the ratio $K_{1}: K_{2}$ should be 6 . The observed ratio is about 3.3 at $\mu=1$, corresponding to about 6.8 at $\mu=0$. (The difference between the last two values is due to the fact that the factors in the function of Bray and Hershey ${ }^{4}$ by means of which $K_{2}$ was extrapolated to $\mu=0$, depend on the valencies of the associating ions.)
The interpretation of the absorption maximum in Fig. 11 as corresponding to the maximum concentration of ferric chloride finds a strong support in the results of Dodson, Forney and Swift ${ }^{17}$ on the effect of hydrochloric acid concentration on the extractability of ferric chloride solutions by ethers, which show, for different ethers, maxima between 6 and $8 \mathrm{~m} . / \mathrm{l}$. (cf. dotted line in Fig. 11). The extreme sharpness of this maximum, as well as the fact that the relative quantity of extracted ferric chloride increases with increasing concentration of iron, seems to indicate that $\mathrm{FeCl}_{3}$, passes into the ether in the form of associated molecules, e. g., $\mathrm{Fe}_{2} \mathrm{Cl}_{6}$. However, this conclusion contradicts the results of the molecular weight determinations of ferric chloride in organic solvents ( $c f$. Gmelin's Handbook ${ }^{18}$ ); on the other hand, it agrees with the results of Schlesinger and van Valkenburgh ${ }^{19}$ concerning the dimerization of $\mathrm{Fe}(\mathrm{CNS})_{3}$ in ether solutions. Spectrophotometric measurements on ferric salt solutions in organic solvents would be of considerable interest in connection with this problem.

[^0]
## Summary

1. Absorption curves have been determined for ferric perchlorate solutions in the presence of different amounts of $\mathrm{OH}^{-}, \mathrm{Cl}^{-}$and $\mathrm{Br}^{-}$ions, at different temperatures and ionic strengths.
2. The absorption curves of ferric perchlorate + perchloric acid systems have been analyzed and the absorption curve of free (hydrated) $\mathrm{Fe}^{3+}$ ions separated from that of $\mathrm{Fe}(\mathrm{OH})^{2+}$ ions (Fig. 2).
3. By a similar procedure, the absorption curves of solutions containing hydrochloric acid or hydrobromic acid have been analyzed. They show several successive association steps. The absorption curves of $\mathrm{FeCl}^{2}+, \mathrm{FeCl}_{2}+$ and $\mathrm{FeCl}_{3}$, as well as of $\mathrm{FeBr}^{2+}$, have been derived (Fig. 11). All these species are yellow, ferric chloride being the most intensely colored. The complex anions ( $\mathrm{FeCl}_{4}^{-} \ldots$ ) are only formed in very concentrated chloride solutions and are less strongly colored than ferric chloride.
4. The equilibrium constants $K_{1}=4.2, K_{2}=$ 1.3, $K_{3}=0.04, K_{\mathrm{Br}}=0.5$ (all for $\mu=1$ ) of the formation of $\mathrm{FeCl}^{2+}, \mathrm{FeCl}_{2}{ }^{+}, \mathrm{FeCl}_{3}$ and $\mathrm{FeBr}^{2+}$, have been derived from the effects of changes in the concentrations of $\mathrm{Fe}^{3+}, \mathrm{Cl}^{-}$and $\mathrm{Br}^{-}$on the spectra; the distribution of $\mathrm{Fe}^{\mathrm{III}}$ between the several ionic species at different chloride concentrations has been calculated (Fig. 13).
5. The effect of heating on the absorption curves has been measured and the heats and entropies of formation of $\mathrm{FeOH}^{2+}, \mathrm{FeCl}^{2+}$ and $\mathrm{FeBr}^{2+}$ determined (Table I).
Cambridge, Mass. Received October 3, 1941
[Contribution from the Baker Laboratory of Chemistry, Cornell University, and Tusculum College]

# A New Method for Determining Dineric Distribution ${ }^{1}$ 

## By Wilder D. Bancroft and Stephen S. Hubard

The primary object of the present investigation was to develop a perfectly general and convenient method for determining the composition of conjugate phases in systems of three liquid components containing two immiscible or slightly miscible components, each of which is consolute with the third liquid. The method to be described is essentially graphical. It is superior to that of

[^1]chemical analysis in cases where this is tedious or unreliable, and seems to us more convenient than the refractive index schemes which have been used by some workers.

