of experimental conditions. The N_2 to H_2 ratio decreased with time (Figure 6) from 17 toward a constant value of 15 at 222° C. and 300 p.s.i., and from approximately 10 to 5 at 250° C. and 430 p.s.i. The ratio decreased by 5 per 100 p.s.i. increase of pressure at 222° C. and by 1.4 per 100 p.s.i. at 250° C.

The N_2 to H_2 values indicated that a substantial part of the decomposition proceeded by Equation 1:

$$3N_2H_4 \rightarrow 4NH_3 + N_2 \tag{1}$$

The small quantities of hydrogen that formed are due in about equal amounts to the dissociation of ammonia (Equation 2) and probably hydrazine (Equation 3):

$$2NH_3 \rightarrow N_2 + 3H_2 \tag{2}$$

$$N_2H_4 \rightarrow N_2 + 2H_2 \tag{3}$$

For the purpose of establishing the extent to which Equation 2 contributes to the N_2 to H_2 ratio, an upper limit was obtained by calculating the amounts of N_2 and H_2 that should have resulted from the dissociation of ammonia under experimental conditions. In this way, it was possible to account for about one-half of the hydrogen found among the products. If the analytical N_2 and H_2 data are used in the general Equation 4,

$$3N_2H_4 \rightarrow 4(1 - x)NH_3 + (1 + 2x)N_2 + 6xH_2 \tag{4}$$

for the decomposition of hydrazine into ammonia, nitrogen, and hydrogen, the value of x when N_2 to H_2 tends to become constant (Figure 6) was 0.017 at 222° C. and 300 p.s.i. pressure. This value at 250° C. and 430 p.s.i. pressure was 0.034.

The results relating to the stoichiometry of decomposition suggested a changing reaction mechanism at the higher temperatures. This observation is based on the variation of the N_2 to H_2 ratio with reaction parameters and the inability to account for all of the hydrogen by the dissociation of ammonia. It was not possible to obtain indications of competing processes from the rate-temperature relation (Figure 5) because of the incomplete nature of these data. If the decomposition process involves competing reactions, a calculated activation energy from Figure 5 would have doubtful meaning. The calculated activation energy was ≈ 73 kcal. per mole, which is greater by a factor of 2 than the reported values (*1*, *4*). Hydrazine is relatively stable under the conditions described. Results such as those found in Figures 4 and 5 suggest that there are pressure and temperature conditions which determine the reaction mechanism and hence control the rate of decomposition. The 222° C.–300 p.s.i. and 250° C.–430 p.s.i. conditions apparently are in the regime of changing mechanisms. It appears that up to 250° C. the total pressure should exceed the vapor pressure of hydrazine by at least 200 p.s.i. if the rate of decomposition is to be confined to relatively low values.

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Prediction of Boiling Points of Liquid Mixtures

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KNOWLEDGE of vapor-liquid equilibrium of a mixture is necessary in distillation calculations. It is practical to predict multicomponent vapor-liquid equilibria only from the data for pure components and their binary combinations to save further experimentation. There are generally two types of methods to correlate vapor-liquid equilibrium data. One involves the vapor phase imperfections and the liquid phase activity coefficients as a thermodynamically consistent function of liquid composition in various empirical forms of representation. In this case the effect of temperature on the activity coefficient also should be taken into consideration. This method is exacting, but is laborious even for the prediction of isobaric ternary vapor-liquid equilibria, since this involves the above effects and the correlation of vapor pressure *vs.* temperature. The other method uses several different empirical algebraic equations, which correlate compositions of vapor phase directly with those of liquid phase without the use of the composition–boiling point relationship. Thus, one can avoid the complexities in dealing with the activity coefficient and the temperature dependence of the vapor pressures of pure components (*32*). The main advantage of those algebraic equations which have been proposed so far consists in simplicity of their expressed forms. However, the fact that those equations do not have temperature terms seems to be unreasonable.

This article presents an empirical method to correlate boiling temperatures of a binary liquid mixture with its equilibrium compositions by such an algebraic equation. The method is applied for the prediction of boiling points of ternary systems.

