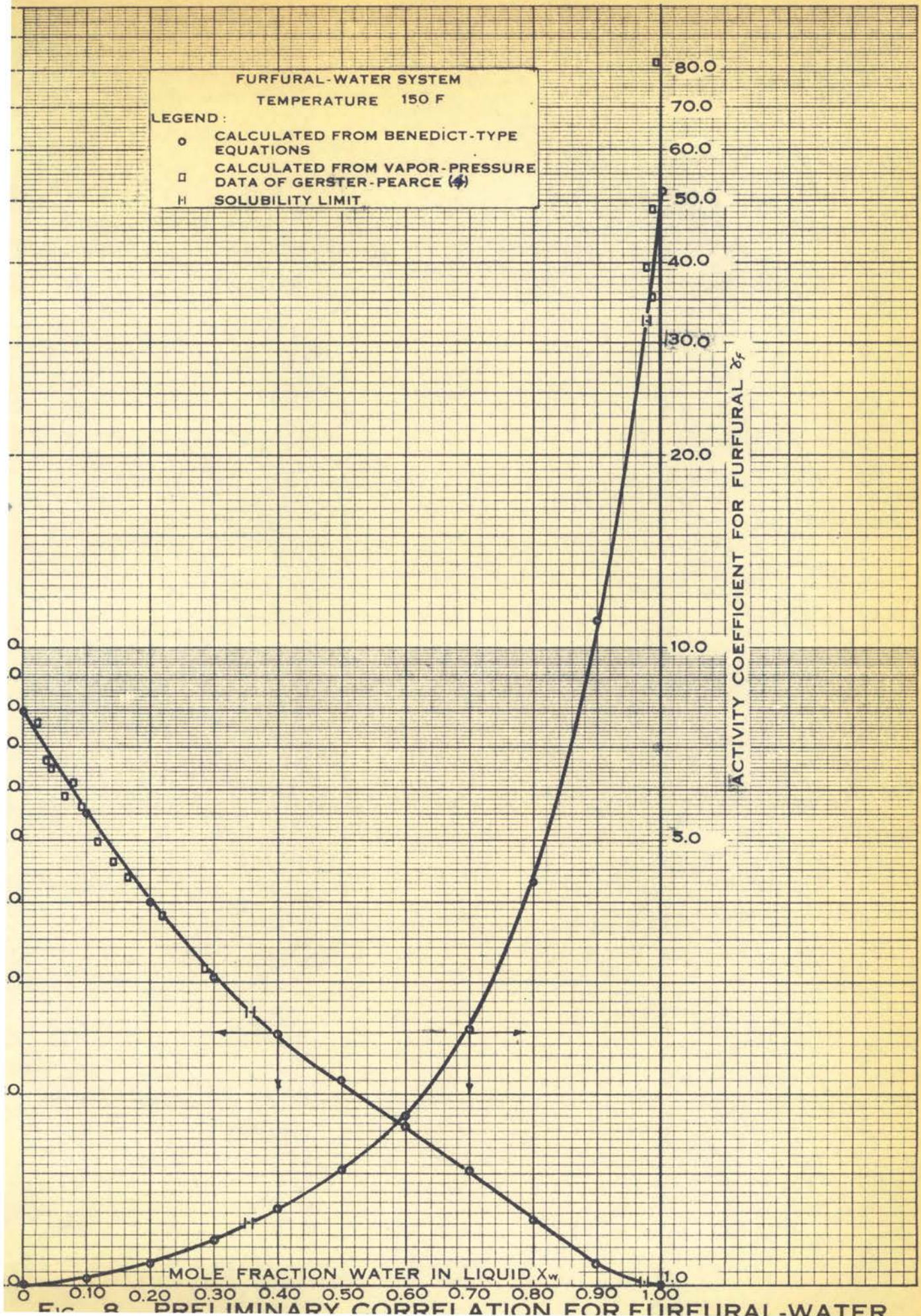
B. Vapor-Liquid Equilibria

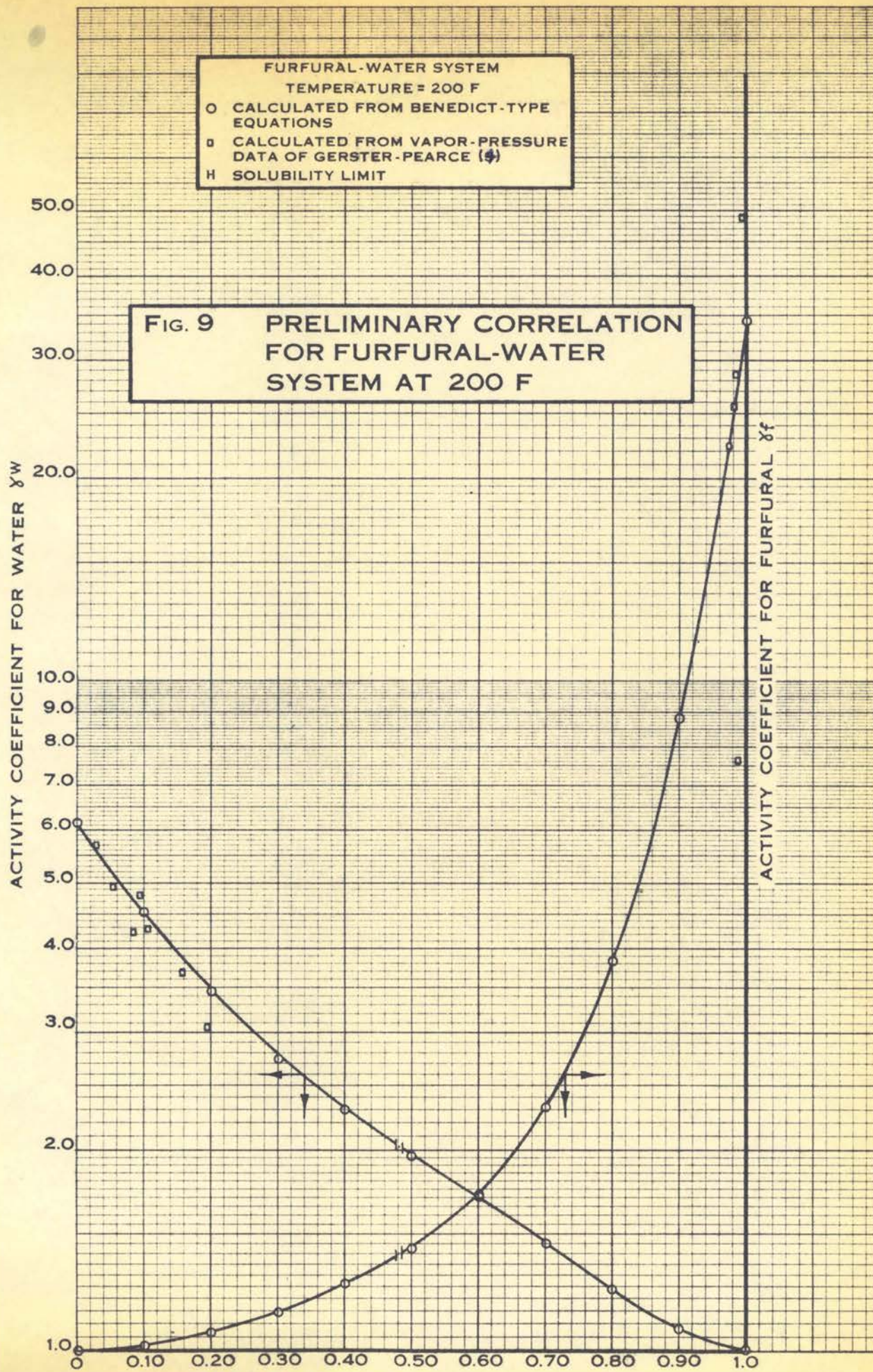
The vapor liquid equilibria of Mains at atmospheric pressure and Phillips' Research Division data at 64.2 psia do not lend themselves to the same treatment accorded the vapor pressure data. First, the bulk of Mains work was done in the water-rich rather than the furfural-rich region as with the Gerster-Pearce data. Second, the only data available covering the entire concentration range were reported as being in error by Mains due to fractionation during the equilibrium determinations. Third, the Phillips 64.2 psia data are above the critical solution temperature for the system and simultaneous agreement is possible only between the equilibria and the Duhem relationship.