Another object of this work was to show that our distribution data for the systems investigated could be generalized by simple empirical equations; these systems were benzene-alcohol-water and chloroform-acetone-water. This matter will be discussed later in detail, and we shall
present first the principles of the procedure for determining the distribution.

## The Method

Step 1.-If the isothermal diagram for the system at the desired temperature is not available, it must be obtained as the first step. The familiar method of saturating (detected visually by clouding) various known mixtures of each of the consolute pairs with the third liquid is recommended.

Step 2.-After the isothermal diagram has been obtained appropriate ternary mixtures of known total composition (by weight) are prepared, and the resulting conjugate solutions are allowed to reach equilibrium at the desired temperature. (The total compositions should be so chosen that an appreciable volume of each layer is present at equilibrium.)

Step 3.-After equilibrium has been attained, a considerable portion of each layer in a given mixture is removed and weighed. To be concrete, let us call the consolute component alcohol, and the other two components benzene and water, since this system was actually studied. An arbitrary amount of alcohol is then added to each sample (i,e., each phase), and the weight of this alcohol is found by difference. Benzene is then added to the sample of the layer rich in water (the lower layer in this system) until it becomes saturated; water is added in a similar manner to the sample of the layer rich in benzene (the upper layer in this system). The weights of benzene and water are found by difference, of course.

Step 4.-The final step is entirely mathematical, and consists in finding by trial-and-error what original composition of a given phase required the particular amounts of alcohol and benzene (or alcohol and water) added in Step 3 to depart from the isotherm and then return to it. The principles involved in this step can best be explained on a graphical basis. although, as will be seen later, our actual procedure here was more arithmetic than graphical.


Water Benzene
Fig. 1.-- Graphical principle of the method.
The reader is referred to Fig. 1, which is merely schematic. A mixture of total composition $C$, for example, forms the conjugate phases $X$ and $Y$ at equilibrium.

Point $M$ represents the "composition" of the benzene-plusalcohol added to the sample of phase $X$ in Step 3 to produce the final solution of composition $Z$, Since the weights of $X$ and $M$ are known, the ratio $X / M$ is also known, and is equal to the ratio $M Z / Z X$, which we shall call $R$. To determine the composition of $X$ (our ultimate object), a probable composition $Z_{1}$ is assumed for the final solution (of actual composition $Z$, but not yet known). The straight line $M Z_{1}$ is prolonged to the tentative point $X_{1}$, which is so chosen that $M Z_{1} / Z_{1} X_{1}=R$. A similar procedure. is followed for other probable compositions $Z_{2}, Z_{8}$, etc., the ratio $M Z_{\mathrm{x}} / Z_{\mathrm{x}} X_{\mathrm{x}}$ being kept equal to $R$. Since the correct value for $Z$ would give a value for $X$ lying on the isotherm, the points $X_{1}, X_{2}$, etc., may be connected by a smooth curve (almost a straight line if the points are close together) which cuts the isotherm at the true value of $X$. An analogous scheme can be used to determine the composition of phase $Y$, although this is not illustrated in Fig. 1.

It is not really necessary, of course, to determine independently the compositions of both phases, i. e., both $X$ and $Y$, if the total composition $C$ is known. Independent values were obtained in our work, however, to serve as a check on the consistency of the results.

The trial-and-error calculations actually used, and based upon the principles just outlined, will now be illustrated with a case from the system benzene-alcohol-water, in order that the scheme may be clearly understood.

