Since bubble growth rate varies from bubble to bubble, it is not possible by the present method to determine how bubble growth rate varies with the surface temperature. This will require obtaining several bubble photographs during any one temperature drop.

CONCLUSIONS

The following conclusions have resulted from this study.

1. The bubble behavior is consistent with the microlayer vaporization hypothesis of Moore and Mesler. A bubble growing on a surface removes heat very rapidly, a bubble departs from its nucleation site as the surface temperature increases, and the sudden temperature drop corresponds to the initiation of bubble growth.
2. No significant cooling is apparent as liquid returns to the surface during bubble departure. Such cooling is predicted by many hypotheses concerning nucleate boiling.

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Mr. William Lansdown designed a firing circuit for the strobe light used in the initial phase of the research. M. Johnson and Akos Kavács helped the author to take some of the photographs.

NOTATION

D_b = diameter of bubble, in.
D_{tc} = outside diameter of chromel annulus for thermocouple, in.
Q/A = heat flux, B.t.u./(hr.) (sq. ft.)
$t.c.$ = thermocouple
X = horizontal coordinates of oscilloscope trace, time, msec.
Y = vertical coordinates of oscilloscope trace, temperature, °F.
T_{avg} = average temperature of nucleation site or thermocouple temperature, °F.

Greek Letters

ΔT = temperature drop from start of cooling cycle to taking of bubble photograph, °F.
ΣT = total temperature drop from start of cooling cycle to end of cooling cycle, °F.
$\Delta\theta_c$ = time from start of cooling cycle to taking of bubble photograph, msec.
$\Delta\theta_h$ = time from start of heating cycle to taking of bubble photograph, msec.
$\Sigma\theta_c$ = total time from start of cooling cycle to end of cooling cycle, msec.
$\Sigma\theta_h$ = total time from start of heating cycle to end of heating cycle, msec.
$\Sigma\theta_t$ = total time of complete temperature cycle, msec.

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Vapor-Liquid Equilibrium Determination by a New Apparatus

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The prediction of the vapor-liquid equilibria of nonideal systems continues, despite the considerable fundamental research on the interaction between molecules, to be a rather elusive goal. Recourse to experimental measurement will undoubtedly be required for the foreseeable future in order to provide the mass of data necessary for engineering calculations. Such measurements, if they are of sufficiently high accuracy, will also serve the more important function of providing a basis for the development and evaluation of theories describing the liquid state.

Although the vapor-liquid equilibria of mixtures can be obtained by a variety of experimental methods, for example the measurements of the vapor pressure of solutions of known compositions and temperatures as described by Van Ness and Ljunglin (*8*), direct measurement of the *x-y-T-P* data by means of equilibrium stills retains considerable appeal particularly for mixtures more complex than the binary. A summary of the types, construction, and capabilities of the many stills which have been used is provided by Hala et al. (*3*). Although a number of the devices are reported to be quite precise and reliable, they suffer the drawbacks of rather complex construction or difficult experimental requirements. This study was directed to the development and evaluation of an apparatus which would hopefully surmount these objections without sacrificing the accuracy of the measurements.

Previous studies in vapor-liquid equilibrium in this laboratory had led to the development of a modification of the Gillespie apparatus. Although this modified equilibrium still described by Landwehr et al. (*7*) had achieved most of the desired objectives, two undesirable features which it shares with the large majority of existing devices deserved further consideration.