PROPOSED METHOD

Most empirical algebraic equations treat only binary systems. An essential requirement is that the method can treat not only binaries, but also multicomponent mixtures. The most useful is the equation developed by Prahl (*31*). This equation is flexible because it covers the whole range of concentrations of many binary systems by using three constants, and because it can be extended to multicomponent systems (*23*). For binary systems, the equation is expressed as follows:

$$\frac{y_i}{y_j} = \frac{x_i}{x_j}\left(\frac{x_i + x_i a_{ij}}{x_j b_{ij} + x_i c_{ij}}\right) \tag{1}$$

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where y and x are the mole fractions in the vapor and liquid phases, respectively. Subscripts i and j indicate the components of a given binary mixture; a_{ij}, b_{ij}, and c_{ij} are characteristic constants of the mixture. In the present work the boiling points of the mixture in absolute temperature scale, T_m, are calculated by the following equation based on Equation 1

$$T_m = T_i y_{ii} + T_{ij}(y_{ij} + y_{ji}) + T_j y_{jj} \tag{2}$$

where the new variables y_{ii}, y_{ij}, y_{ji}, and y_{jj} are defined as follows:

$$y_{ii} = y_i \frac{x_i}{x_i + a_{ij}x_j} \tag{3}$$

$$y_{ij} = y_i \frac{a_{ij}x_j}{x_i + a_{ij}x_j} \tag{4}$$

$$y_{jj} = y_j \frac{b_{ij}x_j}{b_{ij}x_j + c_{ij}x_i} \tag{5}$$

$$y_{ji} = y_j \frac{c_{ij}x_i}{b_{ij}x_j + c_{ij}x_i} \tag{6}$$

The same values of a_{ij}, b_{ij}, and c_{ij} are used as in Equation 1. Therefore, the following relationship exists.

$$y_{ii} + y_{ij} + y_{jj} + y_{ji} = 1 \tag{7}$$

T_i and T_j are the boiling points of the pure components i and j under the total pressure at which vapor-liquid equilibrium data of the mixture were determined, respectively. T_{ij} is an arbitrary constant and has been so determined as to agree with experimental data in the vicinity of equimolar composition. The value of T_{ij} will be estimated in the sample calculation later. Interchange of the subscripts of a, b, and c yields

$$a_{ij} = \frac{c_{ji}}{b_{ji}} \tag{8}$$

$$b_{ij} = \frac{1}{b_{ji}} \tag{9}$$

$$c_{ij} = \frac{a_{ji}}{b_{ji}} \tag{10}$$

Equations 1 and 2 for each of the component binaries of a ternary system are given by

$$\frac{y_1}{y_2} = \frac{x_1}{x_2}\left(\frac{x_1 + a_{12}x_2}{b_{12}x_2 + c_{12}x_1}\right) \tag{11}$$

$$T_m = T_1 y_{11} + T_{12}(y_{12} + y_{21}) + T_2 y_{22} \tag{12}$$

$$\frac{y_2}{y_3} = \frac{x_2}{x_3}\left(\frac{x_2 + a_{23}x_3}{b_{23}x_3 + c_{23}x_2}\right) \tag{13}$$

$$T_m = T_2 y_{22} + T_{23}(y_{23} + y_{32}) + T_3 y_{23} \tag{14}$$

$$\frac{y_3}{y_1} = \frac{x_3}{x_1}\left(\frac{x_3 + a_{31}x_1}{b_{31}x_1 + c_{31}x_3}\right) \tag{15}$$

$$T_m = T_1 y_{11} + T_{13}(y_{13} + y_{31}) + T_3 y_{33} \tag{16}$$

The y's are calculated by the definition of Equations 3 to 6. If the system deviates only a little from the condition

$$b_{12} \times b_{23} \times b_{31} = 1 \tag{17}$$

Lu, Li, and Ting (*23*) suggested that for the prediction of ternary vapor-liquid equilibria, the components are related in this ratio:

$$\begin{aligned} y_1 : y_2 : y_3 = {} & \left(\frac{b_{31}}{b_{12}}\right)^{1/3} x_1\left(x_1 + x_2a_{12} + x_3\frac{c_{31}}{b_{31}}\right) \\ & : \left(\frac{b_{12}}{b_{23}}\right)^{1/3} x_2\left(x_2 + x_3a_{23} + x_1\frac{c_{12}}{b_{12}}\right) \\ & : \left(\frac{b_{23}}{b_{31}}\right)^{1/3} x_3\left(x_3 + x_1a_{31} + x_2\frac{c_{23}}{b_{23}}\right) \end{aligned} \tag{18}$$

In the present method the boiling points of ternary system are calculated by

$$\begin{aligned} T_m = {} & T_1y_{11} + T_2y_{22} + T_3y_{33} + T_{12}(y_{12} + y_{21}) \\ & + T_{13}(y_{13} + y_{31}) + T_{23}(y_{23} + y_{32}) \end{aligned} \tag{19}$$

