Vapour–liquid equilibria in the ternary system
ethyl acetate–benzene–*cyclo*hexane

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Abstract—The vapour–liquid equilibrium compositions and temperatures covering the entire composition range were determined experimentally under isobaric conditions of 760 mm Hg pressure for the ternary system ethyl acetate – benzene – *cyclo*hexane and its three constituent binaries.

A continuous recirculating equilibrium still combining the best features of Jones and Gillespie stills was used.

Values of activity coefficients and their ratios were correlated by Redlich–Kister equations. A modification of these equations was introduced to satisfy the Gibbs–Duhem equation at constant pressure.

Résumé—Les auteurs ont étudié expérimentalement, sous 760 mm Hg, les courbes de rosée et d'ébullition du système ternaire acétate d'éthyle–benzène–cyclohexane et des trois mélanges binaires.

Ils ont utilisé un ébulliomètre dynamique présentant les principales caractéristiques des ébulliomètres de Jones et Gillespie.

Ils ont déterminé les valeurs des coefficients d'activité et leurs rapports par les équations de Redlich–Kister.

Ils ont introduit une modification de ces équations pour satisfaire à la relation de Gibbs–Duhem.

Zusammenfassung—Zusammensetzungen und Temperaturen des Dampf–flüssig–Gleichgewichts über den ganzen Bereich der Zusammensetzungen wurden experimentell unter isobaren Bedingungen bei 760 Torr für das ternäre System Äthylazetat–Benzol–Cyclohexan und die drei darin enthaltenen Zweistoffsysteme bestimmt.

Verwendet wurde eine kontinuierliche Umlauf–Gleichgewichtsapparatur unter Ausnutzung der besten Vorschläge von Jones und Gillespie.

Werte der Aktivitätskoeffizienten und ihrer Quotienten wurden durch Gleichungen nach Redlich und Kister wiedergegeben. Diese Gleichungen waren abgeändert, um die Gibbs–Duhem–Gleichung bei konstantem Druck zu befriedigen.

OBJECTIVES

MOST of the published data on vapour–liquid equilibria pertain to binary systems. Data covering the entire composition range on relatively few systems have been published. From an industrial standpoint experimental data on ternary systems are essential because of their frequent incidence in chemical processing and their growing importance in azeotropic distillation and solvent extraction. From a theoretical standpoint such investigations are also important in establishing useful relations between the behaviours of multicomponent systems and those of lower-order constituent systems.

This investigation has the following objectives: To determine the vapour–liquid composition-temperature relations at 760 mm Hg pressure of the ternary system ethyl acetate–benzene–*cyclo*hexane and its three binaries; to correlate the experimental data of activity coefficients of the ternary system and its three binaries in terms of composition; and to compare the correlation constants in equations for isobaric vaporization in conventional and corrected forms.

The particular ternary system ethyl acetate–benzene–cyclohexane was selected because of its possible industrial importance in the separation of the benzene–cyclohexane azeotrope by distillation with ethyl acetate. The mixture of benzene and cyclohexane is an industrial product resulting from the catalytic hydrogenation of benzene to form cyclohexane.

The addition of ethyl acetate to the binary system benzene–cyclohexane in fractional distillation results in the separation of benzene from the binary azeotrope of cyclohexane–ethyl acetate. The separation of ethyl acetate from this latter azeotrope may then be made by solvent extraction with water.

Previous Literature

The three binary systems reported in this research have been investigated by TAO [19] at pressures of 1, 10, 20 and 30 atm. The benzene–cyclohexane system has been investigated by SCATCHARD, WOOD and MOCHEL [16] at 39·99° and 69·98°C and by RICHARDS and HARGREAVES [14] at 759 mm Hg. Furfuraldehyde and methyl cellosolve in ternary systems with benzene–cyclohexane have been studied by THORNTON and GARNER [20], [21]. The ternary system selected for this investigation has not been previously reported in the literature.

Equilibrium Still

The continuous equilibrium still used in this investigation (Figs. 1 and 2) is essentially a combination of the JONES [9] and GILLESPIE [5] types.

With reference to Fig. 1, contact between vapour and liquid is secured in the mixing chamber A from which vapour with entrained liquid rises to impinge on the thermowell W_2 located in the separator D. The liquid falls to the trap E, of 23 ml capacity. Liquid overflows from this trap, to the mixing chamber thus completing the circuit for the liquid. Vapour escaping from the separator is totally condensed in condenser F and collected in the condensate trap G from which the condensate flows at a closely controlled rate into the vaporizer K. Upon complete vaporization the vapour bubbles
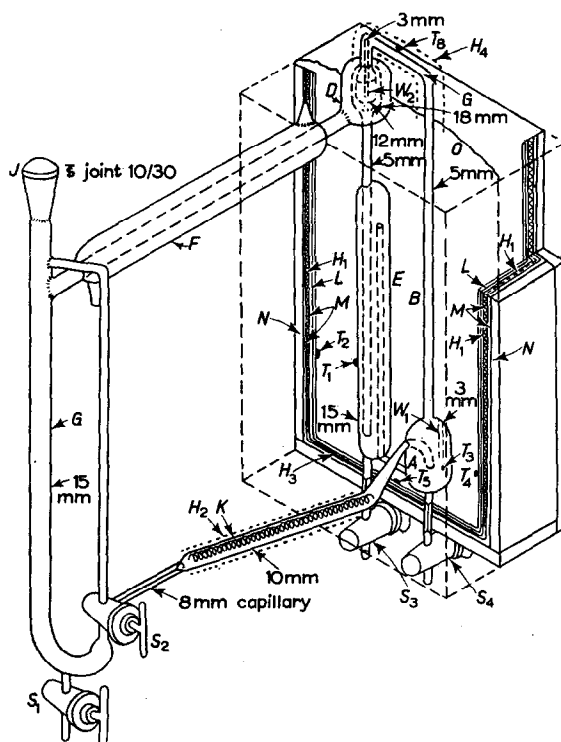

FIG. 1. Equilibrium still.

through the liquid in the mixing chamber A, completing its circuit.

To obtain significant data it is essential to circulate the liquid under adiabatic conditions. For this purpose an insulating jacket encloses the liquid trap and the mixing chamber. The innermost part of the jacket consists of a sheet-metal box L with dimensions $2\frac{1}{4}$ x $4\frac{3}{4}$ x 10 in. Two layers of asbestos fabric M are wrapped around this box with a chromel ribbon heater H_1 placed in between the layers. An outer box made of plywood $\frac{3}{8}$ in. thick encloses the assembly ($3\frac{1}{4}$ x 6 x $10\frac{1}{4}$ in.). The space inside the sheet metal box is filled with Santocel insulation.

