chlorine and phosphate in such liquids (for example, urine) no difficulties were presented, the results being in perfect accord with those obtained by the other methods. The advantages of the electro-titrametric method in these latter instances are, the possibility of an exact analysis of a few cubic centimeters, and at the same time an extremely high degree of precision.

It is necessary here to call attention to the fact that in the determination of $\mathrm{SO}_{4}$ in such liquids certain complications were encountered, which impressed us with the fact that we had to deal with a liquid of different composition from the synthetical solution. Observing certain precautions, as for example, degree of acidity, kind of reagent, etc., we were in some instances able to obtain results which closely agreed with those of gravimetric determinations.

The last curve is an illustration of the acid- and base-binding capacity of a physiological liquid, in this case urine. The previous statement in regard to the use of indicator is especially true in this case. It should not be overlooked, however, that the direction of the curve in such cases is probably not entirely due to the above stated phenomena, because other factors, such as changing viscosity, may affect the total result. It is interesting to note that in this connection successive precipitations were observed after the addition of certain amounts of the reagent.

It is the belief of the writers that such curves may prove to be in some cases a more instructive demonstration of the complex properties of such liquids and that more deductions might be drawn from such curves than those from a turning point of an indicator.

As the nature of this publication is preliminary, the authors wish to reserve the right to develop this field more completely in the near future.

Amerrst. Mass.
[Contribution from the Chemical Laboratories of Clark University.]

## A RAPID LABORATORY METHOD OF MEASURING THE PARTIAL VAPOR PRESSURES OF LIQUID MIXTURES.

By M. A. Rosanoff. C. W. Bacon and R, H. White. ${ }^{1}$
Received July 2, 1914.
Section I.-Introductory Remarks.
It is scarcely necessary to point out that the partial pressures of volatile mixtures are not measured as such. What is really determined, is the composition of the vapor which is in equilibrium with the liquid mixture. The partial pressures are then assumed to be proportional to the molar percentages of the components in the vapor, and their absolute values become known if the total pressures have been determined manometrically.
${ }^{1}$ I gladly acknowledge my indebtedness to my research assistant, Dr. John F. W. Schulze. for valuable help in preparing this paper for publication. M. A. R.

The main difficulty involved is that of analyzing the vapor with sufficient precision. The method that has been most extensively used in the past consists in distilling off a small amount from the given mixture and analyzing the distillate, on the assumption that if the relative amount of distillate is sufficiently small, its composition is very close to that of the first trace of vapor given off by the liquid. As the precision and reliability of this method are in many ways subject to doubt, and as the results obtained have often been found to disagree with those yielded by other methods, it appeared desirable to devise a method, the reliability of whose results should, as far as possible, be free from doubt. Such, we believe, is the method devised by Rosanoff, Lamb, and Breithut, ${ }^{1}$ and worked out in its practical details in these laboratories. ${ }^{2}$ It consists, briefly, in passing a binary vapor of constant composition through a liquid mixture of the same substances; as long as the liquid is not in equilibrium with the vapor, its composition changes, and consequently both its boiling point and the vapor escaping from it change continuously. When the composition of the liquid has finally adjusted itself to that of the vapor employed, and equilibrium has set in, everything becomes constant: the thermometer in the liquid indicates a constant temperature; the escaping vapor has ceased changing, and consecutive fractions of it condensed show the same composition. The attainment of equilibrium is thus attested in two independent ways, and as the condensed fractions can be taken as large as desired, the analytical difficulties disappear, and the composition of the equilibrium vapor becomes known with all precision necessary. Unfortunately, the required apparatus is somewhat complex, and its efficient handling calls for considerable manipulative skill, so that the method can scarcely be recommended for ordinary use, in connection with studies of either the theory of solutions or fractional distillation.
The method just referred to has served to demonstrate that reliable partial pressure data can be obtained by distilling off a small fraction, as has long been practised. Thus, the well-known results obtained by v. Zawidzki ${ }^{3}$ are doubtless very good. Only, on account of the tendency of certain impurities, such as moisture, to accumulate in the first distillate, the organic liquids employed must be exquisitely purified, and the small distillate to be analyzed must be handled with great care, if its composition is not to be grossly affected by evaporation. Furthermore, even v. Zawidzki's apparatus is of somewhat complex construction and calls for no little delicacy of manipulation. Thus a need still remained for a simpler and more rapid, yet sufficiently reliable, laboratory method.

[^0]Such a method is described in the present communication. It was first devised and successfully employed in these laboratories during the year 1910-191i, and a brief preliminary account of it was published in igi. ${ }^{1}$ Since then, however, it has been used here in a number of new cases of both binary and ternary mixtures, and to-day we feel justified in recommending it as the easiest method for ascertaining the composition of vapors in equilibrium with all sorts of liquid mixtures. We believe, further, that it would be especially useful where the available amount of substance is too small for the older methods to yield accurate results.

## Section II.-Principle of the Method.

The problem is to ascertain the composition of the first infinitesimal amount of vapor given off by a liquid mixture of known composition. To this end we subject the given mixture to distillation, carefully avoiding reflux condensation. The amount finally driven over may be as great as 80 or $90 \%$ of the total original weight. And imagine that we have obtained knowledge of what the composition of the distillate was when its weight was, say, I g.; what the composition of the distillate was when its weight had reached 2 g ., then 3 g ., 4 g ., 5 g ., etc. If the composition of the distillates were now plotted against their weights, a curve would be obtained, every point of which would indicate the composition that the distillate would have when its weight has attained any definite amount within the range of the curve. But only a moderate extrapolation backward would lead up to the composition axis, that is, to where the weight of distillate is zero. The point of intersection would obviously indicate the composition of the first indefinitely small amount of distillate, and thus our problem would be solved.