An early attempt to correlate both sets of data at isotherms of 208 F (for the Mains data) and 292 F (for Phillips') by use of Benedict-type equations and the relationship $\gamma_W / \gamma_f = \frac{\alpha_{\text{actual}}}{\alpha_{\text{ideal}}}$ was unsuccessful

because the original Phillips data could not be reproduced. Therefore,







it was decided to calculate the Phillips 64.2 psia data directly using fugacities and to match the Duhem relationship graphically. Such a procedure would yield data over a sufficient temperature range to permit interpolation for other temperatures.

1. Phillips 64.2 psia Data: The 64.2 psia data were smoothed on a temperature-composition diagram and activity coefficients calculated from the following relationships:

$$\gamma_W = \frac{f_W Y_W}{f_W^0 X_W}$$

$$\gamma_f = \frac{f_f Y_f}{f_f^0 X_f}$$

The calculations and estimated fugacities are shown in Table V (Appendix). The γ_W 's were then plotted against X_W on semilogarithmic graph paper and slopes calculated at even 10 per cent concentration intervals. The desired slopes for γ_f were then calculated from the Duhem relationship. The calcu-

$$\frac{\frac{d \ln \gamma_W}{d X_W}}{\frac{d \ln \gamma_f}{d X_W}} = - \left(\frac{1 - X_W}{X_W} \right)$$

lated values for γ_f were then plotted in agreement with the above calculated slopes. Note, however, that it was necessary to smooth some of the calculated values for γ_f near zero water concentration in order to agree with the Duhem relationship. This smoothing does not invalidate the agreement with the original data. The comparison of the original and predicted (from the activity coefficient correlation) equilibria at 64.2 psia may be seen in Fig. 10.