The vapour–liquid tube C that extends above the jacket is wrapped with glass wool and wound with a heating wire H_4 to permit adiabatic performance.

Auxiliary iron–constantan thermocouples for purposes of adiabatic control are attached to the

wall of the mixing chamber, of the residue liquid trap and to the different sides of the sheet-metal box.

The equipment is heated electrically with four chromel ribbon and wire heaters controlled by three Variacs. Heater 1 consists of chromel-A ribbon ($\frac{1}{16}$ x 0·04 in., resistance 2·44 Ω/ft, the total resistance being 160 Ω) wound uniformly on all four sides of the adiabatic jacket which encloses the entire liquid recirculating system. Heater 2 consisting of chromel-A wire (size 30; 6·71 Ω/ft, the total resistance being 68 Ω) supplies heat to the vaporizer. Heater 3 supplies heat to the bottom of the adiabatic jacket. This heater consists of chromel–A wire having a total resistance of 20 Ω as in heater 2; the wire is enclosed between two layers of asbestos fabric as in heater 1. Heater 4 maintains adiabatic conditions in the vapour–liquid tube C which extends above the box enclosure.

To promote even heating a sheet of aluminium foil surrounds the vaporizer; the foil is separated from the heating coil by a layer of glass wool. A closely wound coil of 22 gauge copper wire fits tightly against the inner wall of the vaporizer to act as a liquid distributor. This coil induces a liquid film to form and wet the entire inner surface of the tube.

To maintain the still at constant pressure, a regulating device is attached to the top opening of the condensate trap of the equilibrium still through an auxiliary condenser. This control is effected by bleeding compressed air through a nozzle immersed in water, the depth of immersion being adjusted to compensate for variations in the atmospheric pressure. With this device the pressure in the still may be kept constant within an accuracy of 1·5 mm of water.

The equilibrium temperature was measured by a calibrated copper constantan thermocouple T_B located in thermowell W_2 in the separator; the thermowell being filled with liquid silicone for improved thermal contact. The accuracy of readings was within 0·1°C. Readings of thermocouple T_A located in the mixing chamber A were made for comparison with those of couple T_B.

All auxiliary thermocouples were iron constantan recording to an accuracy of 1°F.

OPERATION OF THE EQUILIBRIUM STILL

In starting operation the adiabatic jacket and the tube to the separator are heated to the anticipated temperature, about 2 hr being required for preheating. Cooling water is admitted to the total condenser, and heat applied to the vaporizer. A voltage of 35 to 40 V is applied to heater 2 for about 5 min before admitting feed to the still. The auxiliary condenser is removed from the still and the stopcock leading to the vaporizer is slightly opened. Then a charge of known composition is fed to the condensate trap through a connection leading to the auxiliary condenser. A mixture of liquid and vapour passes into the mixing chamber; about 68 ml of total liquid charge is required. The liquid should be supplied gradually so that boiling may be continuous in the vaporizer; this insures saturation of the liquid in the liquid trap as soon as the charging operation is completed. Feeding usually takes about 15 min, after which the stopcock S_2 leading to the vaporizer K is partly closed to its normal operating position. The auxiliary condenser is restored and the cooling water circulated. A constant pressure of 760 mm Hg is applied to the still.

During operation adiabatic conditions are maintained by adjusting the adiabatic heaters H_1, H_3, H_4 so as to equalize the temperature readings of thermocouples T_1 and T_3 and those on the adiabatic jacket. Thermocouples T_1 and T_3 show no disagreement after a short period of operaton. Temperatures on the different parts of the adiabatic jacket may vary by 2°F, a range which is adjusted to include the temperatures of thermocouples T_1 and T_3; thus the temperature difference across the Santocel insulation is in every case less than 2°F.

Heat to the vaporizer is controlled so as to cause the last trace of condensate to disappear just at the end of the vaporizer, a condition which can be observed visually. The sensitivity of this observation is enhanced by the V-shape of the vaporizer permitting traces of liquid to be easily seen in the bottom of the V.

Equilibrium conditions were usually reached within 1 hr of operation. It was customary to

operate 90 min before taking equilibrium readings.

At the end of each run, the stopcock S_2 leading to the vaporizer is closed and the vaporizer heater turned off. The stopcocks below the condensate trap and the liquid trap are opened to sampling bottles after purging the line with 8 ml of the liquid. When samples have been withdrawn the entire content of the still is emptied in preparation for the next run.

No difficulty was encountered in securing leak-proof operation of the two stopcocks S_1 and S_2 of the condensate trap; these stopcocks were not greased. However, difficulty was experienced with the two stopcocks S_3 and S_4 below the mixing chamber and the liquid trap. It was found necessary to use high vacuum grade cocks to obtain good service; these required lubrication. A thin layer of silicone lubricant was applied, but it was necessary to assure that no contamination resulted from this source. To verify the absence of contamination the three pure liquids used in this study were tested separately. The first 5 ml of liquid withdrawn from the sampling port were collected, but only in the case of benzene was the first 5 ml sample found different from the liquid in the trap. Further samples showed exactly the same refractive index as the original feed. Contamination of the first 5 ml in the case of benzene corresponds to a change of 0·0001 in refractive index. The capillary tube connection to the greased stopcocks prevented contamination by diffusion. To insure no contamination 8 ml of liquid were purged from the line before liquid samples were taken for analysis.

ESTABLISHMENT OF EQUILIBRIUM

An inherent advantage of the vapour recirculation still is that the two phases retain their separate compositions and flow rates, with no net vaporization or condensation. Thus a steady state attained under conditions of recirculation is an unmistakable sign of equilibrium. The following five conditions of operation were essential to assure the establishment of equilibrium conditions.

(1) One manifestation of steady state is the constancy of the boiling point of the liquid as measured by thermocouple T_B. Variation in this reading usually disappears after about 80 min operation.

(2) Constancy of composition of the vapour and liquid streams throughout is another indication of steady state and equilibrium. Since the amount of material circulating in the still must be maintained within close limits it is not possible to withdraw samples sufficiently large for analysis and to continue operating at the same time. The volume of liquid in the still is critical for proper operation of the vapour lift, and the amount of condensate is critical in furnishing the proper hydrostatic head to force the liquid into the vaporizer. A series of runs were made on about the same mixture of benzene and ethyl acetate in order to determine variation in composition of liquid in the still with residence time.

Mixtures of benzene and ethyl acetate containing about 30 mole per cent of ethyl acetate were charged to the still. Successive runs of different time intervals were made and the results are given in Table 1.