This is, in fact, our procedure. Only, instead of allowing the distillate to accumulate in the receiver, we remove seven or eight consecutive fractions of it, and weigh and analyze them separately. Knowing the weights and compositions of Fractions 1 and 2, we can readily calculate the weight and composition that would have been found if they had been allowed to form a single combined fraction. Similarly, knowing the weights and compositions of 1,2 and 3 , we can easily calculate what the weight and composition would have been if these three distillates had been allowed to form a single fraction, and so forth for the rest of the distillates obtained.

The extrapolation just mentioned indicates, as stated, the composition of the first infinitesimal amount of vapor evolved by the given liquid mixture. But the same experiment yields also further information. Suppose that eight distillates have been collected and that the composition of the residue had been found by analysis. Knowing, again, the weights and compositions of Fractions 8 and 7 , we can calculate the weight
${ }^{1}$ Rosanoff, J. Franklin Inst., 172, 527 (1911).
and composition that would result if the two were mixed, or if they had been allowed to form a single fraction. Similarly, we can find the combined weight and composition of Nos. 8, 7, and 6, then of Nos. 8, 7, 6, and 5, etc. Suppose now that the weight of No. 8 is entered as an abscissa and the composition of No. 8 as the corresponding ordinate; that the combined weight of Nos. 8 and 7 is taken as a second abscissa, and their combined composition as a second ordinate, etc. A new curve would thus result, and this curve again we would extrapolate to intersection with the composition axis. The point on the curve corresponding to distillate No. 8 may be thought of as the composition of the mixture returned to the residue when the weight returned, as if by a reversal of the actual distillation, is that of No. 8. Similarly, the point of intersection on the composition axis would represent the composition of the first infinitesimal amount returned to the residue. But this is evidently nothing else than the composition of the slight amount of vapor still in contact with the residue. In this manner our one actual distillation teaches, not only what vapor is in equilibrium with the original mixture, but also what vapor is in equilibrium with the final residue. It would be easy to show that simple enough calculation could further reveal the composition of the vapors in equilibrium with mixtures intermediate between the original and the residue. But we will not insist on this point, as we have not made use of it in our practical work.

## Section III.-Apparatus and Manipulation.

In applying experimentally the simple principle just stated, an apparatus was devised in which reflux condensation is practically impossible. The apparatus, drawn to scale in cross section, is shown in Fig. i. It consists of a pear-shaped vessel with a long neck, near the upper end of which are four circular openings for the escape of the vapor. A glass jacket, fused on to the rim of the neck, surrounds the flask and ends below in a tube through which the vapors escape into a powerful worm condenser, and thence, in liquid aform, into a receiver having several compartments for the convenient collection of consecutive fractions. The receiver communicates with the atmosphere through a tube filled with calcium chloride, to keep out moisture. The neck of the pearshaped boiling-vessel is permanently stoppered above with a cork, which is made thoroughly vapor- and liquid-tight with shellac and sealing-wax. The cork carries an electric heater of platinum wire, and, for the introduction and withdrawal of liquid, an adapter-tube reaching nearly to the bottom of the boiling-vessel. Liquid is introduced and withdrawn with the aid of a separatory-funnel fitted by means of a tight cork into the upper part of the adapter-tube, as shown in the diagram. During operation the boiling-vessel is thus surrounded by the vapor of the boiling liquid itself, and thus reflux condensation is prevented. But to make doubly sure
of this, the jacketed distillation vessel is all but completely immersed in a bath, whose temperature, roughly constant, is somewhat above the highest temperature that may be attained by the boiling mixture experimented upon.

The manipulation is very simple. A mixture of known composition is introduced into the distilling vessel and is set boiling by means of the electric heater. There being no reflux, the distillation is usually very rapid, each fraction taking only a minute or two to collect. The fractions are received in small, carefully weighed glass-stoppered bottles, and in scarcely half an hour, during which the apparatus requires little attention, the run is complete. Now a sample of the residue is withdrawn for analysis, the several distillates are weighed (with a precision of about 0.05 g .), and finally the residue and the distillates are analyzed as stated above.

We have not mentioned the dimensions of the distillation apparatus. In our earlier work the pear-shaped boiler had a capacity of about 300 cc . and was almost filled with the liquid mixture for a run. To prevent the protrusion of the platinum heater above the liquid, the distillation was usually interrupted when about 100 cc . of liquid still remained in the vessel. More recently a smaller apparatus has been employed here, the pearshaped boiler having a capacity


Fig. 1. of only 125 cc. , and the shape of the platinum heater was modified to permit of leaving a residue of barely 25 cc . There is, however, no reason why a still smaller apparatus should not be employed when only a scanty amount of experimental material is available.

## Section IV.-Analytical Method.

The composition of our binary mixtures was determined on the basis of their refractive indices by an interpolation method first recommended by Ostwald and since used by von Zawidzki and also in this laboratory. The indices of a number of mixtures of exactly known composition are determined, and from these the percentages are calculated which would correspond to these indices if the latter obeyed the rule of additivity. The differences between the true and these "ideal" percentages are plotted as ordinates against the ideal percentages themselves. The resulting curve gives the correction to be algebraically added to the ideal percentage, the latter being calculated in any given case from the equation:

$$
\text { Ideal percentage }=\frac{100\left(i-i_{2}\right)}{i_{1}-i_{2}}
$$

where $i_{1}$ is the refractive index of the isolated component whose ideal percentage in the mixture is sought, $i_{2}$ is the index of the second component in the isolated state, and $i$ is the observed index of the mixture.

Tables I-III give the corrections for a number of ideal percentages in the case of three pairs of liquids; the data of Tables I and II are based on new measurements; the data of Table III are calculated from the measurements of von Zawidzki. ${ }^{1}$ Corrections for other percentages than those given in the tables will readily be found by graphic interpolation. All these corrections lead to the true composition of the mixtures expressed in molar percentages.