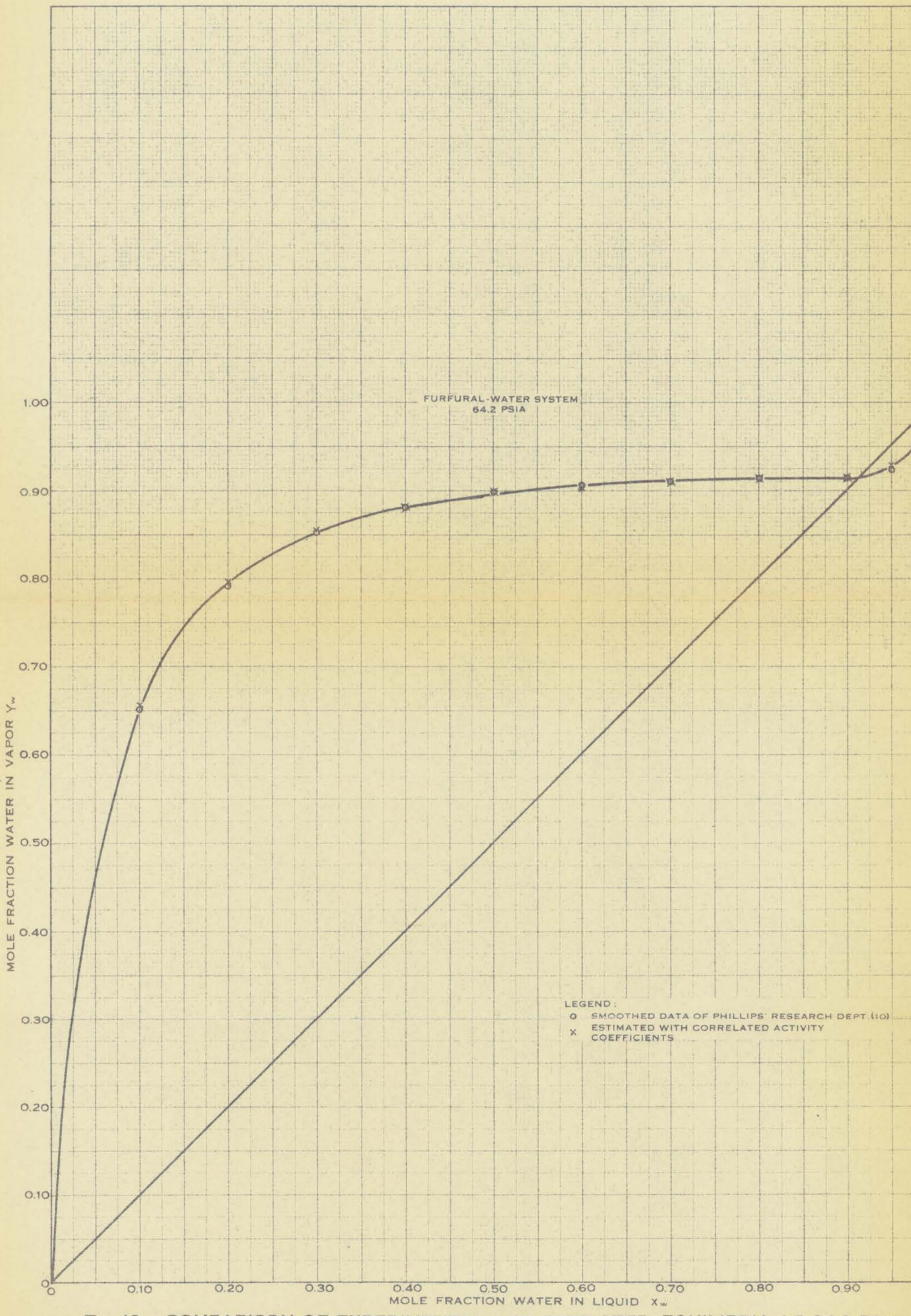


FIG. 10 COMPARISON OF EXPERIMENTAL AND PREDICTED EQUILIBRIA AT 64.2 PSIA

2. Mains Atmospheric Pressure Data: As mentioned above, the atmospheric pressure equilibria of Mains are in error because of still-head fractionation. If this were true, the calculated activity coefficients should be slightly high. A direct calculation of the γ_w 's for temperatures of 210 to 229 F shows them to be 20-30 per cent greater than the Gerster-Pearce values for 200 F. This is shown in Fig. 11 and Tables IV and VI. It seems improbable that still-head fractionation could account for such a large discrepancy. Also shown in Fig. 11 are the 208 F γ 's calculated from the relationship

$$\gamma_w/\gamma_f = \frac{\alpha_{\text{actual}}}{\alpha_{\text{ideal}}}, \text{ a Benedict-type equation, and liquid-liquid solubility.}$$

These values are practically identical to the 200 F Gerster-Pearce values at water concentrations of 20 per cent and greater. This is as it should be. The discrepancy below 20 per cent water concentration could be due to the smoothing of the α curves and/or the temperature corrections used, but it is not considered serious. Sufficient points are available to complete the correlation.

RATHMORE PARCHMENT

100% RAG - U.S.A.

FURFURAL-WATER SYSTEM
 TEMPERATURE = 200 F (PLUS)
 LEGEND:
 ○ CALCULATED FROM SMOOTHED MAINS DATA AT ATMOSPHERIC PRESSURE: TEMPERATURE SHOWN
 □ CALCULATED FROM 200 F GERSTER-PEARCE DATA WITH BENEDICT-TYRE EQUATIONS
 X CALCULATED FROM MAINS DATA (TEMPERATURE CORRECTED TO 208 F) WITH α RELATIONSHIP

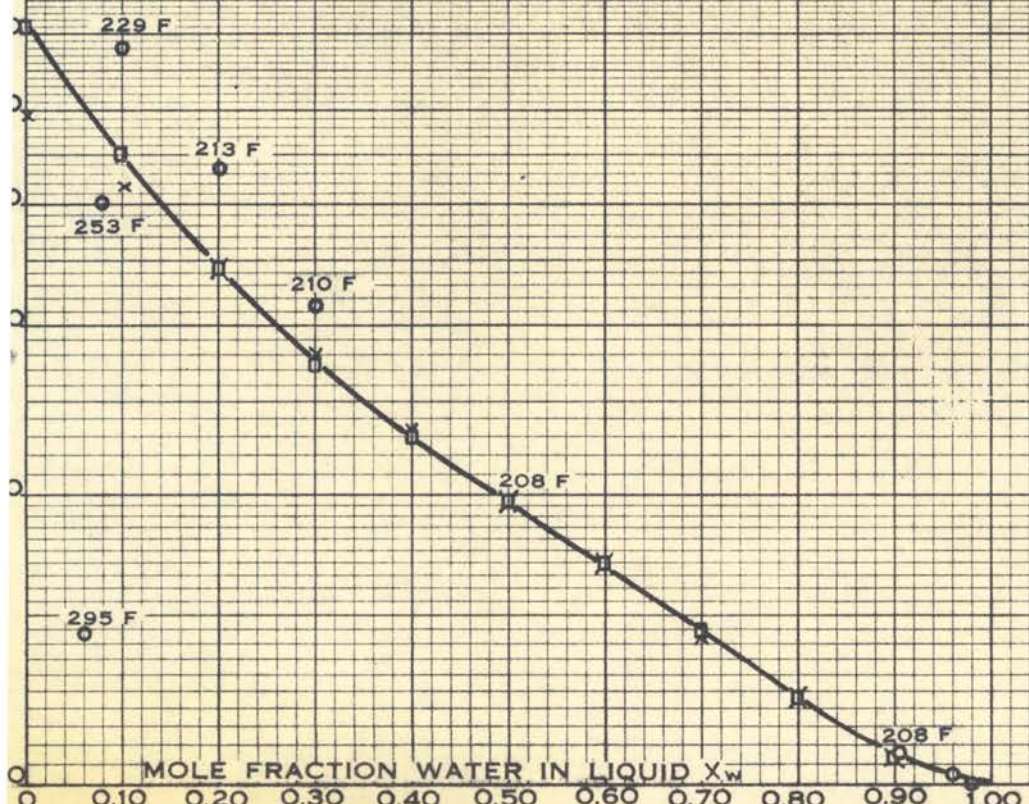


FIG. 11 COMPARISON OF ACTIVITY COEFFICIENT VALUES

CHAPTER V

THE FINAL CORRELATION

The desired final correlation is one showing activity coefficients as isothermal functions of concentration. This was accomplished by preparing graphs of activity coefficients versus temperature for equal concentration increments and smoothing the values as in Figs. 12, 13, and 14. The final values for 250 and 300 F from these smooth curves were drawn in agreement with the Duhem relationship on the final correlation. Since these temperatures are above the critical solution temperature, simultaneous agreement with liquid-liquid solubility is not possible. The smooth values for 200 F were adjusted slightly so as to be in simultaneous agreement with the Duhem relationship and liquid-liquid solubility. The final values for 100 and 150 F were not changed by the smoothing process, and hence retain their original agreement with liquid-liquid solubility and the Duhem relationship. The complete correlation on Fig. 15 for temperatures of 100, 150, 200, 250, and 300 F shows only the real portions of the curves, i.e., regions of immiscibility have been omitted.

