where $T$ is the absolute temperature and $a$ and $b$ are constants. The constants for Equation 6 were determined to fit the authors' data, and those from each of the previous investigations, by a least squares calculation. These results are shown in Table II.

Goodwin and Mailey gave only smoothed data from a linear plot of fluidity as a function of temperature, and Lorenz and Kalmus gave only data from a smoothed curve. To obtain an idea of how well Goodwin and Mailey's smoothed data represented their experimental values, we calculated Dantuma's data and our data for Calibration C (with 10 points well distributed over the temperature range investigated) as

$$1/\eta = a + bT \qquad (7)$$

This relation gave a better fit to the authors' data than did Equation 6. The fit with Dantuma's data was about the same for the two relations. From this, we presume that Goodwin and Mailey's actual data are well represented by the smoothed data they reported.

The methods and calculations used by each group were reviewed in an attempt to determine their probable reliability and to provide a better basis for comparison of the previous results with each other and with ours. Fawsitt used a rather crude oscillating disk viscometer before the theory of this type of apparatus was well understood. His results are probably the least reliable and were omitted from consideration.

Goodwin and Mailey and Lorenz and Kalmus used capillary viscometers and considered most, but not all, of the necessary corrections to the data. For example, the effect of surface tension was ignored in both investigations, and Lorenz and Kalmus used a linear (rather than time) average hydrostatic head correction. Despite these criticisms, the results obtained by these two groups should be reliable within a few per cent.

Dantuma's work has been considered to be as good as any viscosity determination on fused salts. $KNO_3$ was originally chosen as a calibration material because the authors found no grounds for criticism when they reviewed Dantuma's work, and assumed his values to be exact within 1%. Murgulescu and Zuca (*9*) used essentially a duplicate of Dantuma's apparatus. They determined the viscosity of $KNO_3$ to check their results against Dantuma's and, therefore, gave viscosity values at only four temperatures (357° to 413° C.).

The five values of the temperature dependence listed in Table II fall into two groups. The three values determined with capillary viscometers agree within experimental error and the values determined with oscillating sphere viscometers also agree with each other, but not with the first group.

The review and analysis of the techniques used by the earlier investigators yielded no explanation for the discrepancy between the results obtained with capillary viscometers and those obtained by Dantuma or Murgulescu and Zuca. The neglect of some small corrections could easily account for the earlier capillary viscometer results giving a slightly lower temperature dependence than we found, but these errors could not account for the temperature dependence being 6 to 7 % too low.

In conclusion, it is not possible to judge which results are more correct since either type of determination could be in error because of some unrecognized effect. However, the authors' results should best represent those to be expected in the calibration of capillary-type instruments.

## ACKNOWLEDGMENT

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# Isobaric Ternary Vapor-Liquid Equilibria System

## Acetone–Carbon Tetrachloride–Benzene

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PRECISE DETERMINATION of the vapor-liquid equilibrium data is essential if the distillation and the contacting equipment designed using this experimental data are to operate to the predicted specifications. The need for reliable vapor-liquid equilibrium data is further increasing with the development of extractive and azeotropic distillation processes as potential methods of separating close-boiling mixtures. The present investigation on this system was carried out to obtain reliable vapor-liquid equilibrium data, to correlate the data so obtained, to see to what extent the ternary effect is a contributing factor in the evaluation of ternary vapor-liquid equilibria, and to see whether benzene could be used as a third component in the separation of azeotropic mixtures of acetone and carbon tetrachloride.