The data chosen are for the lower layer derived from mixture no. 5 ( $c f$. Table IV and Fig. 2). The total composition of this mixture and the position of tie-line no. 4 (Fig. 2) indicated that the percentage of water in the lower layer probably fell in the range $50-55 \%$. The sample of the layer weighed 18.894 g ., and the weight of the final solution after adding (see Step 3) alcohol ( 5.937 g .) and saturating with benzene ( 2.435 g .) was 27.266 g . Since the ratio of the weights of the sample and of the final solution was about 0.7 , the percentage of water in the latter probably lay between 35 and $39 \%$. (This deduction was possible because the actual weight of water present did not change during the addition of alcohol and benzene; therefore, the percentages of water in the sample and in the final solution were inversely in the same ratio as the total weights of the two solutions.)

A tentative value of $36 \%$ water in the final solution was chosen, the percentages of alcohol and benzene at this point on the isotherm being 51.9 and 12.1 , respectively. On this basis the weights of water, alcohol, and benzene in the final solution would be, respectively, $9.817 \mathrm{~g} ., 14.158 \mathrm{~g}$.. and 3.300 g . The original sample would therefore have contained 9.817 g . water, 8.221 g . alcohol (i.e., 14.158 g . minus the 5.937 g . added in Step 3), and 0.865 g . benzene (i. e., 3.300 g . minus the 2.435 g . added in Step 3). The corresponding percentages are $51.94,43.50$, and 4.58 .

Since these values gave a point lying near the isotherm but not falling upon it, a value of $37 \%$ water in the final solution was next chosen, and a similar calculation was performed. A point was obtained which lay still closer to the isotherm than the previous one. After repeating this procedure for a value of $38 \%$ water in the final solution, three tentative compositions were available. When plotted, they fell on a straight line (broken line in Fig. 2) intersecting the isotherm at $53.9 \%$ water, $43.0 \%$ alcohol,


Fig. 2.-Benzene-alcohol-water at $25^{\circ}$ : open circles, Hubard; solid circles, Lincoln; squares, Varteressian and Fenske: broken line and crosses, tentative data for lower phase of no. 5 .
and $3.1 \%$ benzene-the true composition of the lower phase of mixture no. 1. The tentative values (percentages) used in deducing this are summarized in Table I.

## Table I

Tentative compositions of lower


| Water | Alcohol | Benzene | Water | Alcoture | Benzene |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 36.0 | 51.9 | 12.1 | 51.94 | 43.50 | 4.58 |
| 37.0 | 51.7 | 11.3 | 53.39 | 43.19 | 3.42 |
| 38.0 | 51.4 | 10.6 | 54.8 | 42.7 | 2.41 |

True value (from diagram) $53.9 \quad 43.0$
3.1

The compositions of all water-rich layers were determined according to the scheme just described. The only differences involved in working with benzene-rich layers are that benzene, not water, is the component whose actual weight remains constant throughout Step 3, and that water, not benzene, is the saturating liquid. It therefore seems unnecessary to work out one of these cases in detail. The application of the method to the system chloroform-acetone-water is also left to the reader.

There are, however, several additional general points which should be borne in mind if one wishes to avoid shooting in the dark. For example, the tie-line nearest the benzene-water axis in the ternary diagram (no. 1 in Fig. 2) was determined first, since the possible range of its slope is obviously more restricted than that of any other tie-line (that is, before any of the tie-lines have been determined). Consequently, there was a minimum amount of
guess-work involved in finding the composition of the conjugate phases. In the second place, one should not forget that the location of one tie-line fixes qualitatively the slope of the others: that is, it shows whether alcohol is dissolved preferentially in the benzene-rich layer or the waterrich layer. With one tie-line determined and the general pitch of the others indicated, it was possible to estimate the water or benzene content of any succeeding conjugate phase within $\pm 2-3 \%$ in carrying out the calculations in Step 4.