Table I.
Chloroform-Toluene.

Table II.
Acetone-Toluene.

Table III.
Ethyl Iodide-Ethyl Acetate.
The index of the iodide is 1.51009. That of the acetate is $\mathbf{1 . 3 7 0 1 2}$. Temp. $25.2^{\circ}$.

Ideal \% Correc-

| Ideal $\%$ <br> $(\mathrm{CH})_{2} \mathrm{CO}$ <br> 0 | Correc- <br> tion. | Ideal <br> $\mathrm{C}_{2} \mathrm{H}_{5}$ \%. | Correc- <br> tion. |
| :---: | :---: | :---: | :---: |
| 0 | 0 | 0 | 0 |
| 10 | +3.03 | 10 | +4.12 |
| 20 | +3.56 | 20 | +6.96 |
| 30 | +7.35 | 30 | +8.68 |
| 40 | +8.56 | 40 | +9.4 I |
| 50 | +9.16 | 50 | +9.42 |
| 60 | +9.12 | 60 | +8.70 |
| 70 | +8.31 | 70 | +6.21 |
| 80 | +6.52 | 80 | +5.36 |
| 90 | +3.56 | 90 | +2.96 |
| 100 | 0 | 100 | 9 |

${ }^{1}$ Von Zawidzki, Loc. cit., p. 145.

Tables for the analysis of mixtures of carbon disulphide and carbon tetrachloride may be found in a former communication. ${ }^{1}$

Ternary mixtures, whose partial pressures were determined by the present method, have been analyzed according to the procedure described by Schulze. ${ }^{2}$

## Section V.-Purification of the Substances.

Our substances were purified as follows: Carbon disulfide was thoroughly shaken with lime, allowed to stand for some time in contact with mercury, dried with calcium chloride, and distilled; a large middle fraction collected for use passed over within less than o.1 ${ }^{\circ}$. Kahlbaum's carbon tetrachloride required no further treatment than drying with calcium chloride and redistilling, the fraction collected for use boiling again within o. ${ }^{\text { }}$. Chloroform from a well-known American manufacturer was washed with dilute sulfuric acid, then with caustic potash, and next, five times with water. After drying with calcium chloride, it was distilled in dim light, a large middle fraction, boiling between $60.9^{\circ}$ and $61.0^{\circ}$, being kept for use. A high-grade commercial toluene was thoroughly washed with water, dried with calcium chloride, and distilled, the utilized fraction passing over between $109.5^{\circ}$ and $109.6^{\circ}$. A quantity of commercial acetone was boiled for ten hours with an excess of solid potassium permanganate, distilled off, dried with potassium carbonate, and redistilled; the fraction kept for use passed over within $0.1^{\circ}$. The ethyl iodide was prepared by ourselves, from resublimed iodine, absolute alcohol, and pure red phosphorus; the crude product was washed with a solution of caustic potash and with water, then dried with calcium chloride, distilled, and preserved in contact with finely divided ("molecular") silver; the preparation distilled over completely between $72.6^{\circ}$ and $72.8^{\circ}$. Finally, a good grade of commercial ethyl acetate was washed with a $50 \%$ solution of calcium chloride, then dried with fused calcium chloride, and distilled, the utilized fraction passing over between $76.6^{\circ}$ and $76.7^{\circ}$.

| No. of distillate. | Table IV.-Run Weight of distillate. Grams. | A. <br> Index of refraction. | $\mathrm{Molar} \%$ of CS . |
| :---: | :---: | :---: | :---: |
| 1. | 16.48 | 1.53177 | 59.35 |
| 2. | 19.43 | 1.53108 | 58.96 |
| 3. | 15.86 | 1.52815 | 57.21 |
| 4. | 16.00 | 1.52491 | 55.25 |
| 5. | .. 23.75 | 1.52088 | 52.73 |
| 6. | .. 17.80 | 1.51639 | 49.85 |
| 7. | 25.23 | 1.51181 | 46.79 |

It would have been advantageous to express the composition of the dis-

[^1]tiallates, not in molar, but in weight percentages, as the former complicate the calculations unnecessarily. We will, however, reproduce all results in this paper in the form in which they were originally obtained and used.
From the figures of Table IV, calculation gives the following:


The original mixture (refractive index $=1.49780$ ) contained 36.77 molar per cent $\mathrm{CS}_{2}$. The third column of Table V shows, by graphic extrapolation, that the vapor in equilibrium with the original mixture contained 60.35 molar per cent $\mathrm{CS}_{2}$.


Fig. 2.-Carbon"disulphide-carbon tetrachloride.

The residue (refractive index $=$ 1.48000) contained 22.18 molar per cent $\mathrm{CS}_{2}$. The sixth column of Table V shows, by graphic extrapolation, that the vapor in equilibrium with the residue contained 44.85 molar per cent $\mathrm{CS}_{2}$.
The results of Table V are shown graphically by the pair of curves marked $A$ in Fig. 2. The curves, it will be seen, are very smooth, and the slight extrapolation introduces practically no uncertainty. Only the first point on the upper curve, corresponding to the first distillate, fails to agree with the rest. The cause of this was doubtless a trace of moisture contained in the original mixture, and if one distillate only had been examined, as is done in the older procedures, an error of at least $1 \%$ would have been introduced, probably more. On the other hand, the shape of our curve and its extrapolation are scarcely rendered less certain by the irregularity of that one point.
Table VI.-Run B.

| No. of distillate. | Weight of distillate. Grams. | Index of refraction. | $\underset{\text { of } \mathrm{CS}_{2} .}{\text { Molar }} \%$ |
| :---: | :---: | :---: | :---: |
| 1. | 13.67 | I. 55285 | 70.78 |
| 2. | 18.01 | 1.55168 | 70.19 |
| 3. | 16.22 | 1.54901 | 68.80 |
| 4. | 21.43 | I . 54582 | 67.14 |
| 5 | 12.14 | 1. 54200 | 65.08 |
| 6. | . 17.76 | 1. 53890 | 63.43 |

Table VII.