The first of these was concerned with the vapor condensate sampling cell which was of the conventional overflow design. The vaporization of liquid at the liquid-vapor

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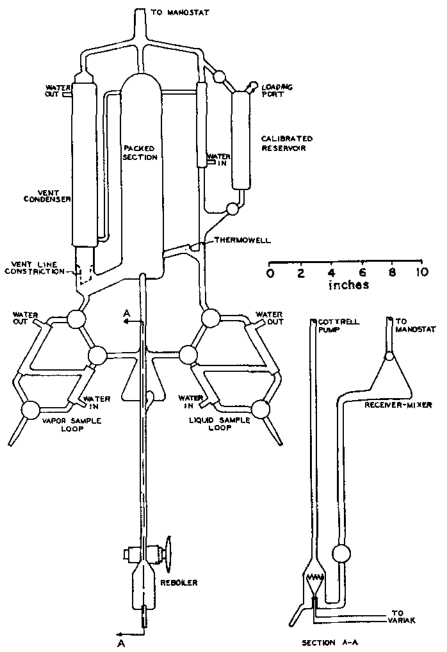

Fig. 1. Equilibrium still.

interface of such a cell was shown in subsequent experiments to affect the composition of the gross contents of the sampling cell to an extent which depended on the relative volatility of the components and on the length of time following the termination of recirculation prior to sample removal. Although the quantitative effect for most binary mixtures of moderate volatility and for short delay time was small, the effect on the x-y data for a system such as ethylbenzene-methanol was quite pronounced.

The second characteristic was of a more fundamental nature in that a degree of internal inconsistency of the measured liquid and vapor concentrations of the order of ± 0.002 in mole fraction was observed in the course of reproducibility tests. Since vapor and liquid recirculation was employed, some degree of instability would be expected. Nevertheless it was felt that an effort to reduce the internal inconsistency was justified.

THE PROPOSED EQUILIBRIUM APPARATUS

The equilibrium still, Figure 1, represents an additional modification of the apparatus described by Landwehr. It remains basically a vapor and liquid recirculation device. Its most distinguishing feature is to be found in the details of the separation chamber, Figure 2. The vapor-liquid mixture emerging from the Cottrell tube is directed downward through a short column packed with ⅛-in. Fenske helices and is disengaged only after the mixture has passed through the column in concurrent flow. The liquid streams past a thermometric element, in this case a thermocouple, and overflows to the liquid sampling cell. The vapor flows upward around the packed column and thence downward around the entire separation chamber providing a thermal barrier surrounding the crucial separation region. The vapor stream then passes into a condenser, the condensate from which flows to the vapor condensate sampling cell. The overflows from the liquid and vapor condensate cells are combined in the main liquid reservoir which is kept well mixed by a magnetic stirrer before returning to the reboiler.

Three principal modifications have been made to the predecessor apparatus.

1. The incorporation of the short packed column in the equilibrium train. This feature, which Heertjes (*4*) has also made use of, is intended to accomplish two objectives. First the apparatus shares with all vapor and liquid recirculation devices the severe handicap that equilibrium of the liquid and vapor must be achieved in a single pass through the equilibration train (continued recirculation serves to achieve equilibrium on a gross basis), in this case, the reboiler, the Cottrell tube, and the separation chamber. The short packed column, providing additional contact as well as enhancing interfacial surface, is intended to bring the two phases into a closer approach to equilibrium that can be obtained in the Cottrell tube itself. Second the vaporization process occurring in the reboiler is quite chaotic. Viewed from the standpoint of a small element of liquid moving into the proximity of the surface of the immersion heater there is very little certainty of the extent to which this element will be vaporized before being swept away. The small packets of vapor and liquid swept into the Cottrell tube may very well be close to equilibrium on a local basis but certainly may be far removed from it on a gross or integral basis. The packed column serves to smear out these local fluctuations, to homogenize and mix the vapor and liquid streams, and hopefully to insure that equilibrium will be more closely approached on a gross basis.

2. The use of the vapor phase as a thermal barrier around the separating chamber. As Rose and Williams (*9*) have shown it is essential that heat effects in the separation region be reduced to an absolute minimum. They chose to use the recycle liquid stream to lag the Cottrell tube. In this design only the upper portions of the tube are lagged so to speak, the lower portion being left unlagged in order to facilitate the loss of any superheat which may be present. The choice of the vapor phase as a thermal barrier fluid was predicated on two considerations: an effective thermal barrier for all regions of the separating chamber can be obtained since the vapor flow can be more easily directed, and the latent heat of condensation appears more attractive from a lagging point of view than the sensible heat of the recycle liquid.