The accuracy of the composition deduced for any conjugate solution is greater, the closer to $90^{\circ}$ is the angle between the isotherm and the plot of the tentative values. A fairly wide angle can be assured by bringing the final solution back to the isotherm (see Step 3) as far as possible from the original composition of the sample. For this reason, it proved desirable to add relatively large quantities of alcohol to the samples-enough to give a final solution weighing one and one-half to two times as much as the sample. The precision of the method is probably about $\pm 0.2 \%$ in most cases, although the accuracy of the actual compositions is, of course, dependent also upon the reliability of the isothermal diagram.

## The Systems Benzene-Alcohol-Water and Chloroform-Acetone-Water

Materials and Experimental Procedure.-Absolute alcohol, benzene of thiophene-free grade, and acetone and chloroform of reagent grade were dried with pure calcium oxide and fractionally distilled into receivers protected
with tubes of ascarite. The distilled water was freshly boiled. The various liquids were stored in bottles connected to burets which were filled with rubber hand-pumps, and a tube of ascarite was inserted between the pump and the rest of the delivery system in each case.

All mixtures were prepared in glass-stoppered flasks and allowed to reach equilibrium in a thermostat maintained at $25 \pm 0.1^{\circ}$. The conjugate solutions were sampled with pipets provided with fine openings. In sampling a lower layer, contamination by the upper layer was prevented by maintaining a slight positive pressure on the pipet until the tip was below the iaterface. In determining saturation the end-point was approached with great caution. and was taken as the first appearance of cloudiness (when water was the saturating liquid). or the first appearance of tiny drops of a second phase (when benzene or chloroform was the saturating liquid). When a flask was removed from the thermostat either for sampling or titrating, it was slipped quickly into a beaker containing water taken directly from the bath, in order that its temperature should not change appreciably during the operation.


Fig. 3.-Logarithmic plots of the isotherms: Plot I, $\mathrm{C}_{6} \mathrm{H}_{6}-\mathrm{EtOH}-\mathrm{H}_{2} \mathrm{O}$; open circles, Lincoln; solid circles. Hubard; squares, Varteressian and Fenske. Plot II, $\mathrm{CCl}_{3} \mathrm{H}-\mathrm{Me}_{2} \mathrm{CO}-\mathrm{H}_{2} \mathrm{O}$, open circles, Hubard: solid circles. Brancker, et al.

The Isotherms.-The data for benzene-alco-hol-water are presented in Table II and the diagram is shown it1 Fig. 2. Most of the values were obtained in a very careful investigation by Lincoln ${ }^{2}$ many years ago; the remaining data were obtained by the present authors and, in two cases, by Varteressian and Fenske. ${ }^{3}$

[^2]Table II
Benzene-Alcohol-Water at $25^{\circ}$ : Data for the Isotherm
Unlettered compositions were recalculated on a percentage basis from Lincoln's data; H refers to data by Hubard, and V to data by Varteressian and Fenske.

|  | Beazene | Percentag Alcohol | Water |  | Benzene | Percentage Alcohol | Water |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $V$ | 0.10 | 9.98 | 89.92 |  | 22.20 | 51.90 | 25.90 |
| $V$ | 0.36 | 24.88 | 74.76 |  | 23.93 | 51.47 | 24.60 |
| H | 1.09 | 34.11 | 64.79 | H | 27.99 | 50.25 | 21.77 |
|  | 3.34 | 43.45 | 53.21 |  | 28.04 | 50.19 | 21.77 |
|  | 4.39 | 45.98 | 49.63 |  | 44.30 | 42.44 | 13.26 |
|  | 5.75 | 47.97 | 46.28 | H | 54.71 | 36.04 | 9.27 |
|  | 6.90 | 49.14 | 43.96 | H | 69.39 | 25.70 | 4.91 |
|  | 9.18 | 50.58 | 40.24 |  | 69.79 | 25.42 | 4.79 |
|  | 11.76 | 51.92 | 36.32 |  | 82.17 | 15.75 | 2.08 |
|  | 14.80 | 52.35 | 32.79 |  |  |  |  |