## CHEMICALS USED

Acetone, Baker Analyzed; carbon tetrachloride, British Drug House Ltd, London—0.0015% nonvolatile matter, 0.0025% absorbed oxygen, 0.0005% carbon disulfide, 0.02% water; and benzene, Veb Berline, Germany, were used in the present investigation after further purification. Acetone was treated with fused anhydrous calcium chloride to remove traces of moisture and subjected to fractional distillation in a laboratory glass fractionating column. Product boiling at 56.1° C. at 760 ± 1 mm. of Hg pressure was collected and used. Carbon tetrachloride and benzene were also subjected

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**Reliable vapor-liquid equilibrium data obtained with a modified Colburn equilibrium still are presented for the ternary system, acetone–carbon tetrachloride–benzene at 760 ± 1 mm. of Hg total pressure. These data have been correlated satisfactorily with Wohl's three-suffix Margules equations using a ternary constant, $C = -0.028$, estimated from the binary constants in accordance with Wohl's suggestion. No ternary azeotrope was noticed. The equilibrium curve drawn for the system, acetone–carbon tetrachloride, on a benzene-free basis with per cent benzene as the parameter, showed that the azeotrope of this system disappeared at 50% benzene.**

to fractional distillation. Carbon tetrachloride boiling at 76.7° C. at 760 ± 1 mm. of Hg pressure and benzene boiling at 80.1° C. at 760 ± 1 mm. of Hg pressure were collected and used.

## EXPERIMENTAL AND ANALYTICAL DATA

The experimental vapor-liquid equilibrium data were obtained at 760 ± 1 mm. of Hg total pressure using a modified Colburn equilibrium still (*8-13, 15*). The boiling points of the mixtures were read accurately to ±0.1° C. Each run was conducted for 3 to 3-½ hours until equilibrium was attained between vapor and liquid samples as tested by intermittent analysis of the samples. Refractive index and specific gravity were used for analyzing the system. The refractive indices of the various samples were read to the third decimal place accurately and with an eye approximation to the fourth decimal place using Abbe's Refractometer. The liquid and vapor samples could be analyzed with an accuracy of 0.5% in all composition ranges. The analytical data for this system were obtained by the same method as described earlier (*14*).

If $A$, $B$, and $C$ represent the three components of a ternary system, then known mixtures of the three components were prepared at intervals of approximately 10 mole % $A$ at constant selected values of $100B/(B + C)$. Refractive indices and specific gravities of the mixtures were determined at 30° C. Conical flasks containing the mixtures were placed in a constant temperature bath maintained at 30 ± 1° C. for about half an hour, after which they were removed from the bath and the refractive index and specific gravity of the mixture contained in them were determined immediately. The refractive index *vs.* mole % $A$ plot was prepared with values of $100B/(B + C)$ as parameters resulting in a family of curves.

Similarly, specific gravity *vs.* mole % $A$ plot was prepared with values of $100B/(B + C)$ as parameters. From these two plots, smoothed typical plot data were obtained at constant values of refractive indices and specific gravities. The typical ternary plot was then prepared with lines of constant refractive index and specific gravity and this was subsequently used in determining the compositions of the unknown mixtures. To test the validity of this analytical method, several known mixtures were analyzed using the ternary typical plot and the results agreed to within less than 0.5% in all composition ranges. The ternary standard plot is shown in Figure 1.

## CALCULATIONS

The activity coefficient data of the experimental runs were calculated by the following relation:

$$\gamma_i = \frac{Z_i P y_i}{P_i^\circ x_i}$$

The vapor phase nonideality correction factor was estimated for all the runs by the following relation (*6*).

$$Z_i = \text{exp.}^{10} \frac{(P_i^\circ - P)(V_i - \beta_i)}{2.303\, RT}$$

The vapor pressure data of the chemicals were obtained at the desired temperatures using Antoine-type vapor pressure equations taken from literature and they are reproduced below with their source.

| | | Ref. |
|---|---|---|
| Acetone: | $\log_{10} P^\circ = 7.84311 - \dfrac{1633.65}{t + 273.16}$ | (*1*) |
| Carbon Tetrachloride: | $\log_{10} P^\circ = 7.53127 - \dfrac{1627.23}{t + 273.16}$ | (*1*) |
| Benzene: | $\log_{10} P^\circ = 6.89745 - \dfrac{1206.35}{t + 220.237}$ | (*2*) |