Corresponding vapor (by extrapolation)................................ $62.30 \% \mathrm{CS}_{2}$

The results of Table VII are shown graphically by the pair of curves $B$ in Fig. 2.


The results of Table IX are shown graphically by the pair of curves $C$ in Fig. 2.


The results of Table XI are shown graphically by the pair of curves $D$ in Fig. 2.

Table XII.—Run E.

| No. of distillate. | Weight of distillate. Grams. | Index of refraction. | $\%_{0}^{\text {Molar }} \mathrm{CS}_{2}$ |
| :---: | :---: | :---: | :---: |
| 1. | 18,09 | I. 59875 | 91.00 |
| 2. | 18.28 | I. 59848 | 90.88 |
| 3. | 21.23 | 1.59751 | 90.51 |
| 4. | 15.70 | 1.59634 | 90.06 |
| 5. | 15.78 | 1. 59520 | 89.60 |
| 6. | 17.78 | 1. 59370 | 89.02 |



The results of Table XIII are shown-graphically by the pair of curves $E$ in Fig 2. The relation between the composition of liquid and vapor is, on the basis of all the data given in this section, exhibited by the curves of Fig. 3. Here the lower curve indicates the boiling points of the various


Fig 3.
mixtures. Any horizontal line through the two curves will indicate the composition of a vapor (point of intersection with the upper curve) and of the liquid (point of intersection with the lower curve) in equilibrium with it.

The case of carbon disulfide-carbon tetrachloride was experimentally a somewhat difficult one, owing to the two liquids interdiffusing rather slowly. Nevertheless, the results obtained by the present method are in satisfactory agreement with those yielded by the standard method mentioned above. ${ }^{1}$

[^2]
## Section VII.-Results for Chloroform-Toluene.

Table XIV.-Run A.
Weight of
distillate
No. of distillate.
Grams.
Index of refraction. Molar $\%$ of $\mathrm{CHCl}_{3}$.

| 1 | 16.37 | 1.44482 | 97.00 |
| :---: | :---: | :---: | :---: |
| 2. | 20.32 | 1.44503 | 96.68 |
| 3. | 24.32 | 1. 44532 | 96.18 |
| 4. | 17.07 | 1. 44552 | 95.84 |
| 5. | 20.51 | 1. 44562 | 95.68 |

TABLE XV.


| Original mixture (refractive index $=1.4$ | 85.88\% CHCls |
| :---: | :---: |
| Corresponding vapor (by extrapolation) | 97.25\% CHCl |
| Residue (refractive index $=1.45523$ ) | $79.54 \% \mathrm{CHCl}_{3}$ |
| Corresponding vapor (by extrapolation) | 95.40\% CHCl ${ }_{3}$ |



Fig. 4.-Carbon disulphide-carbon tetrachloride.
The results of Table XV are shown graphically by the pair of curves $A$ in Fig. 4.

Table XVI.—Run B.
Weight of
No. of distillate.
distillate Grams. Index of refraction. Molar \% of $\mathrm{CHCl}_{3}$.

| 1 | 13.24 | 1. 44945 | 89.36 |
| :---: | :---: | :---: | :---: |
| 2 | 15.86 | 1. 44958 | 89.12 |
| 3. | 15.80 | 1.45013 | 88.21 |
| 4. | 20.88 | I. 45098 | 86.79 |
| 5. | 17.06 | 1.45183 | 85.38 |
| 6. | 20.05 | 1.45293 | 83.53 |

Table XVII.

| Distillates combined. | Combined weight. Grams. | Combined composition. Molar $\% \mathrm{CHCl}_{3}$.) | Distillates combined | Combined weight. Grams. | $\begin{gathered} \text { Combined } \\ \text { compo- } \\ \text { sition } \\ \binom{\mathrm{Molar}^{\circ} \%}{\mathrm{CHCl}_{3} .} \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| No. 1. | 13.24 | 89.36 | No. 6. | 20.05 | 83.53 |
| Nos. $1+2$. | 29.10 | 89.23 | Nos. $6+5$. | 37.11 | 84.37 |
| Nos. $1+2+3$ | 44.90 | 88.87 | Nos. $6+5+4$ | 57.99 | 85.24 |
| Nos. $1+2+3+4$. | 65.78 | 88.21 | Nos. $6+5+4+3$. | 73.79 | 85.88 |
| Nos. $1+2+3+4+5$ | 82.84 | 88.87 | Nos. $6+5+4+3+2$. | 89.65 | 86.45 |
| Nos. $1+2+3+4+5+6$. | 102.89 | 86.82 | Nos. $6+5+4+3+2+$ | 102.89 | 86.82 |
| Original mixture (refractive index $=1.46295$ ) $\ldots \ldots . . . . . . . .95 .33 \% \mathrm{CHCl}_{4}$ |  |  |  |  |  |
| Corresponding vapor (by extrapolation).................... $89.53 \% \mathrm{CHCh}_{3}$ |  |  |  |  |  |
| Residue (refractive index $=1.47015$ ) $\ldots \ldots \ldots \ldots \ldots \ldots \ldots . .$. |  |  |  |  |  |
| Corresponding vapor (by extrapolation)..................... $82.55 \% \mathrm{CHCl}_{2}$ |  |  |  |  |  |

The results of Table XVII are shown graphically by the pair of curves $B$ in Fig. 4.

| No. of distillate. | Table XVIII.—Run C. |  |  |
| :---: | :---: | :---: | :---: |
|  | Weight of distillate. Grams. | Index of refra | Molar \% of |
| 1. | 16.74 | 1.44712 | 93.20 |
| 2 | 16.11 | I. 44743 | 92.68 |
| 3. | . 18.69 | I. 44783 | 92.01 |
| 4. | . 20.98 | I. 44833 | 91.19 |
| 5 | 16.81 | I. 44883 | 90.36 |
| 6. | . 19.51 | 1. 44958 | 89.12 |

TABLE XIX.