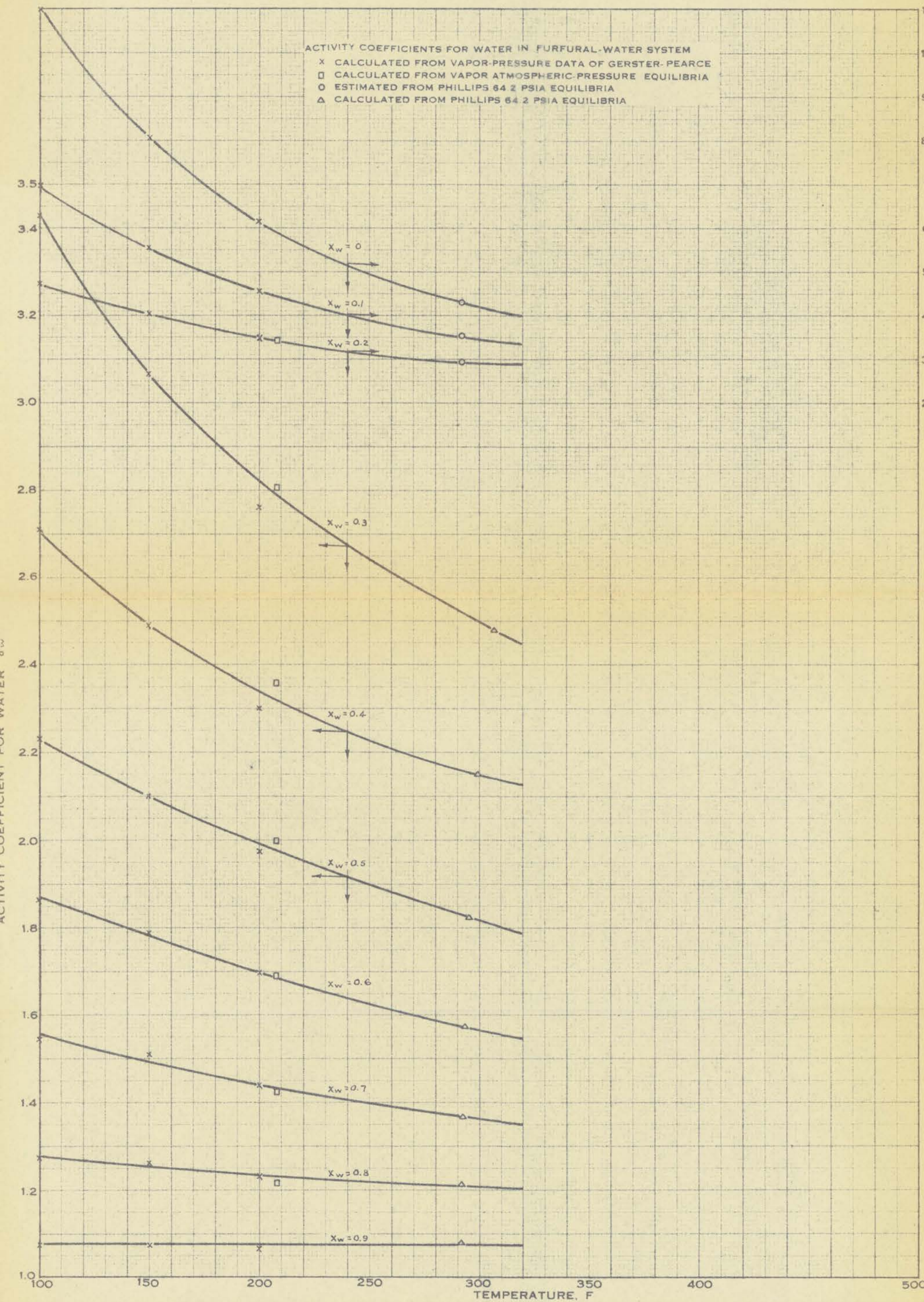


FIG. 12 ACTIVITY COEFFICIENTS FOR WATER IN FURFURAL-WATER SYSTEM

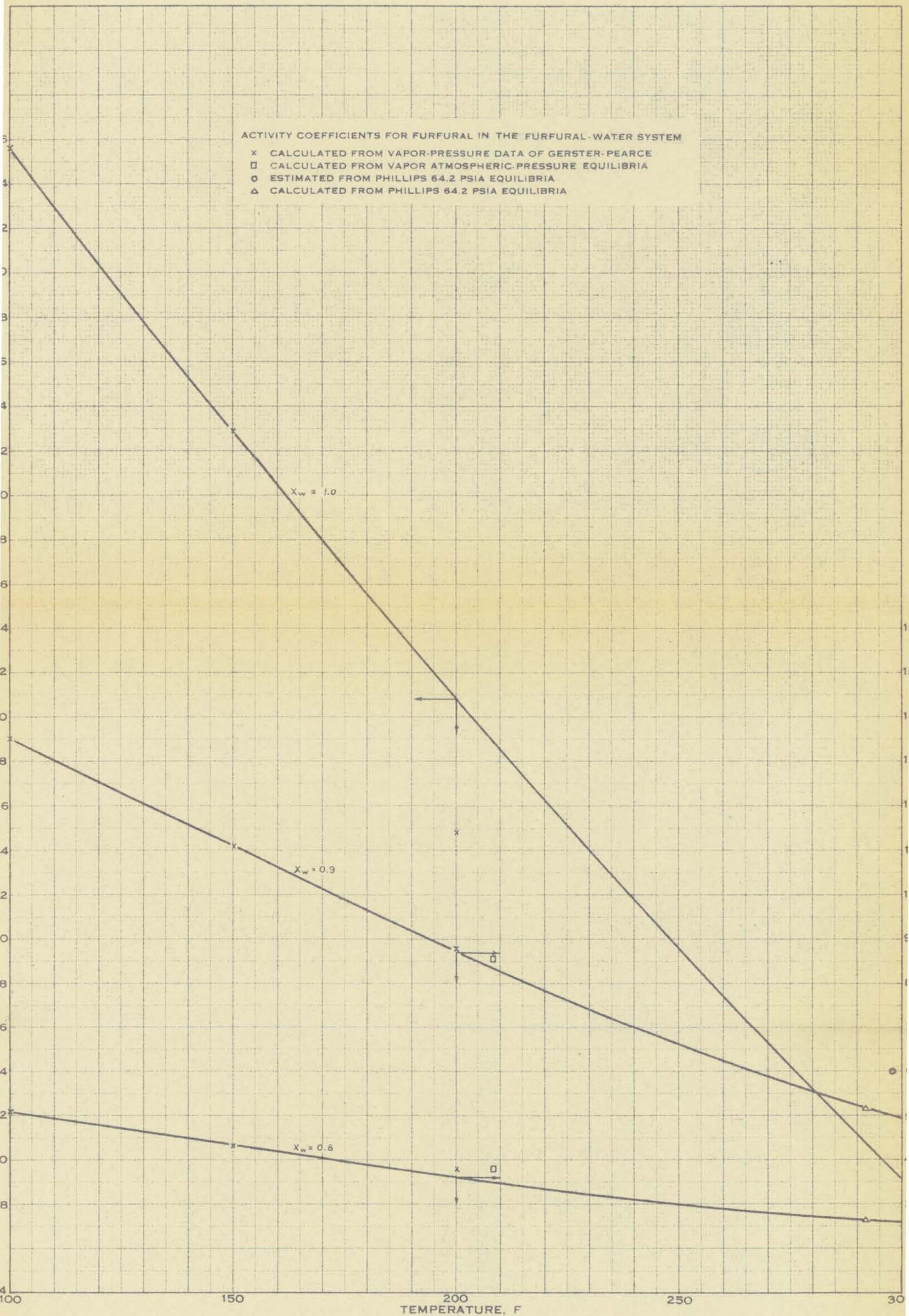


FIG. 13 ACTIVITY COEFFICIENTS FOR FURFURAL IN THE FURFURAL-WATER SYSTEM (HIGH VALUES)

ACTIVITY COEFFICIENTS FOR FURFURAL - WATER SYSTEM