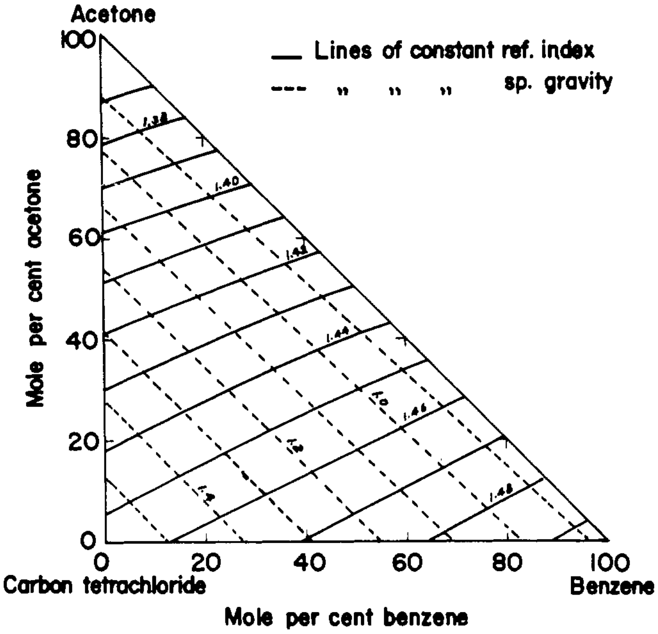

Figure 1. Ternary standard plot

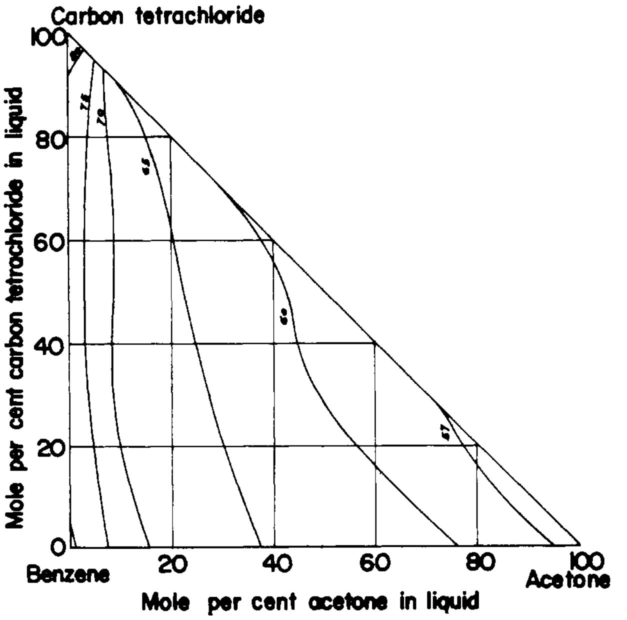

Figure 2. Boiling point diagram

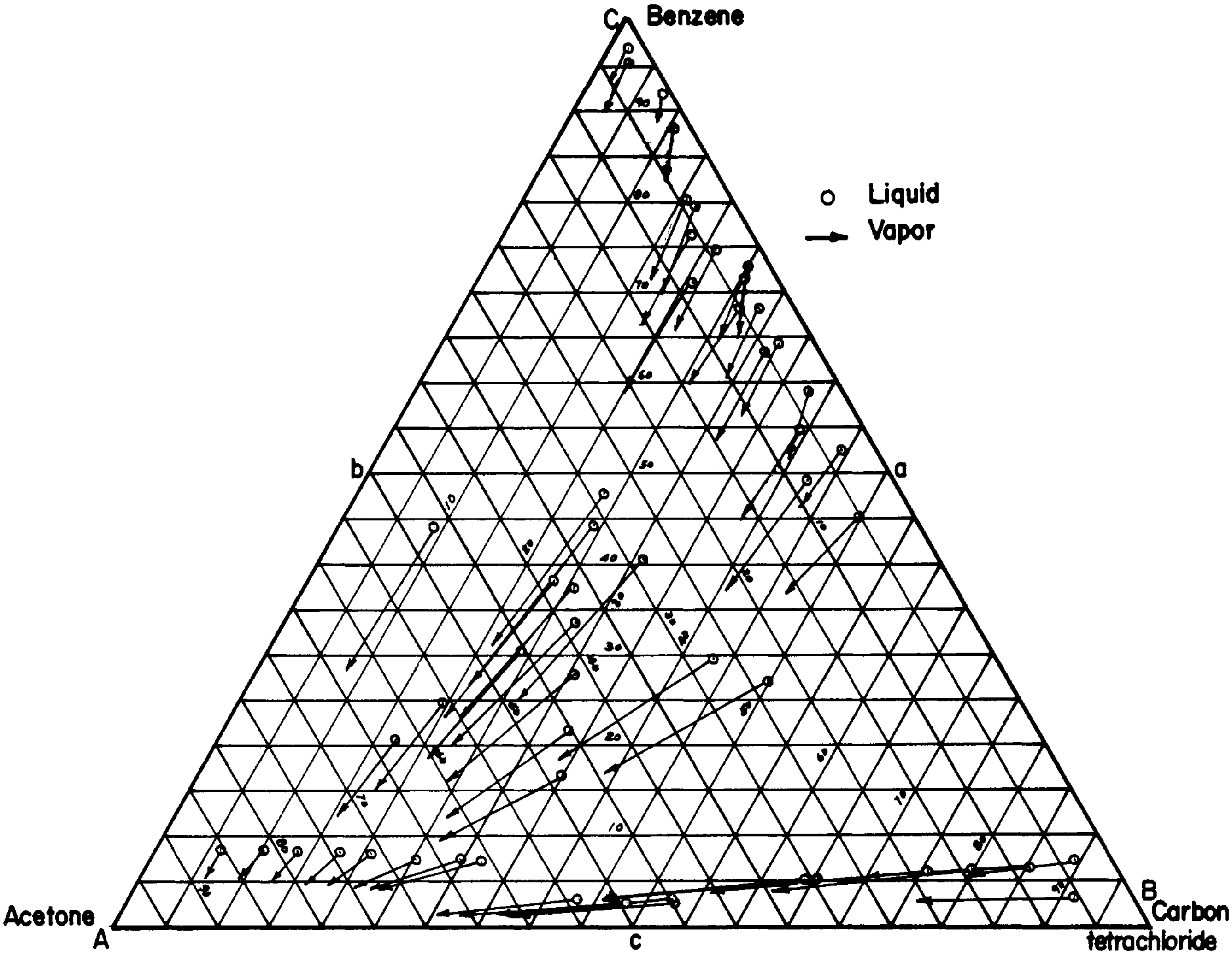

Figure 3. x-y diagram

Liquid molal volumes were calculated at the desired temperatures by the method of Lydersen, Greenkorn, and Hougen (*5*), using the values of pure liquid density at 30° C. The second virial coefficients, $\beta$, were calculated at the desired temperatures using the relation given by Wohl (*19*). The critical constants required in the estimation of the second virial coefficients were taken from literature (*3, 7*).

## PRESENTATION OF RESULTS

Table I compares the physical properties of the purified chemicals with the literature values. Table II presents the experimental *t-x-y* data and a comparison of the calculated and the experimental activity coefficient data. The compositions in Table II are reported to ±0.1% only for purposes of consistency and not to indicate the true degree of accuracy of the data. The ternary analytical typical plot is shown in Figure 1. The boiling point diagram is plotted in Figure 2 in which the base grid represents the liquid compositions and the superimposed across are lines of constant temperature. The *x-y* diagram for the system is plotted in Figure 3.

## DISCUSSION AND CORRELATION OF RESULTS

Experimental vapor-liquid equilibrium data were correlated by Wohl's three-suffix Margules equations (*18*) using a ternary constant. The applicability of the ternary Van Laar (*18*), Li and Coull (*4*), or White (*17*) equations is restricted by the condition,