The results of Table XIX are shown graphically by the pair of curves $C$ in Fig. 4.

| Table XX.-Run D. |  |  |  |
| :---: | :---: | :---: | :---: |
| No. of distillate. | Weight of distillate. Grams. | Index of refraction. | $\% \text { of } \stackrel{\text { Molar }}{\mathrm{CHCl}} .$ |
| 1 | 15.19 | I. 45393 | 81.80 |
| 2 | 16.74 | I. 45473 | 80.40 |
| 3. | 18.05 | 1. 45563 | 78.83 |
| 4. | 14.75 | 1. 45693 | 76.50 |
| 5 | 17.31 | 1.45818 | 74.23 |
| 6. | 22.70 | 1.46012 | 70.65 |

TABLE XXI.


The results of Table XXI are shown graphically by the pair of curves $D$ in Fig. 4.

Table XXII.-Run E.

| Weight of <br> distillate. <br> Grams. | Index of <br> refraction. | $\%$ |
| :---: | :---: | :---: |
| 14.47 | 1.45853 | 73.60 |
| 15.49 | 1.45982 | 71.2 I (Molar |
| 14.02 | 1.4609 I | 69.18 |
| 19.31 | 1.46255 | 66.09 |
| 13.44 | 1.46450 | 62.37 |
| 14.55 | 1.46649 | 58.50 |

Table XXIII.


The results of Table XXIII are shown graphically by the pair of curves $E$ in Fig 4.

| No. of distillate. | Table XXIV.-R Weight of distillate. Grams. | N F . <br> Index of refraction. | Molar \% of CHCl . |
| :---: | :---: | :---: | :---: |
| 1. | 8.05 | I. 46559 | 60.26 |
| 2 | 7.41 | 1. 46589 | 59.68 |
| 3. | . 5.82 | I.46813 | 55.31 |
| 4. | . 6.04 | I. 46837 | 54.83 |
| 5. | ... 5.38 | 1. 46926 | 53.06 |
| 6. | .. 7.93 | 1. 47030 | 51.00 |

TAble XXV.

| Distillates combined. | Combined weight. Grams. | Combined composition. <br> (Molar \% CHCls.) |
| :---: | :---: | :---: |
| No. 1. | 8.05 | 59.97 |
| Nos. $1+2$. | 15.46 | 59.98 |
| Nos. $1+2+3$. | 21.28 | 58.70 |
| Nos. $1+2+3+4$. | 27.32 | 57.84 |
| Nos. $1+2+3+4+5$. | 32.70 | 57.04 |
| Nos. $1+2+3+4+5+6$. | 40.63 | 55.83 |
| Original mixture (refractive index $=1.48074$ ) Corresponding vapor (by extrapolation)....... |  | $29.13 \% \mathrm{CHCl}_{8}$ |
|  |  | $61.47 \% \mathrm{CHCl}_{3}$ |

The residue in this case could not be analyzed.
The results of Table XXV are shown graphically by the upper curve of pair $F$ in Fig. 4.

Table XXVI.—Run G.

| No. of distillate. | Weight of distillate. Grams. | Index of refraction. | $\stackrel{\text { Molar }}{\% \text { of } \mathrm{CHCl}_{3} .}$ |
| :---: | :---: | :---: | :---: |
| 1. | 7.98 | 1.47261 | 46.34 |
| 2 | 9.75 | 1.47344 | 44.65 |
| 3 | 4.87 | 1. 47526 | 40.86 |
| 4. | 5.62 | 1. 47535 | 40.68 |
| 5 | 6.79 | I. 47624 | 38.81 |
| 6. | 6.48 | 1.47712 | 36.95 |

Table XXVII.

| Distillates combined. | Combined weight. Grams. | Combined composition. (Molar \% CHCls.) |
| :---: | :---: | :---: |
| No. 1. | 7.98 | 46.34 |
| Nos. $1+2$. | 17.73 | 45.41 |
| Nos. $1+2+3$. | 22.60 | 44.42 |
| Nos. $1+2+3+4$. | 28.22 | 43.67 |
| Nos. $1+2+3+4+5$. | 35.01 | 42.72 |
| Nos. $1+2+3+4+5+6$. | 41.49 | 41.80 |
| Original mixture (refractive index $=1.48483$ ) $\ldots \ldots \ldots \ldots \ldots \quad 19.99 \% \mathrm{CHCl}_{1}$ Corresponding vapor (by extrapolation)....................... . . $47.23 \% \mathrm{CHCl}_{3}$ |  |  |
|  |  |  |

The residue in this case could not be analyzed.

The results of Table XXVII are shown graphically by the upper curve of pair $G$ in Fig. 4.

The results of all our measurements in the case of chloroform-toluene are exhibited by the curves of Fig. 5 .