The variables y_{11}, y_{12}, and y_{13} are defined as

$$y_{11} = y_1 \frac{x_1}{x_1 + x_2a_{12} + x_3\dfrac{c_{31}}{b_{31}}} \tag{20}$$

$$y_{12} = y_1 \frac{x_2a_{12}}{x_1 + x_2a_{12} + x_3\dfrac{c_{31}}{b_{31}}} \tag{21}$$

$$y_{13} = y_1 \frac{x_3c_{31}/b_{31}}{x_1 + x_2a_{12} + x_3\dfrac{c_{31}}{b_{31}}} \tag{22}$$

y_{22} and others are calculated similarly, and among these variables the following correlations hold:

$$\sum_{ij} y_{ij} = y_{11} + y_{12} + y_{13} + \ldots = 1 \tag{23}$$

The condition (17) for an n-component system is

$$b_{12} \cdot b_{23} \ldots b_{ij} \ldots b_{n1} = 1 \tag{24}$$

Then a generalized equation from Equation 18 is suggested as follows:

$$\begin{aligned} & y_1 : \ldots y_i : \ldots y_n \\ & = (b_{n1} \times b_{n-1\,1} \ldots b_{i1} \ldots b_{21})^{1/n} x_1\left(x_1 + x_2a_{12} \ldots x_ia_{1i} \ldots + x_n\frac{c_{n1}}{b_{n1}}\right) \\ & : b_{1i} \times b_{2i} \ldots b_{ni})^{1/n} x_i\left(x_i + x_1\frac{c_{1i}}{b_{1i}} \ldots + x_ja_{ij} \ldots x_na_{in}\right) \\ & : (b_{1n} \ldots b_{in} \ldots b_{n-1\,n})^{1/n} x_n\left(x_n + x_1a_{n1} \ldots + x_i\frac{c_{in}}{b_{in}} + \ldots\right) \end{aligned} \tag{25}$$

The boiling points of the system are calculated by

$$T_m = \sum_i T_iy_{ii} + \sum_{i \neq j}\sum T_{ij} \times y_{ij} \tag{26}$$

Here the subscripts of T are interchangeable. The variable y_{ij} is defined as

$$y_{ij} = y_i \frac{x_ja_{ij}}{x_i + x_1\dfrac{c_{1i}}{b_{1i}} \ldots + x_ja_{ij} \ldots + x_na_{in}} \tag{27}$$

PREDICTION OF BOILING POINTS OF TERNARY SYSTEMS FROM BINARY DATA

To demonstrate the utility of the present method, data at atmospheric pressure for 33 typical binary systems from the available literature, which can be represented accurately by Equation 1, have been tested. Table I gives the values of the constants determined and used in this investigation, the boiling points and compositions of the azeotropes, and the average deviations of calculated values from smoothed