$$A_{32}/A_{23} = (A_{31}/A_{13})(A_{12}/A_{21})$$

and this condition was not satisfied for the present system. Therefore, an attempt was made to correlate the data of this system by Wohl's ternary three-suffix Margules equations (*18*), which utilize six binary constants and one ternary constant. The ternary constant, *C*, was assumed to be zero as a first approximation and the activity coeficients were calculated, but good agreement between the calculated and experimental values was not obtained. Therefore, to obtain a more satisfactory fit of the experimental data, ternary constants were evaluated using the experimental data at low values of one component and equal values of the other two components by appropriate equations as suggested by Wohl (*18*). The data were correlated using these various ternary constants, using an average of these ternary constants as well as the ternary constant evaluated with the binary constants as suggested by Wohl (*18*). Good agreement with the experimental data was obtained using a ternary constant, $C = -0.028$, evaluated from the binary constants in accordance with Wohl's suggestion, in the three-suffix Margules equations. The binary constants used in the correlation were taken from literature and are reproduced below with their source:

| | Ref. |
|---|---|
| $A_{12} = 0.4$; $A_{21} = 0.35$ | (*15*) |
| $A_{23} = 0.052$; $A_{32} = 0.046$ | (*7*) |
| $A_{13} = A_{31} = 0.176$ | (*7*) |

Subscripts 1, 2, and 3 stand for acetone, carbon tetrachloride, and benzene, respectively. By inserting the seven constants into the three-suffix Margules equations of Wohl (*18*),

## Table I. Physical Properties of the Chemicals

| Chemical | Density at 30° C. | | Ref. Index at 30° C. | | Boiling point in ° C. at 760 ± 1 mm. of Hg | |
|---|---|---|---|---|---|---|
| | Expt. | Lit. (*16*) | Expt. | Lit. (*16*) | Expt. | Lit. (*16*) |
| Acetone | 0.7790 | 0.77933 | 1.3540 | 1.35417 | 56.1 | 56.11 |
| Carbon tetrachloride | 1.5746 | 1.5748 | 1.4547 | 1.45475 | 76.7 | 76.7 |
| Benzene | 0.8682 | 0.86836 | 1.4948 | 1.49486 | 80.1 | 80.05 to 80.15 |

## Table II. Experimental and Estimated Vapor-Liquid Equilibrium Data at 760 ± 1 mm. of Hg Total Pressure

(System: Acetone (I)-Carbon Tetrachloride (2)–Benzene (3) Composition on Mole % Basis)