Fig. 5.-Acetone-toluene.
Section VIII.-Results for Acetone-Toluene.
Table XXVIII.-Run A.

| No. of distillate. | Weight of distillate. Grams. | Index of refraction. | Molar \% of acetone. |
| :---: | :---: | :---: | :---: |
| 1. | 10.42 | 1. 36086 | 98.10 |
| 2 | 12.57 | 1.36104 | 98.01 |
| 3 | 9.61 | 1.36130 | 97.89 |
| 4 | 10.12 | 1. 36148 | 97.82 |
| 5 | I 1.48 | 1.36175 | 97.72 |
| 6. | 11.29 | 1. 36219 | 97.52 |




| Table XXXI. |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Distillates combined. | Combined |  |  | Combined |  |
|  | compo-sition. |  |  | compo- |  |
|  | weight | (Molar \% | Distillates | weight. | Molar \% |
|  |  | acetone.) | combined. |  | acetone.) |
| No. 1. | 9.19 | 96.27 | No. 6. | 10.63 | 95.19 |
| Nos. $1+2$. | 18.62 | 96.25 | Nos. $6+5$. | 20.05 | 95.29 |
| Nos. $1+2+3$. | 30.04 | 96.18 | Nos. $6+5+4$. | 31.88 | 95.50 |
| Nos. $1+2+3+4$. | 41.87 | 96.08 | Nos. $6+5+4+3$. | 43.30 | 95.63 |
| Nos. $1+2+3+4+5$. | 51.29 | 95.94 | Nos. $6+5+4+3+2$. | 52.73 | 95.74 |
| Nos. $1+2+3+4+5+6$. | 61.92 | 95.82 | Nos. $6+5+4+3+2+$ | 61.92 | 95,82 |
| Original mixture | efractiv | index $=1.3$ | 38294) | $\%$ acetone |  |
| Corresponding va | or (by | trapolation) |  | \% acetone |  |
| Residue (refractiv | index | 1.39361).. |  | acetone |  |
| Corresponding va | or (by | trapolation |  | \% acetone |  |



Table XXXIII.

| Distillates bined. | Comweight Grams | Combined composition. <br> (Molar \% <br> acetone.) | $\begin{gathered} \text { Distil- } \\ \text { lates } \\ \text { com- } \\ \text { bined. } \end{gathered}$ | Comweight. Grams. | Combined composition. (Molar \% acetone.) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| No. 1 | 8.62 | 94.07 | No. 6. | 10.22 | 92.14 |
| Nos. $1+2$. | 21.30 | 94.02 | Nos. $6+5$ | 19.75 | 92.37 |
| Nos. $1+2+3$ | 32.88 | 93.90 | Nos. $6+5+4$ | 33.20 | 92.69 |
| Nos. $1+2+3+4$. | 46.33 | 93.73 | Nos. $6+5+4+3$ | 44.78 | 92.94 |
| Nos. $1+2+3+4+5$. | 55.86 | 93.50 | Nos. $6+5+4+3+2$. | 57.46 | 93.17 |
| Nos. $1+2+3+4+5+6$ | 66.08 | 93.29 | Nos. $6+5+4+3+2+$ | 66.08 | 93.29 |
| Original mixture (refractive index $=1.39651$ ) $\ldots \ldots \ldots \ldots . .$. . $9.02 \%$ acetone |  |  |  |  |  |
| Corresponding vapor (by extrapolation).................... . $94.10 \%$ acetone |  |  |  |  |  |
|  |  |  |  |  |  |
| Corresponding vapor (by extrapolation).................... 91.70\% acetone |  |  |  |  |  |

Thble XXXIV.—Run D.

| Weight of <br> distillate. <br> Grams. | Index of <br> refraction. | Molar \% <br> of acetone. |
| ---: | ---: | :---: |
| 9.90 | 1.37534 | 91.23 |
| 10.22 | 1.37558 | 91.10 |
| 10.57 | 1.37651 | 90.61 |
| 11.84 | 1.37790 | 89.88 |
| 12.00 | 1.37950 | 89.01 |
| 12.12 | 1.38167 | 87.82 |

Table XXXV.


| Original mixture (refractive index $=1.41202$ ) | $68.64 \%$ acetone |
| :---: | :---: |
| Corresponding vapor (by extrapolation) | 91.55\% acetone |
| Residue (refractive index $=1.43452$ ) | $51.85 \%$ acetone |
| Corresponding vapor (by extrapolation) | 87.00\% acetone |

Table XXXVI.-Run E.

| No. of distillate. | Weight of distillate. Grams. | Index of refraction. | Molar \% acetone. |
| :---: | :---: | :---: | :---: |
| 1. | 10.44 | 1.38191 | 87.68 |
| 2 | 12.12 | I. 38280 | 87.20 |
| 3. | 11. $5^{2}$ | I. 38470 | 86.10 |
| 4 | 11.56 | I. 38499 | 85.95 |
| 5 | II 4.46 | I. 38965 | 83.22 |
| 6. | II 1.80 | 1.39312 | 81.11 |

## Table XXXVII.



Table XXXVIII.—Run F.

| No. of distillate. | Weight of istillate mis. | Index of refraction. | Molar \% of acetone. |
| :---: | :---: | :---: | :---: |
| 1 | 4.58 | 1. 39302 | 81.16 |
| 2 | 5.71 | I. 39574 | 79.49 |
| 3 | 3.85 | I. 39943 | 77.18 |
| 4. | 5.80 | 1. 39943 | 77.18 |
| 5 | 3.44 | 1.40041 | 76.54 |
| 6. | 3.80 | I . 40247 | 75.19 |

TABLE XXXIX.


The residue in this case could not be analyzed.
Table XL.—Run G.

| No. of distillate. | Weight of distillate. Grams. | Index of refraction. | Molar \% of acetone. |
| :---: | :---: | :---: | :---: |
| 1.................. . . . | 3.04 | 1.42067 | $7 \quad 62.40$ |
| 2. | 4.27 | 1. 42267 | 760.92 |
| 3 | 5.53 | 1. 42762 | 27.18 |
| 4. | 4.74 | 1.43197 | $7 \quad 53.83$ |
| 5 | 4.33 | 1. 43518 | $8 \quad 51.33$ |
| 6. | 5.79 | I . 43994 | $4 \quad 47.55$ |
| Table XLI. |  |  |  |
| Distillates combined. | Combined weight. Grams. |  | Combined composition. <br> (Molar \% acetone.) |
| No. 1.. | 3.04 |  | 62.39 |
| Nos. $1+2$. | 7.31 |  | 61.54 |
| Nos. $1+2+3$. | 12.84 |  | 59.68 |
| Nos. $1+2+3+4$. | 17.58 |  | 58.14 |
| Nos. $1+2+3+4+5$. | 21.91 |  | 56.83 |
| Nos. $1+2+3+4+5+6$. | 27.70 |  | 54.95 |
| Original mixture (refractive i | $=1.47359$ | ........... | 18.70\% acetone |
| Corresponding vapor (by ext | ation).... | ............ | 63.60\% acetome |