Table I. Primary Information and Average Deviations

First Component	Second Component	T_1, ° C.	T_2, ° C.	a_{12}	b_{12}	c_{12}	T_{12}	Azeotropic Data, Exptl. x_a	Azeotropic Data, Exptl. T_a, ° C.	Azeotropic Data, Calcd. x_a	Azeotropic Data, Calcd. T_a, ° C.	Av. Dev.	Data Source
Acetone	Benzene	56.2	80.1	0.966	0.332	0.659	337.5					0.2	*(4, 12, 33)*
	Chloroform[a]	56.2	61.2	0.419	0.734	0.424	348.3	0.355	64.5	0.354	64.5	0	*(4, 16, 33)*
	Ethanol	56.2	78.3	1.298	0.383	0.708	334.6					0.5	*(2, 4, 14)*
	Methanol[b]	56.2	64.7	2.208	0.951	1.314	327.1	0.800	55.7	0.800	55.5	0.1	*(2, 4, 13)*
	4-Methyl-2-pentanone	56.2	115.9	0.808	0.171	0.106	356.6					0.2	*(16)*
Benzene	Cyclohexane[b]	80.1	80.7	1.473	1.015	1.406	348.8	0.545	77.5	0.530	77.6	0.1	*(4, 8, 36)*
	n-Heptane	80.1	98.4	3.259	1.504	0.892	354.7					0.2	*(10, 27, 36)*
2-Butanone	Benzene[b]	79.6	80.1	0.864	0.720	1.168	350.0	0.470	78.2	0.462	78.2	0	*(4, 8)*
	Cyclohexane[b]	79.6	80.7	1.767	0.529	2.375	341.5	0.477	71.4	0.474	71.4	0.2	*(7, 21, 38)*
	n-Heptane[b]	79.6	98.4	4.292	0.805	2.070	348.5	0.767	77.2	0.765	77.2	0.1	*(4)*
	Toluene	79.6	110.6	0.470	0.122	0.484	369.5					0.2	*(4)*
	Trichloroethylene	79.6	86.9	0.486	0.380	0.811	356.5					0	*(20)*
Carbon disulfide	Acetone[b]	46.3	56.2	11.373	2.253	5.495	310.0	0.671	39.0	0.670	38.9	0.2	*(4)*
Carbon tetrachloride	2-Butanone[b]	76.7	79.6	3.107	2.00	1.565	344.1	0.662	73.7	0.662	73.7	0.1	*(11)*
	Trichloroethylene	76.7	86.9	0.813	0.605	0.738	355.3					0.1	*(1)*
Cellosolve	Ethylbenzene[b]	135.3	136.2	2.070	0.641	2.529	398.3	0.480	127.9	0.483	127.8	0.1	*(24)*
Chloroform	Benzene	61.2	80.1	0.960	0.653	0.500	348.1					0.1	*(33)*
Cyclohexane	Ethylene dichloride[b]	79.9	82.4	2.656	0.838	2.549	344.8	0.540	74.1	0.540	74.1	0.1	*(4)*
	n-Heptane	80.7	98.4	1.090	0.647	0.610	361.9					0.1	*(28, 36)*
	Toluene	80.7	110.6	1.209	0.442	0.512	364.2					0.3	*(29, 36)*
Ethanol	Benzene[b]	78.3	80.1	3.356	0.409	4.503	339.3	0.453	68.0	0.457	68.0	0.1	*(10, 22)*
	n-Heptane[b]	78.3	98.4	21.517	0.499	12.50	343.7	0.647	71.0	0.646	71.1	0.3	*(17)*
	Toluene[b]	78.3	110.6	6.433	0.401	2.476	349.4	0.810	77.0	0.803	77.1	0.3	*(22)*
	Water[b]	78.3	100.0	1.513	0.118	1.159	351.1	0.894	78.2	0.898	78.2	1.1	*(4, 30, 34)*
Ethyl acetate	Ethanol[b]	77.1	78.3	3.172	1.392	2.382	343.1	0.562	72.2	0.563	72.2	0	*(4, 25)*
n-Heptane	Toluene	98.4	110.6	1.120	0.611	0.936	373.6					0	*(4, 15, 35, 36)*
Methanol	Ethanol	64.7	78.3	1.091	0.646	0.610	344.6					0.2	*(2, 6)*
	Ethyl acetate[b]	64.7	77.1	3.564	0.823	2.157	333.9	0.702	62.5	0.703	62.5	0.1	*(25)*
	n-Heptane[b]	64.7	98.4	73.217	0.572	25.233	331.7	0.746	58.7	0.750	58.7	0.2	*(3)*
	Toluene[b]	64.7	110.6	9.098	0.188	2.181	337.1	0.883	63.6	0.882	64.1	0.6	*(3)*
	Water	64.7	100.0	0.937	0.120	0.423	350.1					0.4	*(4, 37)*
Methylcyclopentane	Benzene[b]	71.8	80.1	1.208	0.656	1.079	344.5	0.872	71.7	0.875	71.7	0.1	*(4, 28)*
n-Octane	Cellosolve[b]	125.7	135.3	9.540	1.220	5.984	388.2	0.625	116.8	0.625	116.8	0.1	*(24)*

[a] Maximum azeotrope. [b] Minimum azeotrope.

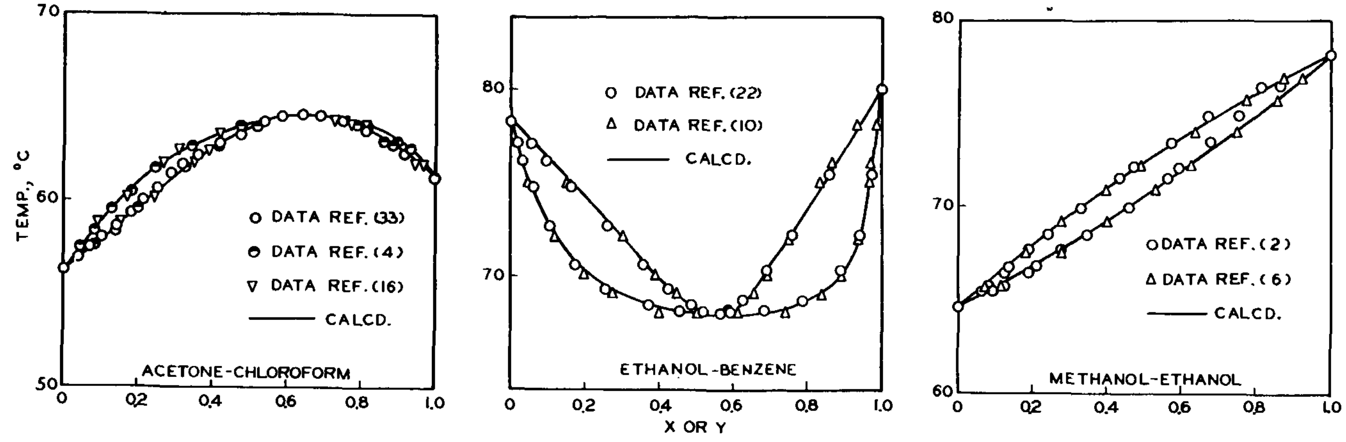

Figure 1. Comparison of calculated and experimental vapor-liquid equilibrium for three systems