3. The sample cells have been redesigned so that continuous flow is maintained through them during the equilibrium process. During steady operation the liquid surface is maintained above the inlet to each cell. The samples can be isolated while the equilibrium still continues in operation and can be cooled in-situ reducing the possibility of stray error during the actual sampling process. The upper three-way bypass valve plug was scored on a glass cutting saw to provide a vent to the atmosphere for the sampling cell when this valve was set into the bypass position. The vent is needed to eliminate contamination of the sample; otherwise the partial vacuum created by shrinkage on cooling may draw extraneous material through the stopcocks.

AUXILIARY APPARATUS, MATERIALS AND PROCEDURE

Pressure control to within ±0.1 mm. Hg was maintained on the system by an electronic unit previously described (*2*). Temperatures were measured with an iron-constantan thermo-

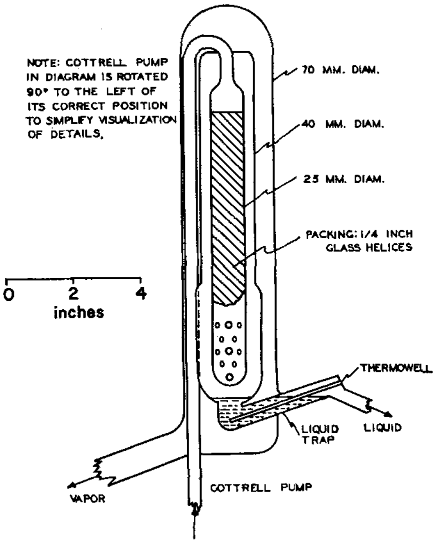

Fig. 2. Details of separation chamber.

Table 1. Experimental Temperature-Composition Data for the System *n*-Heptane-Toluene at 760 mm. Hg

Temperature, °C.	Mole fraction *n*-heptane Liquid	 Vapor
98.41	Pure	*n*-heptane
98.51	0.9700	0.9728
98.58	0.9503	0.9556
98.70	0.9154	0.9245
98.87	0.8771	0.8924
99.07	0.8380	0.8585
99.58	0.7479	0.7845
100.25	0.6525	0.7057
101.47	0.5096	0.5880
101.85	0.4762	0.5594
102.10	0.4474	0.5345
103.33	0.3492	0.4459
104.52	0.2681	0.3672
106.39	0.1622	0.2464
107.57	0.1087	0.1762
108.60	0.0676	0.1162
109.24	0.0445	0.0794
109.80	0.0256	0.0470
110.60	Pure	Toluene

couple calibrated against standard thermometers. A potentiometer permitted a sensitivity of ±0.01°C. in the temperature measurement. Compositions were determined with a precision refractometer capable of detecting differences in the index of refractions of the order of ±0.00003.

The *n*-heptane which was purified by distillation in a 6-ft. column had a refractive index of 1.38505 at 25°C. compared with the value of 1.38511 reported by Timmerman (*13*) and a normal boiling point of 98.41°C. compared with 98.43°C. reported by Timmerman. Chromatographic analysis indicated that the purified *n*-heptane probably had impurities amounting to less than 0.01%. The toluene was employed as received on the basis of chromatographic analysis; its refractive index at 25°C. was 1.49396 and its normal boiling point was determined as 110.60°C. comparing favorably with values of 1.49405 and 110.63°C. reported by Timmerman. Fractional distillation of the *n*-butyl alcohol and benzene produced materials of high purity as determined by chromatographic analysis. The indexes of refraction of the purified materials compared favorably with literature values, 1.49795 vs. 1.49792 (*13*) at 25°C. for benzene and 1.39727 vs. 1.3973 (*13*) for *n*-butyl alcohol.