 X CALCULATED FROM VAPOR-PRESSURE DATA OF GERSTER-PEARCE
 □ CALCULATED FROM VAPOR ATMOSPHERIC PRESSURE EQUILIBRIA
 △ CALCULATED FROM PHILLIPS 64.2 PSIA EQUILIBRIA

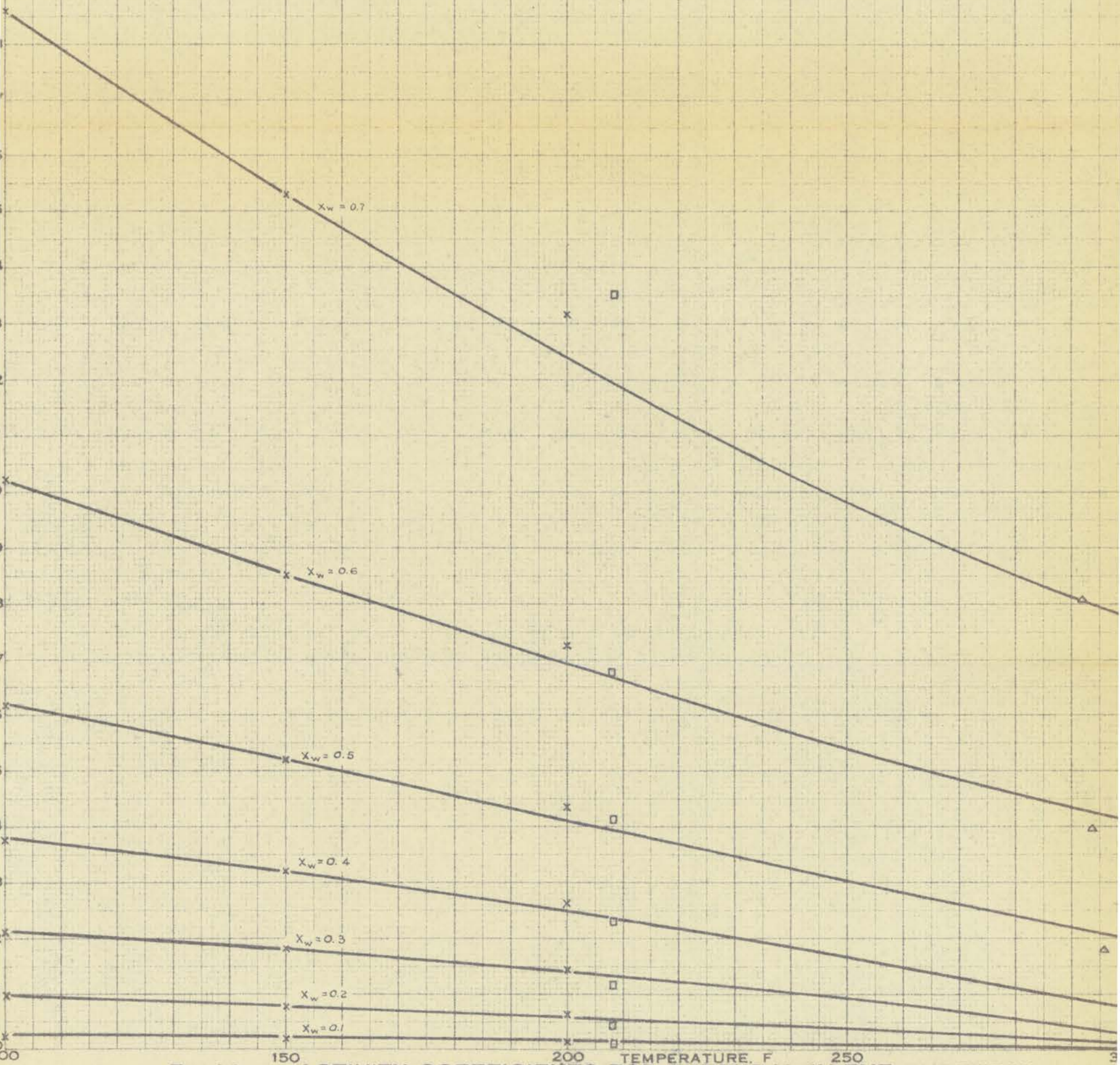
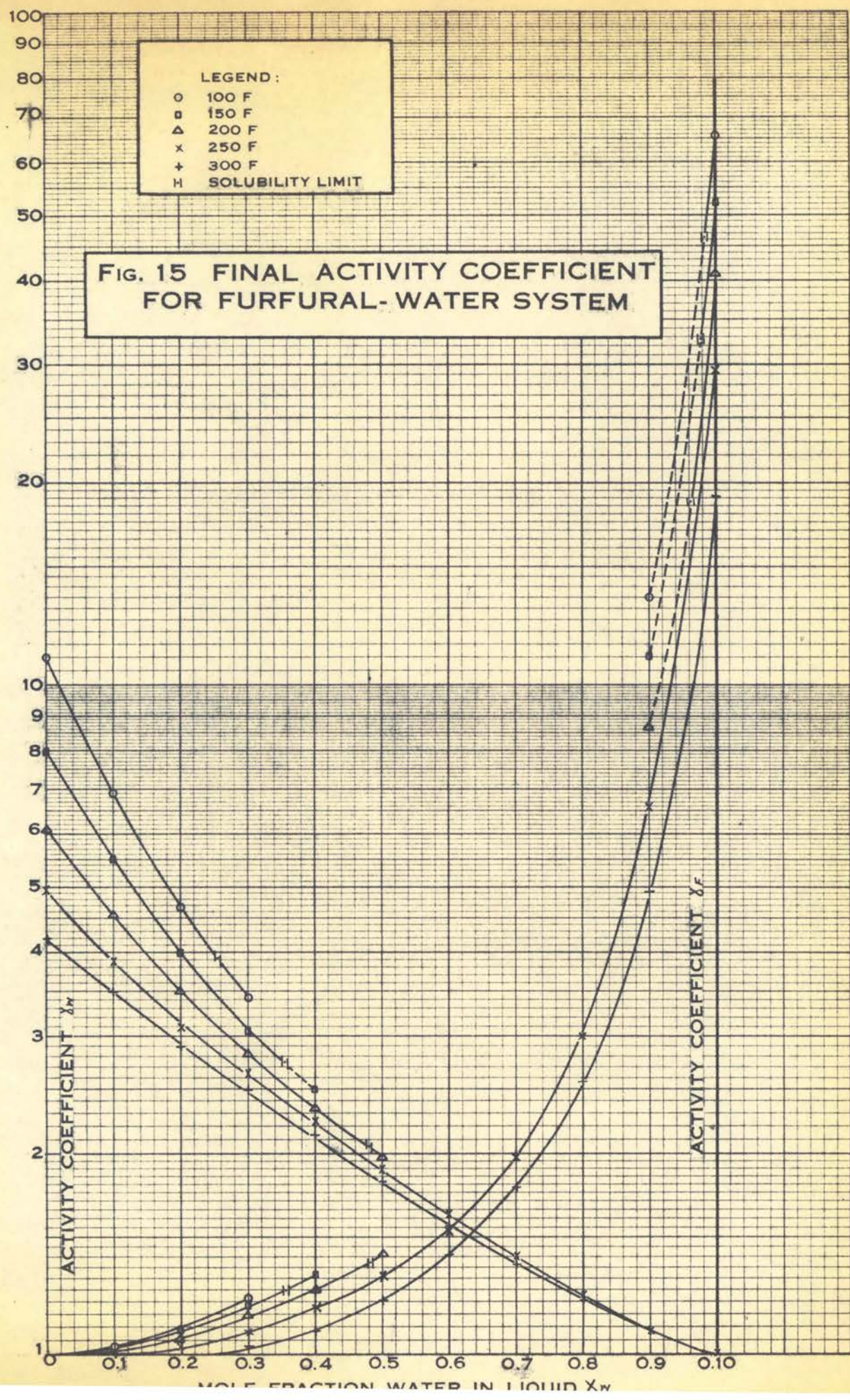