experimental values of nine liquid compositions with intervals of 0.1 mole fraction. The maximum difference between the boiling points of pure components is about 60° C. for nonazeotropic [the acetone–4-methyl–2-pentanone (the acetone-methyl isobutyl ketone)] and 46° C. for azeotropic systems (the methanol-toluene). The average deviations provide a simple measure of the accuracy of the present method. A survey of Table I shows that the ethanol-water system gives poorest agreement and is probably an example of lowest accuracy.

Calculated and experimental results are compared in Figure 1 for three of the tested systems. Normal boiling point data for the pure components were obtained from the same sources as vapor-liquid equilibrium data. When Prahl's equation is inadequate in some cases, a modified equation involving more than three constants can be used with sufficient accuracy (*23*). The present method may be applied by a combination of the modified equations.

Five ternary systems were selected as test systems for prediction of ternary boiling points. Each ternary system is a combination of three binary systems listed in Table I and approximately satisfied the condition (17). They are acetone-chloroform-benzene (*33*), acetone-methanol-ethanol (*3*), 2-butanone-benzene-cyclohexane (*5, 9*), carbon tetrachloride-2-butanone(methyl ethyl ketone)-trichloroethylene (*19*), and cyclohexane–*n*-heptane–toluene (*26*). Table II shows the values of $b_{12}\cdot b_{23}\cdot b_{31}$ and the average deviations of predicted boiling points from experimental values. The components are numbered in the order of increasing boiling points. The results of three of the five systems are shown graphically in Figure 2.

With the acetone-chloroform-benzene system (*33*), the calculated results for the two binaries, acetone-chloroform (*4, 16, 33*) and chloroform-benzene (*33*), are in excellent agreement with the experimental data. The calculated boiling points for acetone-benzene mixture in the benzene-rich range give values slightly lower than the experimental data of Reinders and de Minjer (*33*), but are in good agreement with the recently published data of Free and Hutchison (*12*). The predicted values for this ternary system are in excellent agreement with the observed data.

The predicted and experimental results for the acetone-methanol-ethanol system (*3*) are compared in Figure 2.

The small deviation of the predicted from the observed results in the higher temperature range may be partly due to the fact that in the two binaries, acetone-ethanol and acetone-methanol, the calculated values in the ethanol-rich range are slightly lower than the observed data of Amer, Paxton, and Van Winkle (*2*), because the ternary vapor-liquid equilibrium data must be consistent with the data for its component binaries. However, the boiling point data for methanol-ethanol by Amer, Paxton, and Van Winkle are higher than the observed results of Delzenne (*6*) in high ethanol concentrations (a maximum deviation of about 1° C.), and the calculated data agree with the results of Delzenne as shown in Figure 1.

The 2-butanone–benzene–cyclohexane system consists of three minimum boiling azeotropic systems.

The two sets of experimental data (*5, 9*) for this ternary system are somewhat contradictory. The author's predicted results are in substantial agreement with the observed data of Donald and Ridgway (*9*).

The carbon tetrachloride-2-butanone-trichloroethylene system (*19*) involves a minimum boiling azeotropic system, carbon tetrachloride-2-butanone (*11*), and two ideal systems (*1, 20*). Boiling point data of each binary system are well correlated by the present method. The predicted and experimental results are compared in Figure 2.

In the cyclohexane–*n*-heptane–toluene system (*26*) the predicted and experimental results are in excellent agreement (Figure 2), probably because in each binary system the calculated results agree with the observed data.

DISCUSSION

The vapor phase under atmospheric or subatmospheric pressure is usually regarded as ideal gas, so that the ratio of the mole fractions of two components in the vapor phase is equal to that of the partial pressures of the components, as seen Equation 1—i.e.,

$$\frac{y_i}{y_j} = \frac{p_i}{p_j} = \frac{\pi}{\pi}\,\frac{(k_{ii}x_ix_i + k_{ij}x_ix_j)}{(k_{jj}x_jx_j + k_{ji}x_jx_i)} \tag{28}$$