The apparatus was charged with approximately 200 ml. of pure material and operated over a suitable range of pressure to determine the vapor pressure of the material actually used. The stopcocks were greased with Nonaq for *n*-heptane, toluene, and benzene-rich mixtures and with Silicone grease for the butyl alcohol-rich mixtures. A sufficient amount, usually several milliliters, of the second component to obtain the desired concentration shift was introduced into the system from the pure materials storage reservoir shown in Figure 1. The still was ordinarily operated for some 30 min., except for those studies of the influence of the length of recirculation, during which isothermal conditions were very rapidly established. The vapor condensate and liquid sample cells were isolated from the system, and suitable additions of both pure components were made to the system which was continued in operation with the bypass lines around the sampling cells. The samples were cooled in place, removed, and subsequently analyzed. Approximately one half of the composition range could be studied before the apparatus was emptied and the process repeated starting with the second pure component.

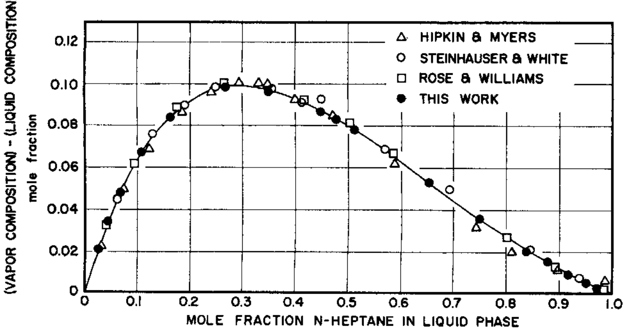

Fig. 3. Equilibrium composition diagram.

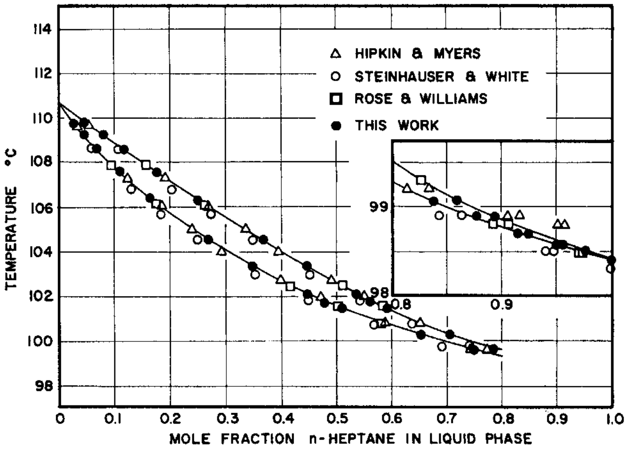

Fig. 4. Temperature-composition diagram.

EXPERIMENTAL RESULTS

Experimental measurements were made to establish the vapor-liquid equilibria of the toluene-*n*-heptane system over the entire range of concentrations and to determine the internal consistency of the apparatus. The experimental *x*-*y*-*T* data at a pressure of 760 mm. Hg are given in Table 1 and are compared with those of other investigators in Figure 3 in terms of vapor and liquid concentrations and in Figure 4 in terms of temperatures and compositions.

Experimental *x*-*y*-*T* data for the system *n*-butanol and benzene at 760 mm. Hg are given in Table 2.

DISCUSSION OF RESULTS

Assessment of the reliability of vapor-liquid equilibrium data is extremely difficult to obtain and can only be estimated by recourse to criteria which might be applied to the situation. For the case at hand three such criteria

Table 2. Temperature-Composition Data for the System of n-Butyl Alcohol and Benzene at 760 mm. Hg