| Temp., ° C. | $x_1$ | $x_2$ | $y_1$ | $y_2$ | $\gamma_1$ Exptl. | $\gamma_1$ Estd. | $\gamma_2$ Exptl. | $\gamma_2$ Estd. | $\gamma_3$ Exptl. | $\gamma_3$ Estd. |
|---|---|---|---|---|---|---|---|---|---|---|
| 57.4 | 78.4 | 13.6 | 82.6 | 12.6 | 1.01 | 1.03 | 1.70 | 1.74 | 1.24 | 1.25 |
| 57.4 | 81.5 | 10.1 | 85.4 | 9.4 | 1.00 | 1.02 | 1.70 | 1.81 | 1.28 | 1.28 |
| 57.4 | 85.7 | 6.3 | 88.6 | 6.2 | 0.99 | 1.01 | 1.81 | 1.90 | 1.34 | 1.33 |
| 57.5 | 74.2 | 17.7 | 79.5 | 16.0 | 1.02 | 1.04 | 1.64 | 1.65 | 1.16 | 1.21 |
| 57.7 | 71.3 | 20.6 | 77.2 | 18.2 | 1.03 | 1.05 | 1.60 | 1.60 | 1.16 | 1.18 |
| 58.0 | 67.4 | 25.2 | 74.8 | 21.0 | 1.04 | 1.07 | 1.49 | 1.53 | 1.15 | 1.15 |
| 58.3 | 61.0 | 31.7 | 72.5 | 23.5 | 1.10 | 1.11 | 1.32 | 1.43 | 1.09 | 1.11 |
| 58.3 | 63.1 | 29.6 | 73.2 | 22.8 | 1.08 | 1.10 | 1.37 | 1.46 | 1.09 | 1.12 |
| 58.5 | 54.0 | 43.1 | 68.2 | 30.3 | 1.16 | 1.18 | 1.24 | 1.32 | 1.03 | 1.06 |
| 59.0 | 49.5 | 48.1 | 66.0 | 32.7 | 1.21 | 1.22 | 1.18 | 1.26 | 1.06 | 1.04 |
| 59.4 | 62.4 | 17.0 | 72.3 | 15.6 | 1.04 | 1.08 | 1.56 | 1.51 | 1.14 | 1.14 |
| 59.5 | 44.6 | 52.9 | 61.0 | 37.6 | 1.22 | 1.28 | 1.21 | 1.21 | 1.10 | 1.03 |
| 59.5 | 45.0 | 52.3 | 62.4 | 36.0 | 1.24 | 1.27 | 1.18 | 1.22 | 1.10 | 1.03 |
| 59.6 | 48.5 | 35.0 | 64.0 | 26.6 | 1.17 | 1.19 | 1.29 | 1.30 | 1.10 | 1.05 |
| 60.1 | 56.0 | 19.6 | 67.4 | 17.6 | 1.05 | 1.11 | 1.50 | 1.43 | 1.17 | 1.10 |
| 60.6 | 45.3 | 33.2 | 62.0 | 26.0 | 1.18 | 1.21 | 1.29 | 1.28 | 1.04 | 1.05 |
| 61.3 | 30.7 | 64.2 | 51.2 | 45.8 | 1.40 | 1.47 | 1.15 | 1.11 | 1.01 | 1.01 |
| 61.6 | 45.1 | 24.4 | 60.4 | 21.0 | 1.12 | 1.18 | 1.37 | 1.31 | 1.10 | 1.06 |
| 61.6 | 41.6 | 30.6 | 59.8 | 24.2 | 1.20 | 1.23 | 1.26 | 1.26 | 1.04 | 1.04 |
| 61.8 | 29.2 | 65.5 | 50.8 | 46.0 | 1.44 | 1.50 | 1.11 | 1.10 | 1.08 | 1.01 |
| 62.4 | 38.9 | 27.9 | 57.2 | 22.8 | 1.20 | 1.24 | 1.27 | 1.25 | 1.05 | 1.04 |
| 62.8 | 24.5 | 69.8 | 46.4 | 50.0 | 1.52 | 1.60 | 1.10 | 1.07 | 1.09 | 1.01 |
| 63.0 | 47.0 | 9.1 | 63.2 | 8.3 | 1.07 | 1.14 | 1.39 | 1.38 | 1.11 | 1.08 |
| 63.1 | 36.7 | 25.9 | 55.0 | 22.0 | 1.19 | 1.25 | 1.29 | 1.24 | 1.05 | 1.03 |
| 63.1 | 38.4 | 23.7 | 56.5 | 20.3 | 1.17 | 1.23 | 1.30 | 1.26 | 1.05 | 1.04 |
| 64.0 | 28.5 | 31.0 | 48.8 | 26.4 | 1.32 | 1.34 | 1.25 | 1.17 | 1.02 | 1.02 |
| 64.1 | 18.4 | 75.7 | 40.7 | 55.5 | 1.70 | 1.74 | 1.08 | 1.04 | 1.07 | 1.02 |