where π is the total pressure of the mixture under consideration, p_i and p_j are the partial pressures of components i and j, respectively, and k_{ii}, k_{ij}, k_{jj}, and k_{ji} are pseudo equilibrium constants. Lu, Li, and Ting (*23*) demonstrated, in their "cluster theory" of vapor-liquid equilibria, that the k's can be defined by the combination of the equilibrium constants between clusters and molecules of the two components in the vapor and the liquid phases. As is easily seen from Equation 28, the partial pressure is the sum of the vapor pressures of like and unlike molecules. Hence the partial pressure of component i can be rewitten in its simplified formula as follows:

$$p_i = \alpha_i P_i x_i x_i + \beta_{ij} P_{ij} x_i x_j \tag{29}$$

Similarly the partial pressure of component j is expressed by the following equation

$$p_i = \alpha_j P_j x_j x_j + \beta_{ji} P_{ji} x_j x_i \tag{30}$$

where α_i, α_j, β_{ij}, and β_{ji} are constants. P_i, P_j, P_{ij}, and P_{ji} are defined below. Therefore, the total pressure π is the sum of the partial pressures of components.

$$\pi = p_i + p_j = \alpha_i P_i x_i x_i + \beta_{ij} P_{ij} x_i x_j + \alpha_j P_j x_j x_j + \beta_{ji} P_{ji} x_j x_i \tag{31}$$

The vapor pressures of the pure components and the mixture are approximately presented in a wide range of temperatures, including normal boiling point, by an integrated form of the Clausius-Clapeyron equation:

$$P_i = A_i \exp.\,(-L_i/RT) \tag{32}$$

$$\pi = B \exp.\,(-L_m/RT) \tag{33}$$

where A_i and B are constants. L_i and L_m are the heats of vaporization of the pure component i and the mixture, respectively. R is the gas constant. Although P_{ij} and P_{ji} are unknown, P_{ij} is assumed equal to P_{ji} and P_{ij} can be expressed by an equation similar to Equation 32—i.e.,

$$P_{ij} = C_{ij} \exp.\,(-L_{ij}/RT) \tag{34}$$

where C_{ij} is constant. L_{ij} corresponds to the heat of vaporization between unlike molecules.

Taking the logarithm of Equation 31 and differentiating it with $1/RT$, one obtains the following relation (*18*).

$$L_m = \frac{L_i\alpha_i P_i x_i x_i + L_{ij}(\beta_{ij} P_{ij} x_i x_j + \beta_{ji} P_{ij} x_j x_i) + L_j \alpha_j P_j x_j x_j}{\pi} \tag{35}$$

Table II. Predicted Results for Ternary Systems

System	$b_{12}\cdot b_{23}\cdot b_{31}$	No. of Points Compared	Av. Dev.	Data Source
Acetone(1)-chloroform(2)-benzene(3)	1.444	85	0.2	(*33*)
Methanol(2)-ethanol(3)	1.603	91	0.6	(*2*)
2-Butanone(1)-benzene(2)-cyclohexane(3)	1.381	85	0.2	(*5, 9*)
Carbon tetrachloride(1)-2-butanone(2)-trichloroethylene(3)	1.169	36	0.4	(*19*)
Cyclohexane(1)-*n*-heptane(2)-toluene(3)	0.894	101	0.2	(*26*)