Temperature, °C.	Mole fraction benzene Liquid	 Vapor
80.23	0.9805	0.9822
80.35	0.9535	0.9617
80.49	0.9265	0.9462
80.64	0.9075	0.9389
80.80	0.8854	0.9283
81.32	0.8255	0.9085
82.37	0.7279	0.8839
84.18	0.5965	0.8501
87.37	0.4329	0.7955
87.89	0.4230	0.7867
92.45	0.3030	0.7129
93.87	0.2683	0.6823
97.67	0.2031	0.6076
97.82	0.1994	0.6026
109.04	0.0647	0.2968
114.57	0.0215	0.1152
115.74	0.0117	0.0693
116.56	0.0062	0.0395

were considered: internal consistency of the experimental data, comparison of the data with results obtained by other investigators employing different experimental methods, and thermodynamic consistency of the measurements. Since each of these criteria represents a necessary but insufficient condition of reliability, these can be employed as the basis for the rejection of measurements and methods which do not satisfy the restraints but cannot serve as a certification, with total certainty, of the validity of the data. Nevertheless the degree to which the experimental data satisfy the criteria is a measure of the likelihood that the measurements are sound.

Internal Consistency

Twenty-five measurements were made in the near vicinity of 0.165 mole fraction heptane in the liquid to ascertain the reproducibility capabilities of the proposed apparatus and to investigate the influence of the rate and duration of recirculation. The conditions under which the data were measured ranged from 15 to 90 min. of isothermal recirculation and from 0.35 to 0.62 ml./sec. of vapor rate expressed in terms of condensate.

The internal consistency of the vapor-liquid composition data is extremely high. If the total deviation from the regression line, whose slope is deduced from the full range composition diagram, were to be assigned to the vapor composition, in no case would it exceed ± 0.0009 in mole fraction. Since the experimental scatter must reflect not only the limitations of the equilibrium apparatus but also those errors incurred during the sampling, transferring, and analysis of the sample, a fuller appreciation of the capabilities of the devices can be obtained if other potential errors are considered. Principal among these is the refractometric error; excluding uncertainties in the lens temperatures and in evaporative losses a potential error in composition of ± 0.00025 in mole fraction for this binary must be recognized as originating from the ultimate precision of the refractometer which is ± 0.00003 in index of refraction. Application of this uncertainty to the vapor and liquid concentrations as given by the regression line provides an estimate of the deviation. Of the four measurements falling outside this band one involved 15 min. of isothermal operation and the remaining three 30 min. Of twelve measurements of 60- and 90-min. duration all fall within the potential refractometric error. No dependence of concentration on the vapor recirculation rate is apparent. When it is considered that other factors may have contributed additional errors, it is concluded that internal inconsistency with respect to composition is extremely small for the proposed apparatus. Although no direct experimental determination of entrainment was made, the high level of replicability of these x-y data demonstrating an independence of vapor velocity suggests that entrainment does not occur.

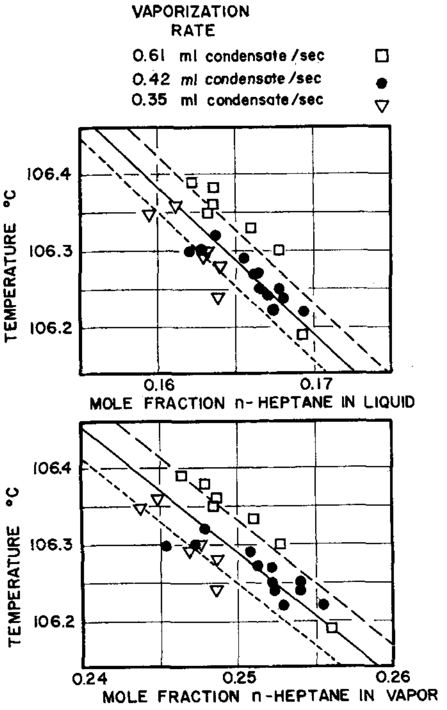

Fig. 5. Temperature-composition diagram at $\bar{x} = 0.1650$.

The temperature-concentration relationships shown in Figure 5 reveal an unexpected dependence of temperature on the vapor recirculation rate. It is noted that the temperatures are internally consistent to ± 0.05°C. or less for each vapor rate but are displaced as a function of the vapor rate. A similar dependence of temperature on vapor circulation rate was later observed with pure toluene. Calculations revealed that a constriction just below the main condenser could result in a 2 mm. Hg pressure drop at the highest vapor velocities and could therefore account for the regular variation of temperature with vapor recirculation rate. In order to avoid random temperature inconsistencies in the full range composition measurements which followed a single vapor recirculation rate corresponding to the maximum reported here was employed. Subsequent to the conclusion of these studies the constriction has been eliminated, and the temperature variations reported here have not been encountered.