Lincoln found that his isothermal data followed a mass law equation of the type

$$
\begin{equation*}
\frac{(b / a)^{n}}{(w / a)}=K \tag{1}
\end{equation*}
$$

in which $b, a$ and $w$ represent the weights or percentages of benzene, alcohol and water, respectively, in a given saturated solution; for when he plotted $\log b / a$ against $\log w / a$, the graph was a straight line. We re-plotted (Fig. 3) Lincoln's data in this way (using $-\log w / a$ for convenience) and found that our own data fell on the same straight line; thus we not only corroborated Lincoln's conclusion, but also showed that our data were consistent with his. One of the two values given by Varteressian and Fenske fell on the line and the other did not; since, however, the latter represented a solution containing only $0.1 \%$ benzene, it is obvious that a very slight experimental error could produce a large error in the term $\log$ $b / a$, and the discrepancy is therefore not important.

The isothermal data for chloroform-acetonewater are listed in Table III and the diagram is

Table III
Chloroform-Acetone-Water at $25^{\circ}$ : Data for the Isotherm
Unlettered data by Hubard; B, data by Brancker, Hunter and Nash.

| Percentage |  |  |  |  | Percentage |  |  |
| ---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Chloroform | Acetone | Water | Chloroform | Acetone | Water |  |  |
| B | 0.6 | 0 | 99.4 | 21.94 | 60.90 | 17.18 |  |
| 0.84 | 20.74 | 78.43 | 25.93 | 61.14 | 12.96 |  |  |
| 1.52 | 34.16 | 64.38 | B 28.5 | 60.5 | 11.0 |  |  |
| 3.06 | 42.98 | 53.97 | 32.82 | 58.74 | 8.42 |  |  |
| 4.85 | 48.33 | 46.80 | B 35.4 | 57.3 | 7.3 |  |  |
| 7.73 | 52.77 | 39.52 | B 43.4 | 52.0 | 4.6 |  |  |
| 9.76 | 55.38 | 34.85 | B 55.2 | 42.3 | 2.5 |  |  |
| 13.08 | 57.50 | 29.44 | 65.86 | 32.63 | 1.54 |  |  |
| 14.54 | 58.08 | 27.39 | B 70.0 | 28.5 | 1.5 |  |  |
| 16.29 | 59.21 | 24.50 | B 80.0 | 18.8 | 1.2 |  |  |
| 20.36 | 61.07 | 18.60 |  |  |  |  |  |


shown in Fig. 4. Brancker, Hunter and Nash ${ }^{4}$ have recently determined this isotherm, but we found it advisable to redetermine a considerable portion of it. The plot of their data was unreasonably flat near the maximum of the curve, and their solutions on the water-rich side contained consistently more chloroform than we found, although their data were concordant with ours on the chloroform-rich side. Several of these latter values are included with ours in Table III.

In contrast to benzene-alcohol-water, the isothermal data for chloroform-acetone-water do not follow a mass law equation of the type represented by Eq. 1. When we plotted $\log c / a$ against $\log w / a$ ( $c, a$ and $w$ representing the percentages of the three components in a saturated solution) the points followed a sort of sigmoidal curve (Fig. 3) instead of a straight line. The flexures in the curve are small, but much larger than can be accounted for by experimental error. So far we have not been able to find a simple equation which describes the curve.
It is not surprising that the present system does not follow the same relationship as does the system benzene-alcohol-water, since we have re-
(4) Brancker, Hunter and Nash, J. Phys. Chem. 44, 683 (1940).
placed a completely non-polar liquid, benzene, by a somewhat polar one, chloroform (the other two liquids are, of course, polar in each case). Thus the solubility relationships might be expected to show considerable differences from those in the first system studied. The changes in slope of the curve for chloroform-acetone-water point, perhaps, to some sort of opposing effects, of an obscure nature at present. It is interesting that the hump in the middle of the curve changes in slope at a point which must be very close to the plait point.