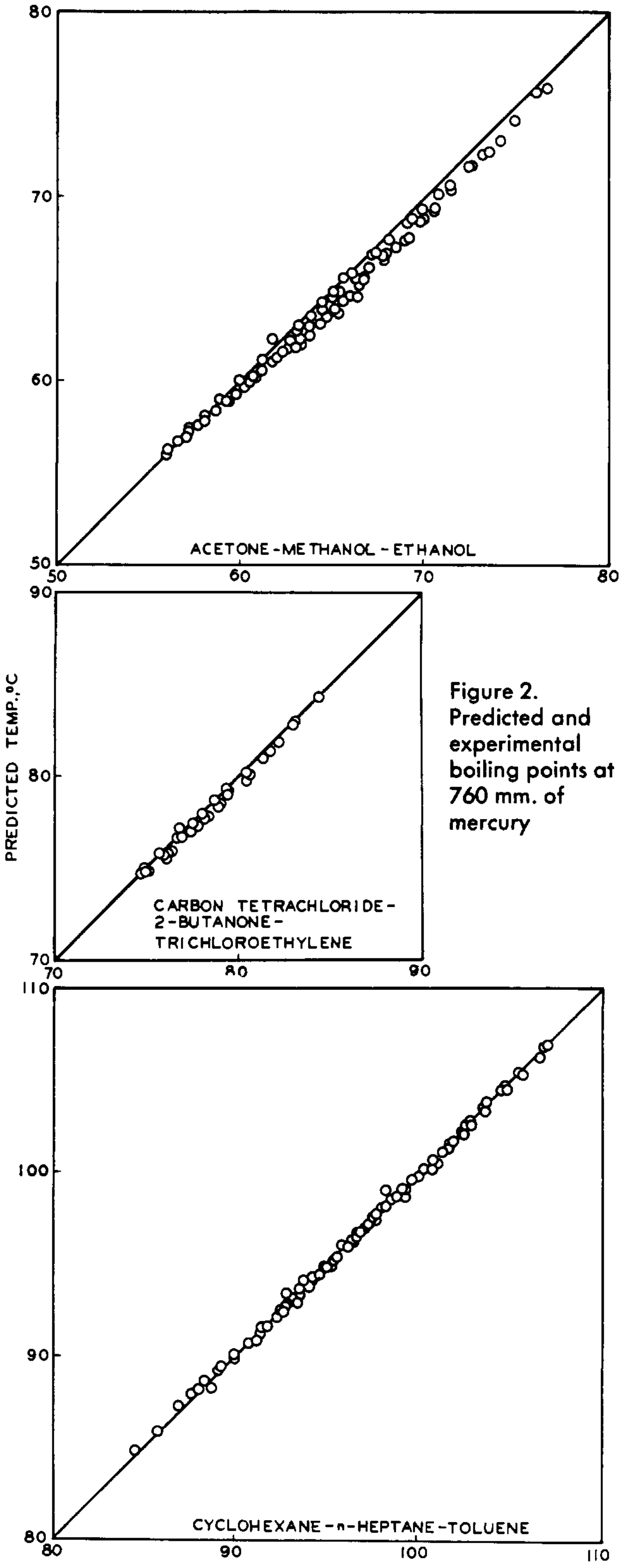

Figure 2. Predicted and experimental boiling points at 760 mm. of mercury

Hence by applying Trouton's rule to Equation 35 and comparing Equation 35 with Equation 1, Equation 2 is obtained.

For an n-component system the partial pressure of component i is expressed by

$$p_i = \alpha_i P_i x_i x_i + \beta_{ij} P_{ij} x_i x_j \tag{36}$$

Therefore, the total pressure π of the system is given by

$$\pi = \sum_i p_i = \sum_i \alpha_i P_i x_i^2 + \sum\sum_{i \neq j} \beta_{ij} P_{ij} x_i x_j \tag{37}$$

where P_i and P_{ij} are given by Equations 32 and 34. Subscripts i and j take every value from 1 to n in an n-component system. For the case, $i = j$, the second right-hand term of Equation 37 vanishes, as this term corresponds to the contribution of unlike molecules.

Taking the logarithm of Equation 37 and dividing it by $1/RT$, one obtains

$$L_m = \frac{\sum_i L\alpha P_i x_i x_i + \sum\sum_{i \neq j} L_{ij} \beta_{ij} P_{ij} x_i x_j}{\pi} \tag{38}$$

Application of Trouton's rule and comparison with Equation 27 yield Equation 26.

SAMPLE PROBLEM

Predict the boiling point for a mixture of 24.6 mole % cyclohexane, 21.3 mole % n-heptane, and 54.1 mole % toluene at 760 mm. of mercury.

Subscripts 1, 2, and 3 indicate cyclohexane, n-heptane, and toluene, respectively. First the constants a_{12}, b_{12}, and c_{12} of Equation 11 are so determined as to agree well with the available experimental x-y data of the cyclohexane-n-heptane binary system (*29, 36*).

The y's are calculated as follows:

From Equation 3

$$y_{11} = y_1 \frac{x_1}{x_1 + a_{12}x_2} = 0.624 \times \frac{0.5}{0.5 + 1.090 \times 0.5} = 0.299$$

From Equation 4

$$y_{12} = y_1 \frac{a_{12}x_2}{x_1 + a_{12}x_2} = 0.624 \times \frac{1.090 \times 0.5}{0.5 + 1.090 \times 0.5} = 0.325$$

From Equation 5

$$y_{22} = y_2 \frac{b_{12}x_2}{b_{12}x_2 + c_{12}x_1} = 0.376 \times \frac{0.647 \times 0.5}{0.647 \times 0.5 + 0.610 \times 0.5} = 0.194$$

From Equation 6

$$y_{21} = y_2 \frac{c_{12}x_1}{b_{12}x_2 + c_{12}x_1} = 0.376 \times \frac{0.610 \times 0.5}{0.647 \times 0.5 + 0.610 \times 0.5} = 0.182$$

The experimental boiling point at the equimolar composition is 88.2° C. from the composition-boiling point curve of this binary system.