Comparison With Previously Reported Data

The experimental vapor and liquid compositions are compared with previously published works as the difference between vapor and liquid concentrations as a function of the liquid composition (that is y-x vs. x) in Figure 3. In general the comparison is favorable, the maximum deviation being less than 0.008 in mole fraction. Agreement with the measurements of Rose and Williams (*9*) who used a modified Gillespie still employing the recirculating liquid phase for self-lagging is excellent over the entire range. General agreement is obtained with the data of Steinhauser and White (*11*) using an Othmer still; however their measurements exhibit some internal inconsistencies. The data of Hipkin and Myers (*5*) obtained by a vapor recirculation apparatus of their own design appear to deviate most seriously from the other three works, their curve oscillating above and below that of the average results.

A comparison of the temperature-composition measurements is provided in Figure 4. It is noted that the data of Steinhauser and White are low over the entire range as they had suspected. Agreement with the data of Hipkin and Myer is good except in the range above 0.85 mole fraction heptane where their temperatures tend to be high. The comparison with the Rose and Williams measurements is excellent over the full range of composition.

The general agreement noted above is most encouraging. It is not likely that the proposed apparatus suffers from basic deficiencies.

Thermodynamic Consistency

The thermodynamic consistency of the experimental data was assessed by the composition resolution test described by Van Ness (*14*). This method, which is extremely sensitive, possesses by virtue of its point-to-point characteristic a distinct advantage over integral or area tests. The latter rely on an overall evaluation in which regional inconsistencies may be obscured by cancellation. The composition-resolution test is to be preferred over the

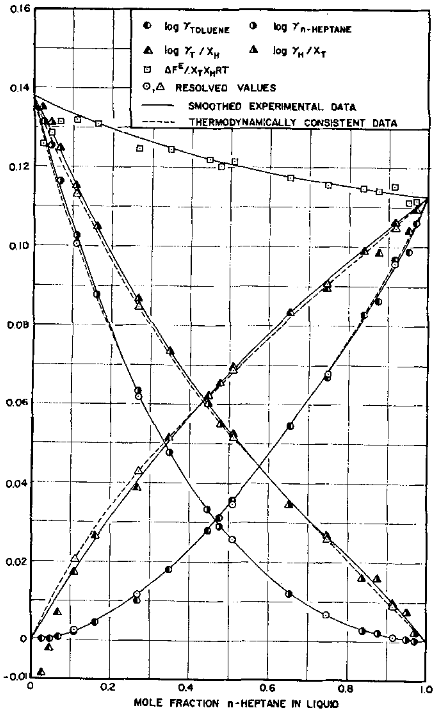

Fig. 6. Comparison of measured and calculated activity coefficients for *n*-heptane-toluene system at 1 atm.

slope test which often gives rise to uncertainties in the test itself which are as great as the uncertainty in the experimental data.

Activity coefficients were calculated from the experimental data by

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P^o} + \frac{(B_{ii} - V_i^L)(P - P_i^\circ)}{RT} \qquad (1)$$

The first term on the right-hand side of (1) corresponds to an estimate of the activity coefficient uncorrected for vapor-phase nonidealities, while nonideal gas behavior is accounted for by the second term.

The virial coefficients for toluene and *n*-heptane were estimated from data for benzene and *n*-hexane presented by Black (*1*). The vapor pressures of the pure components were calculated from expressions recommended by Jordan (*6*) for *n*-heptane and by Thodos (*12*) for toluene. These relations were chosen since they were in closest agreement with the experimental vapor pressures determined with the equilibrium apparatus. In the case of both components small adjustments of temperature were required to mesh the equation and the data at the normal boiling point; these amounted to +0.026°C. for toluene and +0.016°C. for *n*-heptane.