Table 1.

Length of operation (min)	x_A	$y_A - x_A$	Run number
30	0.308	0·025	AB-19
40	0·303	0·028	AB-17
60	0·274	0·029	AB-16
90	0·288	0·029	AB-18

Even though there is no trend in x_A values, the trend in $y_A - x_A$ is evident. Steady state conditions were obtained in from 40 to 60 min. It was concluded that 90 min of operation gave an ample margin of safety.

(8) That equilibrium was attained at the end of the runs was further confirmed by withdrawing samples from the mixing chamber. In all acceptable runs the samples showed the same composition as those taken from the liquid trap. Identity of composition in the liquid trap and in the mixing chamber indicates that equilibrium was established.

(4) In all instances constancy of the liquid level in the condensate trap gives an unmistakable

sign of thermal balance of the liquid recirculation system. This is one of the prerequisites to equilibrium and must be carefully watched throughout operation. In all acceptable runs change in the amount of condensate in the trap was scarcely noticeable, and never exceeded 0·2 ml. Even under the most unfavourable conditions where this change would take place instantly the maximum error that could be made with the most sensitive of the three systems would be 0·1 per cent.

(5). The vapour lift action in this still necessarily induces a temperature change due to variation in hydrostatic pressure with elevation. This pressure reduction is accompanied by vaporization of a portion of the liquid, and this would continuously increase the inventory in the condensate trap and deplete the inventory in the liquid trap. The change in saturation temperature due to hydrostatic head in the still is slight. Thus temperature measurements at the bottom and top of the vapour lift, using thermocouples T_A and T_B, showed a difference of 0·1 to 0·2°C between the two locations under steady conditions. That this hydrostatic effect is not appreciable, but comparable to that of imperfect adiabatic conditions around the liquid recirculation system, is conclusively shown by the constancy of the amount of material in the two separate streams.

The equilibrium pressure was maintained at a standard atmospheric pressure for all runs. Any discrepancy between the prevailing atmospheric pressure and the standard pressure was compensated for by applying compressed air to the system. That the pressure applied to the system though the auxiliary condenser actually represents the equilibrium pressure of the mixture depends on the negligible pressure difference for the vapour flow in the separator and in the condenser. This pressure drop was calculated not to exceed 0·0081 cm of water.

ANALYTICAL PROCEDURE

Analyses of the three binary systems are readily carried out by measurements of refractive index and specific gravity. Measurements of these physical properties against mixtures of known composition were made.

For measuring refractive indices a Baush and Lomb Abbé refractometer was used. All measurements were performed at 25 ± 0.1°C, the precision of refractive index readings being ± 0.0001.

For specific gravity measurements a modified Sprengel type pycnometer was used (Fig. 3). This weighed 17 g and held 10 ml of liquid in a single bulb with capillary connection tubing of 0·7 mm bore. The reproducibility of the specific gravity measurement was ± 0.0001 at 25°C. The compositions of binary systems determined by these two measurements did not differ by more than 0·1 mole per cent.

The physical properties of the standard binary mixtures are shown in Tables 1, 2, and 3, and in Figs. 4 and 5.
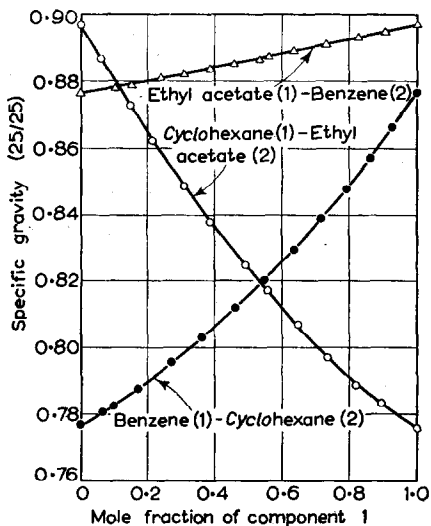

FIG. 4. Specific gravities of binary mixtures.

For calibration purposes specific gravities and refractive indices of ternary mixtures of known composition were measured over the entire composition range at intervals of 10 mole per cent for a total of 66 mixtures; the calibration data are shown in Table 4. By linear interpolation isometric lines were constructed representing loci of constant values for each physical property. (Fig. 6). The isometric lines all merge into terminals on the edge of the triangular diagram coincident with data for the binary mixtures. Linear interpolation between the contour lines
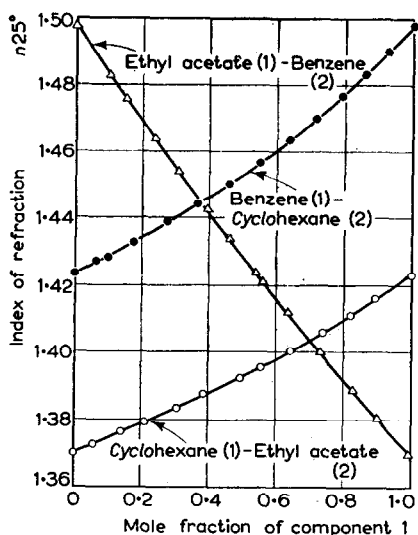
FIG. 5. Refractive indices of binary mixtures.

gives the composition of an unknown sample once its refractive index and specific gravity were determined.
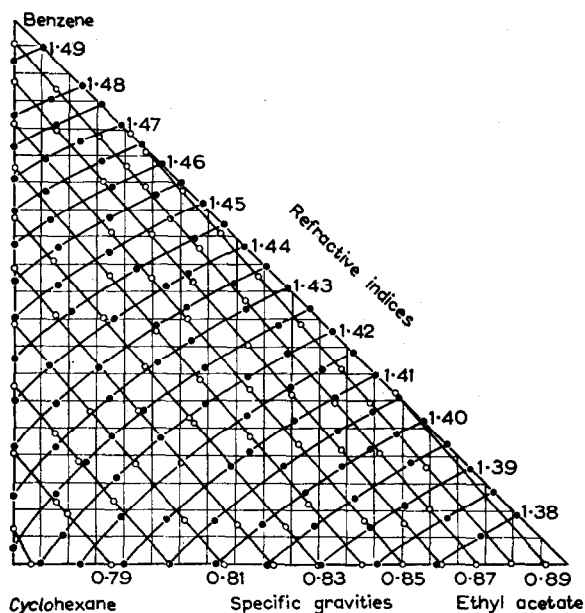

FIG. 6. Refractive indices and specific gravities of the ternary mixtures.

The precision of determining composition is ± 0·1 mole per cent for the binary mixtures and ± 0·2 mole per cent for the ternary mixture.