Distribution Data.-In Table IV are presented for benzene-alcohol-water the total compositions of the mixtures used, and the compositions of the resulting conjugate solutions, obtained according to our new method. The corresponding data for chloroform-acetone-water are shown in Table V. The tie-lines representing the distribution are drawn on the isothermal diagrams in Figs. 2 and 4.

In both systems the distribution was found to follow an equation of a type discussed by Hand ${ }^{5}$ in connection with certain ternary liquid systems. For the system benzene-alcohol-water
(5) Hand. ibid., 34, 1961 (1930).


Table V
Chloroform-Acetone-Water at $25^{\circ}$ : Dineric Distribution

| Mixture по. | Origi <br> Chloroform | al mixtur Acetone | Water | Chlorofor | er layer Acetone | Water | Chloroform | rer layer. Acetore | Water | $\log K$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1. | 37.32 | 23.96 | 38.44 | 0.7 | 17.3 | 82.0 | 68.8 | 29.7 | 1.5 | -0.30\% |
| 2 | 37.58 | 34.16 | 28.25 | 1. 0 | 25.0 | 74.0 | 58.0 | 39.9 | 2.1 | -. 305 |
| 3 | 29.77 | 44.11 | 26.14 | 1.6 | 34.4 | 64.0 | 46.4 | 49.7 | 3.9 | -. 300 |
| 4 | 19.79 | 49.61 | 30.59 | $\because .0$ | 42.8 | 54.2 | 36.4 | 56.8 | 6.8 | -. 300 |
| 5 | 21.92 | 55.99 | 22.09 | 4.8 | 48.0 | 47.2 | 30.1 | 59.9 | 10.0 | -. 298 |
| 6 | 17.76 | 57.93 | 24.31 | 7.4 | 52.5 | 40.1 | 23.3 | 61.2 | 15.5 | -. 311 |
| Equation: $\log a_{1} / w_{1}-1.02 \log a_{2} / c_{2}=\log K^{\circ}$. |  |  |  |  |  |  | Average |  |  | -. 306 |

this equation has the form

$$
\begin{equation*}
\log a_{1} / b_{1}-n \log a_{2} / a_{2}=\log K \tag{2}
\end{equation*}
$$

which is derived from the mass law equation

$$
\begin{equation*}
\frac{a_{1} / b_{1}}{\left(a_{2} / w_{2}\right)^{n}}=\mathbb{K} \tag{B}
\end{equation*}
$$

where $a_{1}$ represents the percentage of alcohol in the benzene-rich layer; $b_{1}$, the percentage of benzene in that layer; $a_{2}$, the percentage of alcohol in the water-rich layer; $w_{2}$, the percentage of water in that layer. Our distribution data are plotted in Fig. 5 as $\log a_{1} / b_{1}$ against $\log a_{2} / w_{2}$. The coefficient $n$ in Eq. 2 was found graphically to be 1.14. This was used to calculate the values of $\log K$ given for the various solutions in Table IV, and it can be seen from the concordance of these results that the distribution is described satisfactorily by Eq. 2. Although the first value for $\log K$ in Table IV is distinctly not in agreement with the others, it corresponds to solutions so dilute that a very slight error in experiment could easily have produced a large error in the logarithmic terms; thus the discrepancy is not disturbing. In fact, even the next two or three values for $\log K$ correspond to solutions so dilute on the benzene-rich side that their good agreement is probably to some extent fortuitous.

Taylor ${ }^{\text {b }}$ determined the volume distribution in this system by a method based upon refractive index measurements, and found that his data fitted a relation similar to Eq. 2. Hand ${ }^{5}$ recalculated Taylor's data on a weight basis, and found a value of 1.20 for the coefficient $n$ and an average value of -0.980 for $\log K$, which differ somewhat from those obtained by us. Taylor's data and his values for $n$ and $\log K$ are perhaps less reliable than ours, because his reagents were measured by volume, not weight, and he made fewer measurements.