The residue in this case could not be analyzed.
Table XLII.-Run H.

| Weight of <br> distillate. <br> Grams. | Index of refraction. | Molar \% of <br> acetone. |
| :---: | :---: | :---: |
| 5.36 | I.44386 | 44.38 |
| 3.86 | 1.44838 | 40.70 |
| 5.99 | 1.45233 | 37.37 |
| 5.90 | 1.45547 | 34.72 |
| 4.94 | 1.45898 | 31.70 |
| 6.64 | 1.46340 | 27.88 |



Fig. 6.-Chloroform-toluene.
TABLE XLIII.

| Distillates combined. | Combined weight. Grams. |
| :---: | :---: |
| No. 1. | 5.36 |
| Nos. $1+2$. | 9.22 |
| Nos. $1+2+3$. | 15.21 |
| Nos, $1+2+3+4$. | 21.11 |
| Nos. $1+2+3+4+5$. | 26.05 |
| Nos. $1+2+3+4+5+6$ | 32.69 |

Original mixture (refractive index $=1.48221$ )
................ $10.77 \%$ acetone
Corresponding vapor (by extrapolation)

Combined composition. (Molar \% acetone.)

### 44.38

42.85
40.73
39.08
37.71 .
35.78
$44.90 \%$ acetone

The residue in this case could not be analyzed.
The results of all measurements in the case of acetone-toluene are exhibited by the curves of Fig. 6.

## Section IX.-Results for Ethyl Iodide-Ethyl Acetate.

| No. of distillate. |  | Weight of distillate. Grams. |  | A. Index of refraction. | Molar \% of $\mathrm{C}_{2} \mathrm{HuI}^{\text {I }}$. |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| I |  | 14 |  | 1.3826I |  | 12.78 |  |
| 2 |  | 11 |  | 1. 38246 |  | 12.64 |  |
| 3. |  | . 12 |  | 1.38210 |  | 12.28 |  |
| 4. |  | 12 |  | 1.38167 |  | 11.86 |  |
|  |  | 13 | . 13 | 1.38133 |  | 11.55 |  |
| 6. |  | 11 | . 66 | 1.38106 |  | 11.28 |  |
| 7. |  | 12 | . 62 | 1.38053 |  | $10.7{ }^{\circ}$ |  |
| Distillates combined. | Combined weight. Grams. | TABLE <br> Combined composition. (Molar \% Ca HsI .) | XLV. <br> Distillates combined. |  |  | Combined weight. Grams. | mbinea <br> compo- <br> sition. <br> Molar \% <br> $\mathrm{C}_{8} \mathrm{H}_{8} \mathrm{I}$.) |
| No. 1. | 14.21 | 12.78 | No. 7. |  |  | 12.62 | 10.76 |
| Nos. $1+2$. | 26.11 | 12.72 | Nos. $7+6$ |  |  | 24.28 | 11.01 |
| Nos. $1+2+3$. | 38.67 | 12.57 | Nos. $7+6$ | +5. |  | 37.41 | 11.20 |
| Nos. $1+2+3+4$. | 51.17 | 12.40 | Nos. $7+6$ | +5+4. |  | 49.91 | 11.36 |
| Nos. $1+2+3+4+5$. | 64.30 | 12.23 | Nos. $7+6$ | +5 + $4+3$. |  | 62.47 | 11.55 |
| Nos. $1+2+3+4+5+6 \ldots$ | . 75.96 | 12.08 | Nos. $7+6$ | +5+4+3+2 |  | 74.37 | 11.72 |
| Nos. $1+2+3+4+5+6+7$. | 88.58 | 11.89 | Nos. $7+6$ | +5+4+3+2 | +1.. | 88.58 | 11.89 |
| Original mixture (refractive index $=1.37875$ ) $\ldots \ldots \ldots \ldots . . .$. . $9.01 \% \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{I}$ |  |  |  |  |  |  |  |
| Corresponding vapor (by extrapolation)..................... $12.95 \% \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{I}$ |  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |  |
| Corresponding vapor (by extrapolation)..................... $10.45 \% \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{I}$ |  |  |  |  |  |  |  |


| No. of distillate. | ble XLVI.—Run <br> Weight of distillate. Grams. | B. <br> Index of refraction. | Molar \% of $\mathrm{C}_{2} \mathrm{HsI}$. |
| :---: | :---: | :---: | :---: |
| I.... | 10.93 | 1. 39167 | 21.26 |
| 2 | 16.39 | 1.39158 | 21.15 |
| 3 | . 15.63 | 1. 39080 | 20.47 |
| 4. | . 14.64 | 1.39023 | 19.94 |
| 5. | . 15.64 | 1.38956 | 19.35 |
| 6. | . 19.62 | 1.38870 | 18.55 |

Table XLVII.