PREPARATION OF MATERIALS

The ethyl acetate of 99·9 per cent purity was obtained from Merck and Co., Inc. The chief impurity, water, was removed by storage over silica gel.

Benzene, of 99·9 per cent purity, was also obtained from Merck and Co. Further purification was obtained by fractional crystallization repeated three times.

*Cyclo*hexane of Research Grade (Lot Number 435), of guaranteed purity 99·94 per cent was obtained from the Phillips Petroleum Co., and used directly.

The physical properties of the purified reagents as measured are tabulated in Table 2 for comparison with literature values.

Table 2.

	Ethyl acetate	*Benzene*	*Cyclo-hexane*
Refractive index at 25°C			
Experimental	1·3698	1·4980	1·4235
Literature	1·37005 [7]	1·49790 [2]	1·42354 [3]
Specific gravity (25°/25°)			
Experimental	0·8970	0·8762	0·7759
Density (25°)			
Experimental	0·8944	0·8736	0·7736
Literature	0·89446 [8]	0·87362 [10]	0·7739 [4]
Boiling point °C			
Experimental	77·2	80·1	80·7
Literature	77·1 [17]	80·1 [17]	80·7 [17]

AZEOTROPES

Because of the very close compositions of liquid and vapour in the equilibrium mixtures of ethyl acetate and benzene at high concentrations of ethyl acetate there is some uncertainty about the existence of azeotropism for this system. RYLAND [15] in 1899 reported the absence of azeotropism. LECAT [11] in 1918 reported an azeotropic composition of 93 mole per cent of ethyl acetate, but the reliability of this finding was questioned by the same author. SWIETOSLAWSKI [18] in 1932 confirmed RYLAND's finding. TAO [19] in 1952 reported an azeotropic composition of 91 mole

per cent of ethyl acetate. To resolve the uncertainty, both Tao's data and the data of this study were plotted in terms of γ_A/γ_B against x_A. On the same figure was plotted the ratio P_B/P_A against x_A, the experimental temperature being used for calculating the vapour pressure ratio. Azeotropism would be indicated by intersection of the two lines. The two sets of data agree up to $x_A = 0.92$. The temperature measurements also agree to within 0·1°C in both investigations. Judging by the trend of the data it is unlikely that an azeotrope exists. The one-constant equation giving a maximum deviation of 0·1 mole per cent for all the experimental measurements supports this observation in not giving any azeotropic composition.

For the binary system *benzene* – cyclo*hexane* the reported values of azeotropic composition and temperature at 1 atm pressure are shown in Table 3.

Table 3

	Benzene (mole per cent)	Temperature °C
Lecat [11]	55	77·5
Richards and Hargreaves [14]	51·6	77·4
Marschner and Cropper [12]	53·7	77·7
Thornton and Garner [20]	53·0	77·6
Tao [19]	50·0	77·4
This investigation	53·7	77·6

For the binary system cyclo*hexane – ethyl acetate* the reported values of the azeotropic composition and temperature at 1 atm pressure are given in Table 4.

Table 4.

	Acetate (mole per cent)	Temperature °C
Lecat [11]	53	72·8
Tao [19]	53·8	72·0
This investigation	54·9	71·6

No azeotrope was found for the ternary system. All the ternary mixtures experimentally studied

boil at a higher temperature than the azeotropic mixture of *cyclo*hexane and ethyl acetate. This binary mixture is indeed the lowest boiling of all the solutions prepared with the three given components. Fig. 11 shows that there is a definite trend for all the equilibrium tie lines on the ternary diagram to converge toward the composition of this binary azeotrope. Data point *ABC*-79 was determined specifically for the purpose of ascertaining if any ternary azeotrope in the neighbourhood of this binary azeotrope might form, but the finding was negative. The liquid phase of this ternary mixture contains only 2·9 mole per cent of benzene, but the boiling point is thereby slightly increased, and the equilibrium vapour contains even less benzene.

THEORETICAL CONSIDERATIONS

Equilibrium between the vapour and liquid of a multi-component system is attained when the pressure and temperature is the same throughout the system and when the fugacity of each component in the two phases is the same, that is $f_{iv} = f_{iL}$. Under these conditions the relation of vapour composition to liquid composition for ideal solution behaviour is expressed as :—

$$y_i f_{iv}^\circ = x_i f_{iL}^\circ \tag{1}$$

where at the temperature and pressure of the system,

f_{iv}° and $f_{iL}^\circ =$ fugacities of pure component i in the respective vapour and liquid phases.

Any lack of ideal solution behaviour in each phase is allowed for by arbitrary terms designated as activity coefficients, γ_{iv} and γ_{iL}, thus :—

$$\gamma_{iv} y_i f_{iv}^\circ = \gamma_{iL} x_i f_{iL}^\circ \tag{2}$$

Here the standard state fugacities f_{iv}°, f_{iL}° are related to pressure by fugacity coefficients $\nu_{i\pi}$ and ν_{ip}, thus :—

$$f_{iv}^\circ = \nu_{i\pi}\pi \text{ and } f_{ip}^\circ = \nu_{ip} P_i \tag{3}$$

$\pi =$ total pressure

$P_i =$ vapour pressure of pure liquid component i at the temperature of the system

At atmospheric pressure and below, the activity coefficient in the vapour phase γ_{iv} is unity and the ratio of fugacity coefficients $\nu_{i\pi}/\nu_{ip}$ is nearly unity, hence

$$y_i \pi = \gamma_{ip} x_i P_i \qquad (4)$$

From measurements of y_i, x_i, P_i, and π the activity coefficient γ_i is evaluated.