For the system chloroform-acetone-water the distribution equation is

$$
\log a_{i} / w_{1}-n \log a_{2} / c_{2}=\log h
$$

where $a_{1}$ represents the percentage of acetone in the water-rich layer (the upper layer); $w_{1}$, the percentage of water in that layer; $a_{2}$, the percentage of acetone in the chloroform-rich layer (the lower layer); and $c_{2}$ the percentage of chloroform in that layer. Our distribution data are plotted logarithmically in Fig. 5. The value of $n$ in Eq. 4 was found graphically to be 1.02 . This was used to calculate the values of $\log K$ for the various solutions in Table $V$, and it can be seen from these results that the distribution is described

[^3]satisfactorily by Eq. 4. Lack of time prevented the investigation of very dilute solutions, where some deviation from Eq. 4 might be expected because of experimental limitations.
Hand ${ }^{5}$ has determined the distribution in this system by chemical analyses of various conjugate solutions. His values for the coefficient $n$ and for $\log K$ are 1.07 and -0.389 (average), which differ appreciably from ours. His data are less consistent than ours, however.

## Discussion of the Distribution Equations

In the usual deduction of the distribution law it is tacitly assumed that addition of the third component causes no increase in the mutual miscibility of the slightly miscible pair of components. This is known not to be true, however, for any finite addition of the third component; consequently the ordinary distribution law is not valid for any considerable range of concentrations. In the preceding sections we have applied to each system a distribution relation which holds even for the most concentrated solutions. The physical significance of the exponent $n$ in Eq. 3 (the coefficient in the logarithmic Eqs. 2 and 4) seems to be that $n$ is related to the increase in mutual solubility of the two immiscible liquids upon addition of the consolute liquid. If this increase in solubility did not occcur, or if it were the same for both liquids, the value of $n$ should be unity. It should be noted that in the system benzene-alco-hol-water, where the isotherm is quite lopsided, $n$ has a value of 1.14; while in the system chloro-form-acetone-water, where the isotherm is more nearly symmetrical, $n$ has a value of $1.02, i$. $e$., closer to 1 . This is in accord with the fact (cf. Tables IV and V) that while there is more benzene in the water layers than water in the benzene layers, and more water in the chloroform layers than chloroform in the water layers, the discrepancy in the first system is much greater than in the second.

The physical significance of $K$ in our equations is, of course, that $K$ is related to the ratio of the


Fig. 5.-Distribution data: Plot I, $\mathrm{C}_{6} \mathrm{H}_{5}-\mathrm{EtOH}-\mathrm{H}_{2} \mathrm{O}$; plot II, $\mathrm{CCl}_{8} \mathrm{H}-\mathrm{Me}_{2} \mathrm{CO}-\mathrm{H}_{2} \mathrm{O}$.
concentrations of the consolute liquid in the two phases (alcohol in the first case and acetone in the second). It is not a direct measure of this ratio because of the exponential form of the fundamental equation.

## Summary

A new and perfectly general method for determining dineric distribution in ternary liquid systems has been described and applied to the systems benzene-alcohol-water and chloroform-acetone-water.
The distribution over the entire range of concentrations in these systems can be described by simple equations of the mass law type. These equations, unlike the ordinary distribution law, do not ignore the increase in mutual solubility of the slightly miscible liquids upon addition of the consolute liquid.
Ithaca, New York Received August 25, 1941
Greeneville, Tennessee


[^0]:    (17) R. W. Dodson, G. J. Forney and E. H. Swift. This Journal. 58, 2573 (1936).
    (18) Gmelin. '"Handbuch der anorganischen Chemie," 8th edition, No. 59B, p. 229.
    (19) H. I. Schlesinger and H. B. van Valkenburgh. This Journal, 53, 1212 (1931).

[^1]:    (1) The funds for this research were provided by the Bancroft Foundation at Cornell University.

[^2]:    (2) Lincoln, J. Phos. Chem. 4. 161 (1900).
    (3) Varteressian and Fonske. Int. Eng. Chem. 28. 228 (1930)

[^3]:    (i) Taylor. J. Phys. Chem., 1. 461 (1897).