| Distillates combined. | Combined weight. Grams. | Combined composition. <br> (Molar \% <br> $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{I}$.) | Distillates combined. |  | mbined composition. (Molar $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{I}$.) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| No. 1. | 10.93 | 21.26 | No. 6. | 19.62 | 18.55 |
| Nos. $1+2$. | 27.32 | 21.19 | Nos. $6+5$. | 35.26 | 18.91 |
| Nos. $1+2+3$. | 42.95 | 20.93 | Nos. $6+5+4$. | 49.90 | 19.21 |
| Nos. $1+2+3+4$. | 57.59 | 20.68 | Nos. $6+5+4+3$. | 65.53 | 19.51 |
| Nos. $1+2+3+4+5$. | 73.23 | 20.39 | Nos. $6+5+4+3+2$. | 81.92 | 19.83 |
| Nos. $1+2+3+4+5+6$. | 92.85 | 20.00 | Nos. $6+5+4+3+2+1$ | 92.85 | 20.00 |


| Original mixture (refractive index | $15.90 \%{ }^{*} \mathrm{C}_{2} \mathrm{H}_{6} \mathrm{I}$ |
| :---: | :---: |
| Corresponding vapor (by extrapolation) | $21.75 \% \mathrm{C}_{2} \mathrm{H}_{s} \mathrm{I}$ |
| Residue (refractive index $=1.38242$ ) | $12.59 \% \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{I}$ |
| Corresponding vapor (by extrapolation) | 18.00\% $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{I}$ |




Fig. 7.-Ethyl iodide-ethyl acetate.
Abscissae $=$ molar per cents ethyl iodide in liquid.

Ordinates $=$ molar per cents ethyl iodide in vapor.

The results in the case of ethyl iodide-ethyl acetate are exhibited by the curve of Fig. 7, in which the abscissae show the composition of the liquid and the ordinates that of the corresponding vapor. Owing to lack of material, only three runs were made in this case, yielding six points, within a range of about $25 \%$ of iodide in the liquid phase.

Section X.-The Boiling Temperatures of the Mixtures.
The boiling point curve of mixtures of carbon disulfide and carbon tetrachloride, shown in Fig. 3, is based on measurements (under 760 mm .) reported in an older communication. ${ }^{1}$ The curvesfor chloroformtoluene (Fig. 5) and acetone-toluene (Fig. 6) reproduce observations tabulated below. In the course of these observations, carried out with the aid of an Oddo ebullioscope and standardized thermometers, the barometric pressure varied irregularly within one or two millimeters. No measures were taken to avoid this, since such variations of pressure could have no appreciable influence on the composition of the vapors.

## ${ }^{1}$ Rosanoff and Easley, Loc. cit., p. 982.

| Table L.-Bolling Points of Mixtures of Chloroform and |  | Table LI.-Bolling Points of |  |
| :---: | :---: | :---: | :---: |
|  |  | Mixtures | of Acetone and |
| Toluene. Bar. Pressure, Toluene. Bar. Pressure, |  |  |  |
| $743.7 \pm 2 \mathrm{~mm}$. |  | $751.3 \pm 0.2$ | mm. |
| Molar \% $\mathrm{CHCl}_{\text {a }}$ | Boiling point. | Molar \% ( $\left.\mathrm{CH}_{8}\right)_{2} \mathrm{O}$. | Boiling point. |
| $\bigcirc$ | $108.92{ }^{\circ}$ | $\bigcirc$ | $109.43{ }^{\circ}$ |
| 7.86 | 103.58 | 14.99 | 88.28 |
| 15.96 | 98.72 | 34.63 | 74.93 |
| 25.46 | 93.38 | 51.42 | 68.77 |
| 34.64 | 88.30 | 65.98 | 64.37 |
| 43.33 | 83.94 | 78.71 | 61.22 |
| 54.44 | 78.17 | 89.99 | 58.71 |
| 64.66 | 73.65 | 100 | 56.50 |
| 74.70 | 69.67 |  |  |
| 86.54 | 65.35 |  |  |
| 100 | 61.33 |  |  |
|  |  |  |  |

A method and apparatus are described for determining the composition of vapors in equilibrium with liquid mixtures; the method is rapid and requires no special experience on the part of the manipulator. Also, results of measurements are given for the following four cases: Carbon disulfide-carbon tetrachloride, chloroform-toluene, acetone-toluene, and ethyl iodide-ethyl acetate. These data were needed here in connection with a study of fractional distillation, and the measurements were therefore carried out isopiestically, under ordinary atmospheric pressure.

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Worcester. Mass.
[Contribution from the W. Gibbs Memorlal Laboratory of Harvard University.]

## THE FREEZING POINT OF BENZENE AS A FIXED POINT IN THERMOMETRY.

By Theodore W. Richards and John W. Shipley.
Received July 3, 1914.
The transition temperatures of hydrated crystalline salts probably afford the most convenient and exact means of fixing points on the thermometric scale between $0^{\circ}$ and $100^{\circ} \mathrm{C}$. A number of these have been determined in this laboratory, chief among which are the transition temperature for sodium sulfate, ${ }^{1}$ the dekahydrate of sodium chromate into hexahydrate and into tetrahydrate, ${ }^{2}$ the dihydrate of sodium bromide into the anhydrous salt, ${ }^{3}$ the transition of manganese chloride from the tetra-
${ }^{1}$ Richards, Am. J.Sci. (1898); Richards and Wells, Proc. Am. Acad., 38, 431 (1902).
${ }^{2}$ Richards and Kelley, Ibid., 47, 171 (1911); This Journal., 33, 847 (1911).
${ }^{3}$ Richards and Wells, Proc. Am. Acad., 4I, $435^{\prime}$ (1906).


[^0]:    ${ }^{1}$ Rosanoff, Lamb, and Breithut, This Journal, 3I, 448 (1909); Z. physik. Chem., 66, 349 (1909).
    ${ }^{2}$ Rosanoff and Easley, This Journal, 3I, 953 (1909); Z. physik. Chem., 68, 641 (Ig10).
    ${ }^{3}$ Von Zawidzki, Z. physik. Chem., 35, 129 (1900).

[^1]:    ${ }^{1}$ Rosanoff and Easley, Loc. cit., p. 970.
    2 Schulze, This Journal, 36, 498 (1914).

[^2]:    ${ }^{1}$ Rosanoff and Easley, Loc. cit., p. 984.