In a binary system at constant pressure and temperature the variation of activity coefficients with composition is related by the Gibbs-Duhem equation :—

$$[(\partial \ln \gamma_1)/(\partial \ln x_1) = (\partial \ln \gamma_2)/(\partial \ln x_2)]_{pT} \qquad (5)$$

The excess free energy μ_i^E of any component i in solution is related to its activity coefficient, thus

$$\mu_i^E = RT \ln \gamma_i \qquad (6)$$

For a binary system :—

$$G^E = x_1 \mu_1^E + x_2 \mu_2^E = RT (x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \qquad (7)$$

For conditions of constant temperature and pressure REDLICH and KISTER [13] have related excess free energy to composition by a series function using terms sufficient to fit the experimental data, thus :—

$$\left\{ G^E = RT x_1 x_2 \left[B' + C' (x_1 - x_2) \right. \right.$$
$$\left. \left. + D' (x_1 - x_2)^2 + \ldots \right] \right\}_{pT} \qquad (8)$$

The terms $x_1 x_2$ provide for the zero value of G^E at compositions corresponding to the separate pure components. Formulations for individual activity coefficients are obtained from equation (8) through the definition of a partial property, thus :—

$$\mu_i^E = [(\partial/\partial n_1) (n_1 + n_2) G^E]_{pT} = RT \ln \gamma_1 \qquad (9)$$

to give :—

$$\left.\begin{aligned}
\ln \gamma_1 &= x_1 x_2 \left[B' + C' (x_1 - x_2) \right. \\
&\quad + D' (x_1 - x_2)^2 + \ldots] \\
&\quad + x_2 \left[B' (x_2 - x_1) + C' (6x_1 x_2 - 1) \right. \\
&\quad + D' (x_1 - x_2) (8x_1 x_2 - 1) + \ldots] \\
\ln \gamma_2 &= x_1 x_2 \left[B' + C' (x_1 - x_2) \right. \\
&\quad + D' (x_1 - x_2)^2 + \ldots] \\
&\quad - x_1 \left[B' (x_2 - x_1) + C' (6x_1 x_2 - 1) \right. \\
&\quad + D' (x_1 - x_2) (8x_1 x_2 - 1) + \ldots]
\end{aligned}\right\} \quad (10)$$

Subtracting the two parts of equation (10) gives :—

$$\ln (\gamma_1/\gamma_2) = B' (x_2 - x_1) + C' (6x_1 x_2 - 1)$$
$$+ D' (x_2 - x_1) (1 - 8x_1 x_2) + \ldots \qquad (11)$$

The same relationship for $\ln (\gamma_1/\gamma_2)$ may be obtained by differentiation of equation 8 with respect to x_1 :—

$$[(\partial/\partial x_1) (G^E/RT) = \ln \gamma_1 - \ln \gamma_2$$
$$= \ln (\gamma_1/\gamma_2)]_{pT} \qquad (12)$$

Thus experimental data on activity coefficients can be correlated by using a single equation in terms of the ratio of activity coefficients without requiring separate expressions for the individual coefficients.

ISOBARIC CONDITIONS

For vapour–liquid equilibrium in a binary system at constant pressure, temperature is fixed by composition and is not an independent variable. Hence the functional form of equation (8) may also be used to express excess free energy under isobaric conditions using slightly different numerical constants. The constants in the equation are then dependent on pressure only. Thus, at constant pressure

$$\left\{ G^E = RT x_1 x_2 \left[B + C (x_1 - x_2) \right. \right.$$
$$\left. \left. + D (x_1 - x_2) + \ldots \right] \right\}_p \qquad (13)$$

In its conventional form the Gibbs–Duhem equation is given at conditions of constant temperature and pressure. IBL and DODGE [6] have extended the Gibbs–Duhem equation to conditions of constant pressure and variable temperature. Since $\ln \gamma$ is at constant pressure, a continuous and single-valued function of temperature and composition, for a binary system in the liquid phase, the following exact differential equations may be written :—

$$[d \ln \gamma_1 = (\partial \ln \gamma_1/\partial T)_{px_1} dT$$
$$+ (\partial \ln \gamma_1/\partial \ln x_1)_{pT} \, d \ln x_1]_p \qquad (14)$$

and similarly for component 2.

The variations of activity coefficients with temperatures at constant pressure and composition are given as follows :—

$$(\partial \ln \gamma_1 / \partial T)_{px_1} = (H_1^\circ - \bar{H}_1)/RT^2 \quad (15)$$

and similarly for component 2. Combining equations (5), (14), and (15) gives :—

$$[(d \ln \gamma_1)/(d \ln x_1) = (d \ln \gamma_2)/(d \ln x_2) + Z]_p \quad (16)$$

where

$$Z = - (\Delta H / RT^2)(dT/dx_1)_p$$

$$\Delta H = H - x_1 H_1^\circ - x_2 H_2^\circ$$

H, H_1°, H_2° = the molal enthalpies of mixtures and components, respectively, each in the liquid phase.

The term ΔH is the integral heat of solution in dissolving liquid components in their standard states to form a liquid solution of given composition at constant pressure and corresponding temperature.

From equation (16)

$$[x_1 \, d \ln \gamma_1 + x_2 \, d \ln \gamma_2 = Z \, dx_1]_p \quad (17)$$

From equations (7) and (16) :—

$$\left. \begin{array}{l} [(d/dx_1)(G^E/RT) = \\ \quad \ln \gamma_1 - \ln \gamma_2 + (d \ln \gamma_1)/(d \ln x_1) \\ \quad - (d \ln \gamma_2)/(d \ln x_2) \\ \quad = \ln \gamma_1 - \ln \gamma_2 + Z]_p \end{array} \right\} \quad (18)$$

The values of Z are difficult to determine experimentally since they involve measurements of the variation of temperature with compositions at constant pressure and the heats of solution which involve hypothetical standard states. These measurements are circumvented by including the effect of Z in the empirical equation for the ratio of activity coefficients, thus retaining the same form as for isothermal conditions but with constants having slightly different numerical values depending upon the magnitude of Z, thus :

$$\ln \gamma_1 / \gamma_2 = b(x_2 - x_1) + c(6x_1 x_2 - 1)$$
$$+ d(x_2 - x_1)(1 - 8x_1 x_2) + \ldots \quad (19)$$

Using identical forms for isothermal and isobaric conditions is not mandatory. This proved satisfactory for the three binary systems under investigation, but it might require additional terms for systems where Z is large. With this particular form, the integral $\int_0^1 \ln (\gamma_1/\gamma_2) \, dx_1$ is zero for both isothermal and isobaric conditions. For isobaric conditions, the integral is not necessarily zero, and might be accounted for by additional terms dissimilar to those in the isothermal equation.