The activity coefficients calculated from the experimental data are shown in Figure 6 in the form of log activity coefficients as a function of the concentration of *n*-heptane in the liquid. Also shown in Figure 6 are the quantities required for the composition-resolution test, namely log γ_i/x_j and $\Delta F^E/x_i x_j RT$. The latter is equivalent to the sum of log γ_i/x_j and log γ_j/x_i.

As shown by Van Ness the thermodynamic consistency of the experimental data can be assessed by resolving the function $\Delta F^E/x_i x_j RT$ obtained from the experimental data into a set of thermodynamically consistent activity coefficient functions. The comparison of the calculated and experimental coefficients provides directly an assessment of the local consistency. The relations required for the resolution are for a binary system

$$\frac{\ln \gamma_A}{x_B} = x_B \frac{2\,\Delta F^E}{x_A x_B RT} - I_o - \delta \qquad (2)$$

and

$$\frac{\ln \gamma_B}{x_A} = x_A \frac{2\,\Delta F^E}{x_A x_B RT} - I_1 + \delta \qquad (3)$$

The quantities I_o and I_1 are intercepts of the tangent to the free energy function at the composition in question. Although it is noted that a graphical construction is required, the specific choice of the free energy relation produces a function of little curvature, and the value of the intercepts is well established. The quantity δ reflects the effect of the heat of mixing for isobaric data and is given by

$$\delta = -\frac{\Delta H_m}{RT^2} \frac{dT}{dx_A} \qquad (4)$$

An estimate of the heat of mixing as $\Delta H_m = x_t x_h$ cal./g.-mole was deduced from data at 25°C. reported by Schnaible, Van Ness, and Smith (*10*). A 10% downward revision in these data was made to reflect the tendency for the heat of mixing of this type of system to decrease somewhat with increasing temperature. For the small temperature gradients involved in the case at hand the effects of the heat of mixing term were generally small, of the order of 1 to 5%. Accordingly a moderate error in the estimate of the heat of mixing would produce a much smaller uncertainty in the final result.

The comparison of the calculated and experimental activity coefficients shown in Figure 6 indicates that the measurements are thermodynamically consistent to within very small limits. It will be noted that the experimental log γ_t/x_h appears to deviate significantly from the resolved values in the range of $x_h < 0.10$. This deviation is less a measure of inconsistency than it is of the sensitivity of the method, since the ratio of log γ_t/x_h is more sensitive to slight errors than is either term. Only a minute adjustment would be required to produce correlation in this region.

The degree of thermodynamic inconsistency is not easily translated into quantitative terms for two reasons. On the one hand the uncertainty may be assigned to a combination of errors in the vapor and liquid compositions and in the temperature. On the other hand the thermodynamically consistent functions with which the experimental data are being compared are but one of a set of such functions which can be obtained by making modest adjustments in the excess free energy function. Referring to Figure 6 one can note that the chosen free energy curve is by no means the only one which might have reasonably been used particularly towards the edges of the diagram. It is specifically in this region that the functions are extremely sensitive to small experimental errors.

Despite the difficulties described above some quantitative estimate of the degree of inconsistency can be obtained by comparing the experimental and calculated data. If the signs for the errors of both components are the same, it is suggested that an adjustment of the free energy function be made to reduce the error. This situation can be interpreted alternately as an indication of a temperature error, since both coefficients are similarly affected. Conversely errors of opposite sign must be associated with concentration uncertainties. In principle then it is necessary to adjust the assumed free energy function within the limits suggested by the experimental data to obtain the best agreement between the resolved coefficients and the smooth curve representing the measurements. The degree of inconsistency is then determined as the variations in concentration and temperature required to account for the error.