FIG. 14

ACTIVITY COEFFICIENTS FOR FURFURAL IN THE FURFURAL-WATER SYSTEM (INTERMEDIATE AND LOW VALUES)



LEGEND:
○ 100 F
□ 150 F
△ 200 F
x 250 F
+ 300 F
H SOLUBILITY LIMIT

FIG. 15 FINAL ACTIVITY COEFFICIENT FOR FURFURAL-WATER SYSTEM

ACTIVITY COEFFICIENT γ_w

ACTIVITY COEFFICIENT γ_f

MOLE FRACTION WATER IN LIQUID X_w

CHAPTER VI

CONCLUSIONS

This Thesis summarizes a correlation of available data on the furfural-water system. Activity coefficients are reported herein (Fig. 15) for temperatures of 100, 150, 200, 250, and 300 F as isothermal functions of concentration. The final correlation should be a valuable engineering tool to aid in the design of equipment for processes involving liquid-liquid extraction and extractive distillation.

A valuable extension to this work would be a correlation of activity coefficients for furfural-hydrocarbon systems. Such a correlation with C_4 hydrocarbons would find application in the extractive distillation processes for the manufacture of butadiene. A correlation with C_5 to C_8 hydrocarbons would find application in liquid-liquid extraction of gasoline fractions. The correlation for hydrocarbons above C_8 would find application in lube oil extractions. The author recommends that these correlations be made.

SUMMARY

This Thesis describes a correlation of activity coefficients for the furfural-water system based on available data for the system, Benedict-type equations, and fugacity correlations for a number of hydrocarbons and water.

The final activity coefficients are reported herein on Fig. 15, page 35, as isothermal functions of concentration. The coefficients are in simultaneous agreement with the Duhem relationship, liquid-liquid solubility (when at temperatures below the critical solution temperature), and the original equilibria.

The Thesis includes a review of theory of the activity coefficient concept, and introduces the exponential-type equation as an improvement over the Margules and Van Laar equations for correlating activity coefficients in binary systems from liquid-liquid solubility measurements.

A correlation is shown by which the fugacity coefficients f/p may be determined for water, furfural and a number of hydrocarbons at saturated conditions from the reduced pressure or temperature. This correlation was deduced by graphical integration of thermodynamic properties and is thought to be an improvement over the generalized correlations of the literature.