Subtracting equation (18) from (7) :—

$$\ln \gamma_2 = (G^E/RT) - x_1 [(d/dx_1)(G^E/RT) - Z] \quad (20)$$

Combining equations (13), (19) and (20) :—

$$\left. \begin{array}{l} \ln \gamma_2 = x_1 x_2 [B + C(x_1 - x_2) \\ \qquad\qquad + D(x_1 - x_2)^2 + \ldots] \\ \quad - x_1 [b(x_2 - x_1) + c(6x_1 x_2 - 1) \\ \qquad\qquad + d(x_1 - x_2)(8x_1 x_2 - 1) + \ldots] \end{array} \right\} \quad (21)$$

Similarly,

$$\begin{array}{l} \ln \gamma_1 = x_1 x_2 [B + C(x_1 - x_2) \\ \qquad\qquad + D(x_1 - x_2)^2 + \ldots] \\ \quad + x_2 [b(x_2 - x_1) + c(6x_1 x_2 - 1) \\ \qquad\qquad + d(x_1 - x_2)(8x_1 x_2 - 1) + \ldots] \end{array}$$

In calculating vapour compositions, temperature sensitivity is minimized by using ratios of activity coefficients and vapour pressures by combining equation (4) for the two components, thus :—

$$\left. \begin{array}{l} y_1 = (\gamma_1 x_1 P_1)/E(\gamma_2 x_2 P_2) \\ y_2 = 1/E \\ E = (\gamma_1 x_1 P_1)/(\gamma_2 x_2 P_2) + 1 \end{array} \right\} \quad (22)$$

For calculating temperatures under isobaric conditions it is necessary to have equations for the separate activity coefficients, and then by trial and iteration to establish the temperature which satisfies the relation $y_1 \pi = x_1 \gamma_1 P_1$ in agreement with the correct value of the vapour pressure of the pure component.

TERNARY SYSTEMS UNDER ISOBARIC CONDITIONS

The excess free energy of a ternary mixture is related to the activity coefficient by the expression :—

$$\begin{array}{l} G_{123}^E = x_1 \mu_1^E + x_2 \mu_2^E + x_3 \mu_3^E \\ \qquad = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2 + x_3 \ln \gamma_3) \quad (23) \end{array}$$

Under conditions of constant pressure :—

$$G_{123}^E = G_{12}^E + G_{23}^E + G_{31}^E \\
+ RT\, x_1\, x_2\, x_3\, [B + C_1(x_2 - x_3) \\
+ c_2(x_3 - x_1) + c_3(x_1 - x_2) + \ldots] \quad (24)$$

Here the first three terms on the right side represent contributions by the separate binaries and the last term represents ternary effects. The binary contributions are related by assigning appropriate constants to equation (13), thus for G_{12}^E :—

$$G_{12}^E = RT\, x_1\, x_2\, [B_{12} + C_{12}(x_1 - x_2) \\
+ D_{12}(x_1 - x_2)^2 + \ldots] \quad (25)$$

As the temperature is fixed by composition the constants in equations (24) and (25) are dependent on pressure only.

The modified Gibbs–Duhem equation for a ternary system under isobaric conditions is given by an expansion of equation (17) thus :—

$$x_1\, d\ln\gamma_1 + x_2\, d\ln\gamma_2 + x_3\, d\ln\gamma_3 \\
= -(\Delta H/RT^2)\, dT \quad (26)$$

On differentiating equation (23) and combining with (26) the individual activity coefficients may be expressed in terms of G^E :—

$$\ln\gamma_1 = \\
\frac{G^E}{RT} + \left[\frac{\partial}{\partial x_1}\left(\frac{G^E}{RT}\right)\right]_{x_2} + \frac{\Delta H}{RT^2}\left(\frac{\partial T}{\partial x_1}\right)_{x_2} \\
- x_1\left\{\left[\frac{\partial}{\partial x_1}\left(\frac{G^E}{RT}\right)\right]_{x_2} + \frac{\Delta H}{RT^2}\left(\frac{\partial T}{\partial x_1}\right)_{x_2}\right\} \\
- x_2\left\{\left[\frac{\partial}{\partial x_2}\left(\frac{G^E}{RT}\right)\right]_{x_1} + \frac{\Delta H}{RT^2}\left(\frac{\partial T}{\partial x_2}\right)_{x_1}\right\} \quad (27)$$

and similarly for the other components. The ratio of the activity coefficients follows :—

$$\ln(\gamma_1/\gamma_2) = \\
[(\partial/\partial x_1)(G^E/RT)]_{x_3} \\
+ (\Delta H/RT^2)(\partial T/\partial x_1)_{x_3} \quad (28)$$

and similarly for the other ratios.

Expressions of activity coefficients and their ratios explicitly in terms of compositions result

upon substituting equation (24) into equations (27) and (28), respectively. The difficulties with the correction terms $(\Delta H/RT^2)(\partial T/\partial x)$ are circumvented by modifying the constants as done with the binary system, thus :—

$$\ln\gamma_1 = (G_{123}^E/RT) + [x_2(x_2 + x_3) \\
- x_1 x_2][b_{12} + c_{12}(x_1 - x_2) + \ldots] \\
- 2x_2 x_3[b_{23} + c_{23}(x_2 - x_3) + \ldots] \\
+ [(x_3 - x_1)(x_2 + x_3) + x_1 x_2] \\
[b_{31} + c_{31}(x_3 - x_1) + \ldots] \\
+ [x_1 x_2(x_2 + x_3) + x_1 x_2^2](c_{12} + \ldots) \\
+ [x_2 x_3(x_2 + x_3) - 2x_2^2 x_3](c_{23} + \ldots) \\
+ [-2x_3 x_1(x_2 + x_3) + x_1 x_2 x_3](c_{31} + \ldots) \\
+ [(x_2 + x_3)(x_2 x_3 - x_1 x_2) \\
- x_2(x_1 x_3 - x_1 x_2)][b + c_1(x_2 - x_3) \\
+ c_2(x_3 - x_1) + c_3(x_1 - x_2) + \ldots] \\
+ x_1 x_2 x_3[(x_2 + x_3)(c_1 - 2c_2 + c_3) \\
- x_2(2c_1 - c_2 - c_3) + \ldots] \quad (29)$$

where G_{123}^E is given by equation (24).

$$\ln(\gamma_1/\gamma_2) = -b_{12}(x_1 - x_2) \\
+ c_{12}[2x_1 x_2 - (x_1 - x_2)^2] + \ldots \\
+ x_3\{b_{31} - b_{23} - c_{23}(2x_2 - x_3) \\
+ c_{31}(x_3 - 2x_1) + \ldots \\
- b(x_1 - x_2) - c_1[x_1(2x_2 - x_3) \\
+ x_2(x_3 - x_2)] \\
- c_2[x_1(2x_2 - x_1) + x_3(x_1 - x_2)] \\
+ c_3[2x_1 x_2 - (x_1 - x_2)^2] + \ldots\} \quad (30)$$

Similarly expressions for the other components are obtained by cyclic advancement of the subscripts in the order 1, 2, 3, 1.