Substitution of the values of y's, T_m, T_1, and T_2 in Equation 12 gives

$$T_m = T_1 y_{11} + T_2 y_{22} + T_{12}(y_{12} + y_{21})$$

$$361.4 = 353.9 \times 0.299 + 371.6 \times 0.194 + T_{12}(0.325 + 0.182)$$

Hence $T_{12} = 361.0$. Primary information on three binaries is given in Table III. This ternary system does not deviate much from the condition (17), as the value of $b_{12} \cdot b_{23} \cdot b_{31}$ is 0.894. The values of y_{11}, y_{12}, and y_{13} are calculated by using Equations 18, 20, 21, and 22 as shown in Table III. The other y's are calculated similarly. Substituting all the the values of y's and T's to Equation 19, one obtains the predicted values of $T_m = 96.0°$ C. The observed value of T_m (*26*) is 95.8° C.

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NOMENCLATURE

a, b, c = constants

Table III. Calculations for Sample Problem

1	x_1	a_{12}	b_{12}	c_{12}	$(b_{31}/b_{12})^{1/3}$	c_{31}/b_{31}	T_1	T_{12}	y_1	y_{11}	y_{12}	y_{13}	$b_{12}\cdot b_{23}\cdot b_{31}$
Cyclohexane	0.246	1.090	0.647	0.610	1.517	1.209	353.9	361.9	0.401	0.087	0.082	0.232	0.894
2	x_2	a_{23}	b_{23}	c_{23}	$(b_{12}/b_{23})^{1/3}$	c_{12}/b_{12}	T_2	T_{23}	y_2	y_{22}	y_{21}	y_{23}	
n-Heptane	0.213	1.120	0.611	0.936	1.019	0.943	371.6	373.6	0.216	0.043	0.048	0.125	
3	x_3	a_{31}	b_{31}	c_{31}	$(b_{23}/b_{31})^{1/3}$	c_{23}/b_{23}	T_3	T_{13}	y_3	y_{33}	y_{31}	y_{32}	
Toluene	0.541	1.163	2.262	2.735	0.646	1.532	383.3	364.2	0.383	0.180	0.095	0.108	

$$y_1 : y_2 : y_3 = (b_{31}/b_{12})^{1/3}\, x_1(x_1 + a_{12}x_2 + c_{31}/b_{31}\; x_3) : (b_{12}/b_{23})^{1/3}\, x_2(x_2 + a_{23}x_3 + c_{12}/b_{12}\; x_1) : (b_{23}/b_{31})^{1/3}\, x_3(x_3 + a_{31}x_1 + c_{23}/b_{23}\; x_2)$$

$$\begin{aligned} 0.401 : 0.216 : 0.383 &= 1.517 \times 0.246 \times (0.246 + 1.090 \times 0.213 + 1.209 \times 0.541) \\ &: 1.019 \times 0.213 \times (0.213 + 1.120 \times 0.541 + 0.943 \times 0.246) \\ &: 0.646 \times 0.541 \times (0.541 + 1.163 \times 0.246 + 1.532 \times 0.213) \end{aligned}$$

$$y_{11} = y_1 \frac{x_1}{x_1 + a_{12}x_2 + c_{31}/b_{31} \times x_3} = 0.401 \times \frac{0.246}{0.246 + 1.090 \times 0.213 + 1.209 \times 0.541} = 0.087$$

$$y_{12} = y_1 \frac{a_{12}x_2}{x_1 + a_{12}x_2 + c_{31}/b_{31} \times x_3} = 0.401 \times \frac{1.090 \times 0.213}{0.246 + 1.090 \times 0.213 + 1.209 \times 0.541} = 0.082$$

$$y_{13} = y_1 \frac{c_{31}/b_{31} \times x_3}{x_1 + a_{12}x_2 + c_{31}/b_{31} \times x_3} = 0.401 \times \frac{1.209 \times 0.541}{0.246 + 1.090 \times 0.213 + 1.209 \times 0.541} = 0.232$$

$$\begin{aligned} T_m &= T_1y_{11} + T_2y_{22} + T_3y_{33} + T_{12}(y_{12} + y_{21}) + T_{13}(y_{13} + y_{31}) + T_{23}(y_{23} + y_{32}) \\ &= 353.9 \times 0.087 + 371.6 \times 0.043 + 383.8 \times 0.383 + 361.9(0.082 + 0.048) + 364.2(0.232 + 0.095) + 373.6(0.125 + 0.108) \\ &= 369.2 \end{aligned}$$

A, B, C = constants
k = equilibrium constant
L = heat of vaporization
p = partial pressure
P = vapor pressure
R = gas constant
T = boiling point
T_{ij} = arbitrary constant
x = mole fraction in liquid phase
y = mole fraction in vapor phase
y_{ij} = variable
α, β = constants
π = total pressure

Subscripts

$1, 2, \ldots\ i, j, \ldots\ n$ = number of component
a = azeotrope
m = mixture

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