The uncertainties as assigned in full to either the vapor or liquid composition or the temperature required to justify the differences between the calculated and the smoothed values range from ±0.0002 to ±0.0007 in composition and less than ±0.05°C. in temperature for the middle range of concentration $0.15 < x_h < 0.85$ in which the experimental data are in virtual agreement with the smoothed data. Only in the dilute region $x_i < 0.15$ does some scatter of the experimental data become evident. In this region however the activity coefficient is extremely sensitive to small errors, and corrections of the order of ±0.0004 or less in composition or ±0.2°C, are sufficient. Since the observed error is most likely to be a consequence of experimental errors on the part of all three parameters, namely vapor and liquid composition and temperature, and since the potential refractometric error itself was of the order of ±0.00025 mole fraction, it is concluded that the vapor-liquid equilibria of this system as measured by the proposed apparatus are quite consistent thermodynamically.

The n-Butyl Alcohol-Benzene Measurements

The extent to which minor design deficiencies in the experimental apparatus can affect the measurements is illustrated by a comparison of isobaric data for the system *n*-butyl alcohol and benzene as determined from this apparatus and that described by Landwehr (*7*). Over the entire range of composition the measurements of Yerazunis (*15*) are too high for butanol and too low for benzene. The source of this error has been determined to be partial vaporization of the vapor condensate in the sampling cell resulting in an enrichment of butanol in the vapor sample. For systems of high relative volatility a significant error in the *x-y* data might well be incurred. The use of sampling cells which can be completely isolated as in the case of the proposed apparatus eliminates uncertainties of this type.

On Figure 7 are shown the measured activity coefficients for the *n*-butyl alcohol-benzene system calculated from the measured vapor pressures without temperature adjustment and corrected for nonideal gas behavior. The calculated values were obtained by integrating the Gibbs-Duhem equation to obtain the benzene activity coefficients from the *n*-butanol data. Since heat of mixing data for this system at temperature are not available, no correction has been made for the variation of temperature which is considerable (~38°C.) in this case. Nevertheless the correction would be in the proper direction. To this extent the experimental results can be considered thermodynamically consistent.

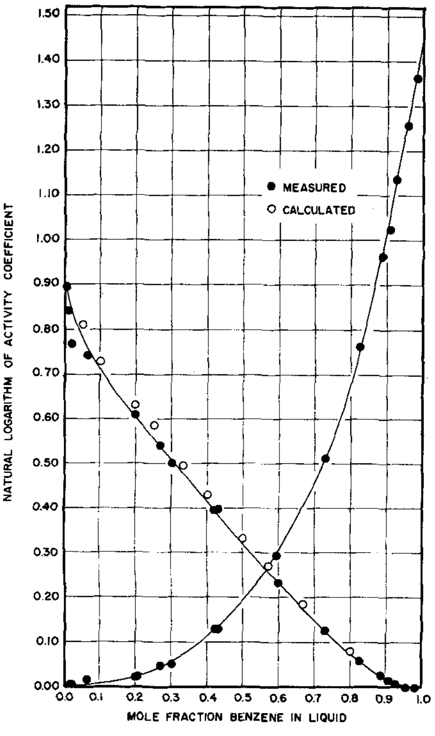

Fig. 7. Corrected activity coefficients for system n-butyl alcohol-benzene.

SUMMARY

The equilibrium apparatus which is proposed has been shown to have a very high degree of internal consistency and to produce measurements which compare favorably with determinations made with devices of different design. The experimental results are found to be extremely consistent with thermodynamic requirements.

The ease of operation, the shortness of the equilibration time (30~45 min.), and the ability to isolate and withdraw samples while the apparatus continues in operation at a new concentration condition are characteristics which make the proposed apparatus attractive from a practical standpoint.

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NOTATION

B_{ii} = virial coefficient for component i
ΔF^E = excess Gibbs free energy of mixing
ΔH_m = heat of mixing for mole of mixture
I_o, I_l = tangent intercepts
P = pressure
P_i° = vapor pressure of component i
R = universal gas constant
T = absolute temperature
V_i^L = molal volume of component i as a liquid
y_i = mole fraction of component i in vapor
x_i = mole fraction of component i in liquid
γ_i = activity coefficient for component i

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