In calculating vapour composition from these equations, temperature sensitivity is minimized by using ratios of activity coefficients and vapour pressures by combining equation (4) for the three components, thus :—

$$y_1 = 1/E \\
y_2 = (\gamma_2 x_2 P_2/\gamma_1 x_1 P_1)\, E \\
y_3 = (\gamma_3 x_3 P_3/\gamma_1 x_1 P_1)\, E \\
E = 1 + \{(\gamma_2 x_2 P_2)/(\gamma_1 x_1 P_1)\} \\
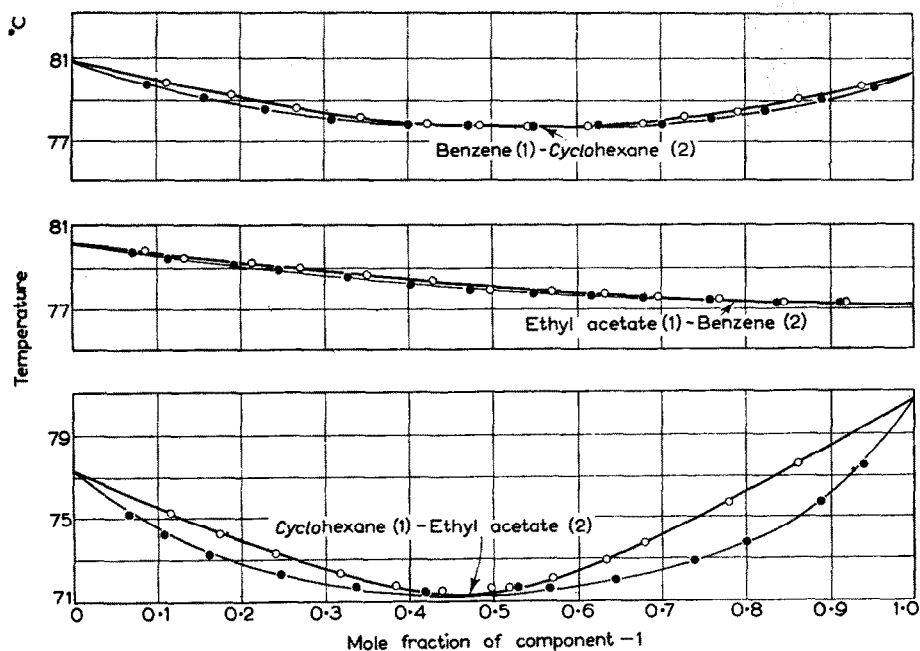+ \{(\gamma_3 x_3 P_3)/(\gamma_1 x_1 P_1)\} \quad (31)$$

255

FIG. 7. Equilibrium temperatures and compositions in the binary systems.

BINARY DATA AND CORRELATION

A total of 18 $x - y - t$ values were measured for each of the three binary systems at 760 mm Hg pressure and for nearly equal intervals of liquid composition. These are presented in Tables 5, 6, and 7 and Figs. 7, 8, 9 and 10. For each binary system the data were correlated with a series of Redlich-Kister equations of increasing complexity, namely, with 1, 2 and 3 constants. These constants were in each case evaluated by the method of least squares using all experimental data.

The following constants were evaluated for equations relating activity coefficient ratios, using logarithms to the base 10 :—

$$\log (\gamma_1/\gamma_2) = b (x_2 - x_1) + c (6x_1 x_2 - 1)$$
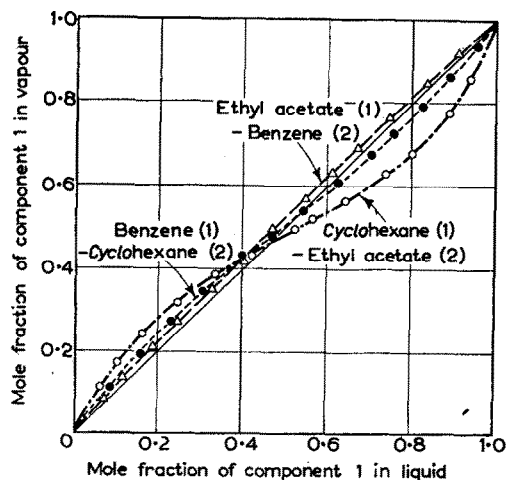$$+ d (x_2 - x_1) (1 - 8x_1 x_2) \qquad (32)$$

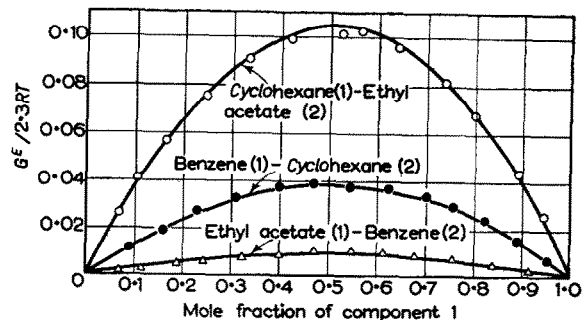FIG. 8. Equilibrium compositions in the binary systems.

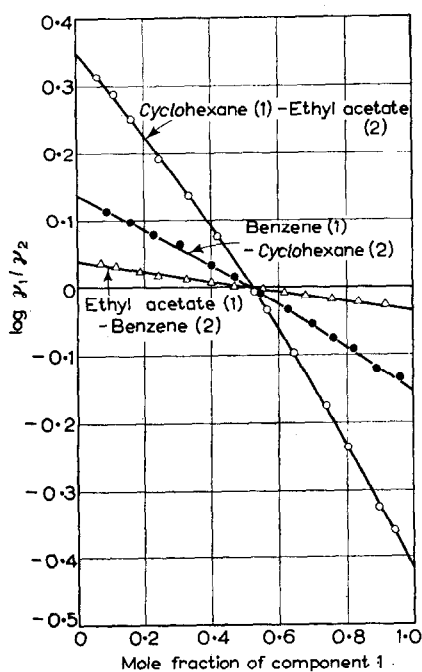FIG. 9. Excess free energy of the binary mixtures.

FIG. 10. Ratio of activity coefficients in the binary systems.

Table 5.

	1-*Constant*	2-*Constant*	3-*Constant*
For ethyl acetate [1] – benzene [2]	b 0·0372	0·0369	0·0369
	c —	— 0·0041	— 0·0042
	d —	—	— 0·0028
For benzene [1] – cyclohexane [2]	b 0·1454	0·1443	0·1444
	c —	0·0100	0·0104
	d —	—	— 0·0029
For cyclohexane [1] – ethyl acetate [2]	b 0·3850	0·3849	0·3848
	c —	0·0321	0·0318
	d —	—	0·0076

Calculated values of vapour composition were compared with experimental values for each binary system, using each correlating equation. The root mean square deviations of calculated values from experimental values of vapour compositions expressed in mole fractions were obtained (Table 6). In these calculations vapour pressure ratios were based upon experimental equilibrium temperatures.