| 64.2 | 31.3 | 24.4 | 52.4 | 21.0 | 1.28 | 1.29 | 1.26 | 1.21 | 0.99 | 1.02 |
| 64.4 | 27.4 | 43.0 | 48.1 | 33.7 | 1.34 | 1.40 | 1.14 | 1.14 | 1.01 | 1.01 |
| 64.9 | 23.4 | 49.8 | 44.1 | 39.0 | 1.42 | 1.49 | 1.12 | 1.10 | 1.02 | 1.01 |
| 65.1 | 28.8 | 23.6 | 48.0 | 21.0 | 1.24 | 1.30 | 1.27 | 1.20 | 1.04 | 1.02 |
| 65.8 | 14.1 | 79.9 | 34.6 | 61.4 | 1.79 | 1.87 | 1.07 | 1.03 | 1.04 | 1.03 |
| 68.4 | 8.1 | 85.3 | 24.8 | 70.0 | 2.07 | 2.06 | 1.06 | 1.01 | 1.12 | 1.05 |
| 71.0 | 3.9 | 89.4 | 14.8 | 79.6 | 2.35 | 2.23 | 1.06 | 1.00 | 1.10 | 1.07 |
| 71.0 | 8.1 | 42.5 | 22.2 | 40.6 | 1.70 | 1.65 | 1.14 | 1.06 | 0.99 | 1.01 |
| 71.7 | 8.4 | 20.6 | 21.0 | 20.0 | 1.53 | 1.51 | 1.13 | 1.10 | 1.07 | 1.00 |
| 72.3 | 6.0 | 39.1 | 16.8 | 38.2 | 1.66 | 1.66 | 1.12 | 1.06 | 1.04 | 1.01 |
| 73.5 | 5.2 | 49.6 | 16.8 | 46.6 | 1.87 | 1.76 | 1.03 | 1.04 | 0.99 | 1.02 |
| 73.5 | 5.7 | 91.3 | 21.0 | 76.2 | 2.11 | 2.20 | 0.92 | 1.01 | 1.14 | 1.07 |
| 74.1 | 5.7 | 17.9 | 15.8 | 18.0 | 1.56 | 1.52 | 1.09 | 1.10 | 1.04 | 1.00 |
| 74.6 | 3.3 | 44.1 | 10.5 | 43.2 | 2.28 | 1.75 | 1.02 | 1.04 | 0.99 | 1.02 |
| 74.7 | 3.8 | 32.1 | 11.0 | 32.8 | 1.61 | 1.64 | 1.09 | 1.06 | 1.03 | 1.01 |
| 75.0 | 5.2 | 31.4 | 14.8 | 31.4 | 1.57 | 1.62 | 1.05 | 1.07 | 0.99 | 1.01 |
| 75.2 | 3.6 | 28.4 | 10.4 | 29.0 | 1.61 | 1.62 | 1.07 | 1.07 | 1.03 | 1.01 |
| 75.3 | 4.4 | 15.3 | 12.2 | 16.4 | 1.50 | 1.53 | 1.12 | 1.10 | 1.03 | 1.00 |
| 75.3 | 5.2 | 26.3 | 14.5 | 25.9 | 1.51 | 1.58 | 1.03 | 1.08 | 1.01 | 1.01 |
| 75.5 | 3.1 | 37.8 | 9.0 | 39.4 | 1.91 | 1.49 | 0.82 | 1.05 | 1.15 | 1.00 |
| 75.6 | 3.1 | 25.3 | 9.1 | 26.2 | 1.59 | 1.61 | 1.07 | 1.07 | 1.03 | 1.01 |
| 76.1 | 4.3 | 21.0 | 12.8 | 21.6 | 1.60 | 1.56 | 1.05 | 1.09 | 0.99 | 1.00 |
| 76.6 | 3.9 | 16.9 | 12.0 | 18.2 | 1.61 | 1.54 | 1.08 | 1.10 | 0.98 | 1.00 |
| 76.8 | 2.1 | 25.3 | 6.5 | 28.0 | 1.60 | 1.62 | 1.10 | 1.07 | 1.00 | 1.01 |
| 78.3 | 2.4 | 2.3 | 7.2 | 2.8 | 1.53 | 1.48 | 1.17 | 1.13 | 1.00 | 1.00 |
| 78.4 | 1.8 | 10.2 | 5.2 | 12.5 | 1.46 | 1.53 | 1.17 | 1.11 | 0.98 | 1.00 |
| 79.4 | 0.9 | 7.2 | 2.8 | 8.9 | 1.56 | 1.53 | 1.13 | 1.11 | 0.98 | 1.00 |
| 79.4 | 1.6 | 1.7 | 5.2 | 1.9 | 1.55 | 1.49 | 1.07 | 1.13 | 0.98 | 1.00 |
| 79.5 | 0.6 | 7.3 | 1.9 | 9.0 | 1.58 | 1.53 | 1.14 | 1.11 | 0.98 | 1.00 |
| 79.7 | 1.6 | 1.7 | 5.2 | 2.0 | 1.54 | 1.49 | 1.07 | 1.13 | 0.97 | 1.00 |