BIBLIOGRAPHY

- (1) Benedict, M., Johnson, C. A., Solomon, E., and Rubin, L. C., Trans. Am. Inst. Chem. Engr. 41, 371 (1945).
- (2) Carlson, H. C., and Colburn, A. P., Ind. Eng. Chem. 34, 581, (1942).
- (3) Evans, W. V., and Aylesworth, M. B., Ind. Eng. Chem. 18, 24 (1926).
- (4) Gerster, J. A., and Pearce, E. J., "Experimental and Theoretical Vapor-Liquid Relationships in the Furfural-Water System", Thesis, University of Delaware, 1949.
- (5) Griswold, J. A., "Status of RuR S.L. 311 at the University of Texas" to Operators Committee on Production of Butadiene from Petroleum, Los Angeles, California, November 4-6, 1946.
- (6) Hachmuth, K. H., "Fractionation", Unpublished Lecture Notes, April 1949.
- (7) International Critical Tables, Vol. III, 388.
- (8) Keenan, J. H., and Keyes, F. G., "Thermodynamic Properties of Steam", First Edition, New York, New York, John Wiley & Sons, Inc. Eighteenth Printing, September 1948.
- (9) Mains, G. H., Chem. & Met. Engr. 26, No. 17, 779 (1922).
- 10) Meissner, H. P., and Redding, E. M., "Prediction of Critical Constants", Ind. Eng. Chem. 34, 521 (1942).
- 11) Phillips Petroleum Company, Unpublished Data.
- 12) Quaker Oats Technical Bulletin No. 2 (1940).

NOMENCLATURE

A	A constant appearing in Margules, Van Laar, and exponential-type equations, defined as the logarithm of the activity coefficient for component i when the concentration of component i in the liquid is zero.
B	The same definition as A except with the substitution of j for i .
C	Compressibility Factor, $C = \frac{PV}{RT}$
D,E,F,G	Coefficients appearing in the Benedict-type equations
K	Equilibrium vaporization constant (ratio) defined as $K = Y/X$
P_r	Reduced pressure = $\frac{P}{P_c}$
PP	Partial Pressure
P_c	Critical pressure
R	Gas constant
T	Absolute temperature
X	Mole fraction of a component in the liquid phase
Y	Mole fraction of a component in the vapor phase
Z	The exponential of the exponential-type equation which is defined mathematically as $Z = \frac{A+B}{B}$
a	The activity of a component in a given phase
f°	Standard fugacity of the liquid. Defined as the fugacity of pure component as a liquid at the temperature and pressure obtaining.
f	Partial fugacity. Assumed to be equal to the fugacity which the pure component would have as a vapor at the temperature and pressure obtaining.
p	Vapor pressure of the component at the temperature obtaining.
v_n	Average molal volume of the liquid.
V	Volume

NOMENCLATURE (CON'T.)

Symbols:

α The relative volatility which is defined as $\alpha = \frac{K_i}{K_j} = \frac{Y_i X_j}{X_i Y_j}$

γ The activity coefficient of a component in the liquid phase, defined as $\gamma = \frac{a}{x}$

$f(0.2)$, $f(0.4)$, etc.

Values for $\log \gamma_i / \gamma_j$ at concentrations X_i of 0.2, 0.4, etc.

π Absolute pressure.

Subscripts:

i, j Component i or j

i_h Component i in the heavy phase

i_l Component i in the light phase

(ideal) Refers to ideal vaporization ratios K defined as f^0/\bar{f}

p Vapor pressure conditions

π Total pressure conditions

sat. liq. Refers to the saturated liquid

W Refers to water

f Refers to furfural

A P P E N D I X

TABLE II

ACTIVITY COEFFICIENT CALCULATIONS FOR 100 F

Mole Fraction* Water in Liquid X_W	Temperature of* Boiling Liquid F	Vapor Pressures mm Hg.		Total Pressure, π^* mm Hg. Abs.	$(PP)_W =$ $\pi - \gamma_f P_f X_f$	$P_W X_W$	$\gamma_W = \frac{(PP)_W}{P_W X_W}$
		Furfural	Water				
0.0962	100.0	4.7	49.2	37.30	32.99	4.73	6.97
0.1813	100.0	4.7	49.2	49.90	45.86	8.93	5.13
0.0325	99.9	4.6	49.0	20.10	15.65	1.592	9.82
0.0752	99.9	4.6	49.0	35.85	31.54	3.68	8.57
0.1204	100.2	4.8	49.5	42.90	38.57	5.96	6.46
0.1138	100.1	4.8	49.3	43.20	38.84	5.60	6.95
0.0243	100.0	4.7	49.2	17.48	12.89	1.197	10.78
0.0484	100.1	4.8	49.3	23.41	18.84	2.38	7.91
0.0783	99.9	4.6	49.0	29.60	25.30	3.84	6.58
0.0831	100.0	4.7	49.2	35.90	31.53	4.09	7.71
0.1053	100.0	4.7	49.2	39.10	34.83	5.19	6.72
0.1472	100.0	4.7	49.2	44.50	40.33	7.25	5.56
0.2037	99.9	4.6	49.0	50.10	46.20	9.98	4.64
0.0198	100.0	4.7	49.2	14.85	10.25	0.975	10.51
0.0450	100.0	4.7	49.2	24.07	19.58	2.215	8.85
0.0429	100.0	4.7	49.2	23.50	19.00	2.11	9.01
0.0700	100.0	4.7	49.2	30.10	25.73	3.44	7.49
0.1064	99.9	4.6	49.0	39.90	35.79	5.21	6.87
0.1630	99.9	4.6	49.0	46.40	42.37	7.99	5.30
0.2148	100.1	4.8	49.3	52.30	48.27	10.60	4.55
0.2058	100.0	4.7	49.2	50.47	46.50	10.11	4.60
0.2383	100.0	4.7	49.2	52.87	49.00	11.74	4.17
					$(PP)_f =$ $\pi - \gamma_W P_W X_W$	$P_f X_f$	$\gamma_f = \frac{(PP)_f}{P_f X_f}$
0.9818	100.0	4.7	49.2	52.3	3.70	0.0855	43.3
0.9900	100.0	4.7	49.2	52.4	3.45	0.0470	73.4
0.9951	100.0	4.7	49.2	51.1	2.14	0.0230	93.1

* Experimental Data of Gerster-Pearce.