Table 6. Root mean square deviations of
$(y_{calc.} - y_{exp.})$

	1-*Constant equation*	2-*Constant equation*	3-*Constant equation*
Ethyl acetate – benzene	0·0007	0·0009	0·0010
Benzene – cyclohexane	0·0022	0·0012	0·0010
Cyclohexane – ethyl acetate	0·0059	0·0022	0·0020

An examination of the above deviations indicates that for the ratio of activity coefficients an optimum correlation is obtained with 2-constant equations for the benzene – cyclohexane and cyclohexane – ethyl acetate systems, and that a 1 – constant equation suffices for the ethyl acetate – benzene system. By optimum correlation is meant that the use of additional terms does not give significant improvement to justify the extra work involved.

For simultaneous correlation of vapour – liquid composition with equilibrium temperature at constant pressure a trial and iteration procedure was employed. Calculation of separate activity coefficients as well as their ratios were required for this purpose. The procedure followed was to calculate vapour pressures of the separate pure components at an assumed temperature from the vapour pressure equations. The vapour composition calculated thus from equation (22) was subsituted into equation (4) to verify the assumed vapour pressure; the second temperature to be assumed was then obtained from this vapour pressure through an equation for vapour pressure. The process was repeated until successive trials gave the same temperature within 0·01°C.

The following equations were obtained for expressing individual activity coefficients in terms of logarithms to the base 10 :—

$$\left.\begin{aligned}
\log \gamma_1 &= x_1 x_2 \left[B + C\left(x_1 - x_2\right)\right] \\
&\quad + x_2 \left[b\left(x_2 - x_1\right) + c\left(6x_1 x_2 - 1\right)\right] \\
\log \gamma_2 &= x_1 x_2 \left[B + C\left(x_1 - x_2\right)\right] \\
&\quad - x_1 \left[b\left(x_2 - x_1\right) + c\left(6x_1 x_2 - 1\right)\right]
\end{aligned}\right\} \quad (33)$$

A comparison of calculated with experimental

Table 7.

	b	c	B	C
For ethyl acetate [1] – benzene [2]	0·0372	0	0·0359	0
For benzene [1] – cyclohexane [2]	0·1443	0·0100	0·1507	0·0100
For cyclohexane [1] – ethyl acetate [2]	0·3849	0·0321	0·4190	0·0149

values for these three equations is shown in Figs. 7, 8, 9 and 10.

The root mean square deviations of calculated from experimental values of temperature and vapour composition are tabulated herewith. A comparison with deviation obtained from the conventional method of correlation is also given. The conventional method does not recognize the difference between the constants in the free energy expression and those in the activity coefficient ratio expression. Those constants are

Table 8.

System	$y_{calc.} - y_{exp.}$ mole fractions		$t_{calc.} - t_{exp.}$ C°	
	Isobaric	Conventional	Isobaric	Conventional
Ethyl acetate – benzene	0·0007	0·0007	0·07	0·07
Benzene – cyclohexane	0·0012	0·0012	0·06	0·13
Cyclohexane – ethyl acetate	0·0022	0·0022	0·13	0·37

then solely determined from the expression of the activity coefficient ratios as in equation (19).

It will be seen that the correlations are nearly the same with isobaric and conventional equations. The calculated temperatures deviate from the experimental values by about 0·1°C for all three systems. Employing two sets of constants did not improve the calculated values of vapour composition but slightly improved the calculated values of temperature.

TERNARY SYSTEMS

Experimental values of vapour–liquid compositions at atmospheric pressure are shown by the lines connecting the vapour with the equilibrium liquid composition (Fig. 11). Values of x, y, and t were measured at 760 mm Hg pressure for 77 ternary compositions uniformly distributed over the entire range of ternary compositions. These were in addition to the 39 compositions for the three binary systems, and were recorded in Table 14.

Table 9. Constants for the ternary system for use in expressing log γ_1/γ_2

	3-Constant equation (1 for each pair)	6-Constant equation (2 for each pair)	9-Constant equation (3 for each pair)	5-Constant equation
b_{AB}	0·0372	0·0369	0·0369	0·0372
b_{BC}	0·1454	0·1443	0·1444	0·1443
b_{CA}	0·3850	0·3849	0·3848	0·3849
c_{AB}		− 0·0041	− 0·0042	
c_{BC}		0·0010	0·0104	0·0100
c_{CA}		0·0321	0·0318	0·0321
d_{AB}			− 0·0028	
d_{BC}			− 0·0029	
d_{CA}			0·0076	

Correlations of ternary data were made similarly to those for the three binary systems, basing them first upon experimental measurements of temperature and then correcting the temperature to give complete correlation for all equilibrium conditions. The first correlation was made with experimental temperature values, using 1-, 2- and 3-constants for each binary pair with corresponding 3-, 6- and 9-constants for the ternary solution. No additional constants were required for ternary effects.

The root mean square deviations of $y_{calc.} - y_{exp.}$ in mole per cent are shown in Table 10.

The accepted equation for relating all three activity coefficient ratios in the ternary system required only 5-constants; for individual activity coefficients at constant pressure, 5 additional constants permitted accurate calculation of temperature. With reference to equations (29) and (30) for activity coefficient

Table 10.

3-*Constant* equation	6-*Constant* equation	9-*Constant* equation	5-*Constant* equation
0·22	0·13	0·16	0·13

Table 12.

	$y_{calc.} - y_{exp.}$ (mole per cent)	$t_{calc.} - t_{exp.}$ °C
Isobaric equation	0·13	0·13
Conventional equation	0·13	0·34

ratios and activity coefficients, the following constants apply. They are given for use with logarithms to the base 10 instead of natural logarithms.

Table 11.

b_{12}	0·0372	B_{12}	0·0359
b_{23}	0·1443	B_{23}	0·1507
b_{31}	0·3849	B_{31}	0·4190
c_{12}	0	C_{12}	0
c_{23}	0·0100	C_{23}	0·0100
c_{31}	0·0321	C_{31}	0·0149

Here 1 = ethyl acetate (also designated as component *A*), 2 = benzene (component *B*), and 3 = *cyclo*hexane (component *C*).

The root mean square deviation of calculated values from experimental measurements are presented in Table 12.

It will be seen that the correlations are nearly the same with isobaric and conventional equations. The temperatures calculated with the isobaric equations deviate from the experimental values by about 0·1°C. Employing two sets of constants did not improve the calculated values of vapour composition but slightly improved the calculated values of temperature.

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