$$\log \gamma_1 = x_2^2\,(0.4 - 0.1\,x_1) + 0.176\,x_3^2 + x_2x_3[(0.48 - 0.012\,x_3 + 0.028\,(1 - 2\,x_1)]$$

$$\log \gamma_2 = x_3^2\,(0.052 - 0.012\,x_2) + x_1^2\,(0.35 + 0.1\,x_2) + x_1x_3[(0.22 + 0.1\,x_2 + 0.028\,(1 - 2\,x_2)]$$

$$\log \gamma_3 = 0.176\,x_1^2 + x_2^2\,(0.046 + 0.012\,x_3) - x_1x_2[(0.128 - 0.012\,x_3 + 0.1\,x_2 - 0.028\,(1 - 2\,x_3)]$$

Table II compares the experimental and calculated activity coefficient data for each experimental run. Excellent agreement was obtained in most cases. The average error between the estimated and the experimental activity coefficients of all the runs expressed as $(\gamma_{\text{cal.}} - \gamma_{\text{expt.}})\,100/\gamma_{\text{cal.}}$ was + 1.72 in $\gamma_1$, − 0.48 in $\gamma_2$, and − 1.13 in $\gamma_3$, and these are within reasonable limits of experimental accuracy.

From the equilibrium curve for the system, acetone–carbon tetrachloride, drawn on a benzene-free basis with per cent benzene as the parameter, the azeotrope for this system disappeared at 50% benzene. This was further confirmed by estimating the relative volatility of acetone to carbon tetrachloride in presence of benzene and on benzene-free basis at this composition.

## NOMENCLATURE

$(A_{12}, A_{21})$ = end values from the plot of logarithms of the activity coefficients *vs.* % composition for 1-2 binary
$(A_{23}, A_{32})$ = end values from the plot of logarithms of the activity coefficients *vs.* % composition for 2-3 binary
$(A_{31}, A_{13})$ = end values from the plot of logarithms of the activity coefficients *vs.* % composition for 1-3 binary
$C$ = ternary constant
$P^\circ$ = pure component vapor pressure
$P$ = total pressure
$R$ = gas constant
$t$ = temperature, ° C.
$T$ = absolute temperature, ° K.
$V$ = liquid molal volume
$x$ = mole fraction of component in liquid
$y$ = mole fraction of component in vapor
$Z$ = correction factor for the nonideality in vapor phase
$\gamma$ = activity coefficient
$\rho$ = density
$\beta$ = second virial coefficient

### Subscripts

$1, 2.\ldots i$ = components $1, 2.\ldots i$

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# Thermodynamic Functions of Aqueous Hydrobromic Acid at Various Concentrations and Temperatures

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**Mean molal activity coefficients of aqueous hydrobromic acid have been calculated from electromotive force measurements over a HBr concentration range from 0° to 70° C. Moreover, the values of the thermodynamic functions of aqueous hydrobromic acid at 25° C. have been determined over the same concentration range.**

THIS investigation has been carried out as a preliminary contribution to research on the electrochemical processes concerning the bromine electrode, within the more general problem of the electrochemical behavior of the halogen-halide systems.

The purpose of this work is to determine the mean molal activity coefficients and the thermodynamic functions of aqueous hydrobromic acid at a wide range of HBr concentrations and temperatures.

Harned, Keston, and Donelson (*7*), Owen and Foering (*14*), Harned and Donelson (*6*), Hetzer, Robinson, and Bates (*8*), and Gupta, Hills, and Ives (*5*) have all studied HBr concentrations lower than 1 molal, at temperatures ranging from 0° to 60° C. Livingston (*10*) has investigated HBr concentrations up to 1.5 molal, at 25° C. Biermann and Yamasaki (*3*) have studied 0.5-, 1-, 2-, and 3-molal HBr at 20°, 25°, and 30° C.

The present investigation covers particularly the HBr