TABLE III

ACTIVITY COEFFICIENT CALCULATIONS FOR 150 F

Mole Fraction* Water in Liquid X_W	Temperature of* Boiling Liquid F	Vapor Pressures mm Hg.		Total Pressure, π^* mm Hg. Abs.	$(PP)_W =$ $\pi - \gamma_f P_f X_f$	$P_W X_W$	$\gamma_W = \frac{(PP)_W}{P_W X_W}$
		Furfural	Water				
0.0246	150.0	22.2	192.3	57.80	36.05	4.73	7.63
0.0491	150.0	22.2	192.3	83.31	61.91	9.45	6.55
0.0658	150.0	22.2	192.3	102.3	81.25	12.65	6.43
0.0925	149.9	22.1	192.1	121.2	100.65	17.79	5.66
0.1198	150.0	22.2	192.3	136.0	115.75	23.00	5.03
0.1434	149.9	22.1	192.1	148.7	128.90	27.60	4.66
0.1658	150.0	22.2	192.3	159.7	140.30	31.85	4.41
0.0397	150.0	22.2	192.3	72.7	51.15	7.64	6.70
0.0793	150.0	22.2	192.3	115.5	94.65	15.28	6.20
0.2192	150.0	22.2	192.3	181.4	162.75	42.15	3.86
0.2856	149.9	22.1	192.1	190.4	172.75	54.90	3.145
					$(PP)_f =$		$\gamma_f = \frac{(PP)_f}{P_f X_f}$
					$\pi - \gamma_W P_W X_W$	$P_f X_f$	
0.9898	149.9	22.1	192.1	200.3	8.00	0.225	35.5
0.9955	149.9	22.1	192.1	199.5	8.27	0.0995	83.1
0.9845	149.9	22.1	192.1	207.7	16.70	0.342	48.9
0.9792	150.0	22.2	192.3	208.6	18.40	0.462	39.8

* Experimental Data of Gerster-Pearce

TABLE IV

ACTIVITY COEFFICIENT CALCULATIONS FOR 200 F

Mole Fraction* Water in Liquid X_W	Temperature of* Boiling Liquid F	Vapor Pressures mm Hg.		Total Pressure, π^* mm Hg. Abs.	$(PP)_W =$ $\pi - \gamma_f P_f X_f$	$P_W X_W$	$\gamma_W = \frac{(PP)_W}{P_W X_W}$
		Furfural	Water				
0.0267	200.0	76.8	595.9	166.5	91.50	15.91	5.74
0.0528	200.0	76.8	595.9	230.2	156.80	31.45	4.98
0.0812	199.9	76.6	595.8	277.3	205.90	48.40	4.25
0.0920	200.0	76.8	595.9	355.9	264.80	54.90	4.82
0.1028	199.9	76.6	595.8	333.2	263.00	61.10	4.30
0.1549	199.9	76.6	595.8	409.4	341.50	92.20	3.70
0.1958	200.0	76.8	595.9	421.4	356.00	116.80	3.05
					$(PP)_f =$ $\pi - \gamma_W P_W X_W$	$P_f X_f$	$\gamma_f = \frac{(PP)_f}{P_f X_f}$
0.9895	200.0	76.8	595.9	598.6	6.1	0.806	7.56
0.9958	199.9	76.6	595.8	610.8	15.8	0.322	49.0
0.9840	200.0	76.8	595.9	623.8	31.8	1.230	25.85
0.9823	200.0	76.8	595.9	630.0	39.0	1.360	28.65
0.9723	200.1	77.0	596.0	635.2	47.2	2.130	22.20

* Experimental Data of Gerster-Pearce

TABLE V

ACTIVITY COEFFICIENT CALCULATIONS FROM PHILLIPS 64.2 PSIA DATA

Mole Fraction* Water in Liquid X_W	Temperature of* Boiling Liquid F	Mole Fraction* Water in Vapor Y_W	Vapor Pressures PSIA		$f^o @ 64.2$ PSIA		$\bar{f} @ 64.2$ PSIA		$\gamma = \frac{\bar{f} Y}{f^o X}$	
			Furfural	Water	Furfural	Water	Furfural	Water	Furfural	Water
0.1	358.7	0.6510	24.40	150.17	23.25	140.29	55.50	62.47	0.925	2.90
0.2	322.6	0.7924	14.20	93.00	13.83	88.54	53.7	62.12	1.005	2.78
0.3	306.8	0.8517	10.90	73.91	10.68	71.00	52.70	61.96	1.048	2.48
0.4	299.6	0.8817	9.75	66.00	9.56	63.53	52.10	61.86	1.077	2.145
0.5	296.0	0.8978	9.24	63.00	9.08	60.75	52.10	61.83	1.178	1.829
0.6	293.9	0.9056	8.95	62.00	8.78	59.80	51.90	61.80	1.395	1.560
0.7	292.7	0.9099	8.78	60.50	8.64	58.40	51.90	61.80	1.805	1.375
0.8	292.1	0.9135	8.69	60.00	8.54	57.90	51.90	61.78	2.630	1.220
0.9	292.1	0.9146	8.69	60.00	8.54	57.90	51.90	61.78	5.190	1.084
0.95	292.6	0.9229	8.76	60.50	8.62	58.40	51.90	61.80	9.29	1.029

* Smoothed Experimental Data From Report 468.44

TABLE VI

DIRECT ACTIVITY COEFFICIENT CALCULATIONS FROM MAINS' ATMOSPHERIC PRESSURE DATA

Mole Fraction* Water in Liquid X_W	Mole Fraction* Water in Vapor Y_W	Temperature of* Boiling Liquid F	Vapor Pressures PSIA		$\gamma = \frac{\pi Y}{P X}$	
			Furfural	Water	Furfural	Water
0.04	0.19	310.64	11.9	78.41	1.042	0.891
0.06	0.36	294.80	9.00	61.96	1.112	1.425
0.08	0.68	252.50	4.40	31.15	1.162	4.02
0.10	0.81	229.10	2.72	20.44	1.141	5.82
0.20	0.89	213.08	1.95	15.02	1.038	4.35
0.30	0.905	209.66	1.80	14.03	1.108	3.16
0.50	0.908	208.22	1.75	13.63	1.548	1.96
0.908	0.908	208.22	1.75	13.63	8.40	1.079
0.96	0.908	208.22	1.75	13.63	19.30	1.020
0.98	0.920	208.52	1.76	13.71	33.4	1.005
0.99	0.945	209.40	1.78	13.96	45.4	1.005

* Smoothed Experimental Data