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ON THE PARTIAL VAPOR PRESSURES OF BINARY MIXTURES.

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1. Introductory.

Partial pressures of binary mixtures, or rather the composition of vapors given off by such mixtures, has hitherto been studied almost exclusively by distilling off a small amount from a comparatively large amount of the binary mixture, on the assumption that the distillate represents the vapor in equilibrium with the liquid.

Recently a new method was proposed by Rosanoff, Lamb, and Breithut,[1] who point out several possible defects in the older dynamic method. A few additional remarks on this subject may not be superfluous. First, the composition of the vapor from a binary mixture varies with the method of heating, and far more so than might be expected. Thus, by employing internal electric heating Richards and Mathews[2] were able to separate the constituents of binary mixtures far more readily than by heating, as usually, with a burner flame from the outside. Again, Brown[3] has pointed out that the composition of a distillate is greatly influenced by the rate of distillation, and Young[4] reproduces some results illustrating this in a striking manner. It is thus clear that the vapors given off by boiling mixtures may have, so to speak, an accidental composition, which can by no means always be considered as the composition of the gaseous

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[1] "A New Method of Measuring the Partial Vapor Pressures of Binary Mixtures (Preliminary Communication)," THIS JOURNAL, **31**, 448 (1909); *Z. physik. Chem.*, **66**, 349 (1909).

[2] THIS JOURNAL, **30**, 1283 (1908); *Z. physik. Chem.*, **64**, 121 (1908).

[3] *J. Chem. Soc.*, **37**, 53 (1880).

[4] *Fractional Distillation* (London, 1903), pp. 158–159.

phase in true equilibrium with the liquid at the given temperature. The following statement of Brown's[1] will, therefore, surprise no one: "The composition of the vapors given off by spirit of different strengths, together with the boiling points of such mixtures, have been determined by Gröning and many other observers; the discrepancies of the different tables to be found in works on alcoholometry are, however, so great that I thought it simpler to make the necessary experiments myself." Of course, there was no guarantee that Brown himself would find the true equilibrium values.

The method employed in obtaining the results of the present communication is free from the doubt attaching to the older methods. The principle of the new method may be re-stated in a few words as follows: When a liquid mixture is boiled, it will ordinarily lose one of its components (which may be conveniently designated as "the more volatile" component) more rapidly than the other. The composition of the vapor will change correspondingly. If the composition of both liquid and vapor is to remain constant, the more volatile component must be gradually added to the mixture in certain amounts during the distillation. If this is done, and the vapor of constant composition obtained is introduced into a liquid mixture of the same substances, the composition and temperature of the liquid will change in such a manner that the partial pressures of the constituents may become respectively equal to the partial pressures prevailing in the vapor. Then all change will cease. In other words, perfect equilibrium will have been established between liquid and vapor, with reference both to temperature and to partial and total vapor pressures. The vapor may then be condensed in any desired quantity for analysis. On the other hand, a sufficient sample of the liquid mixture may be removed and analyzed, and the problem of determining the composition of liquid and vapor in equilibrium at the temperature involved (namely, the lowest temperature at which the constant-composition vapor can exist without undergoing condensation) is solved.

The fundamental principle of this method had been experimentally established by Rosanoff, Lamb, and Breithut,[2] when the research reported in the present communication was commenced. It remained, however, to develop the fundamental principle into a practical working method, which still required a great deal of experimenting. The method, with all its essential working detail, is described below.

The new method completely under control, we undertook to determine by means of it the composition of the vapors in equilibrium with a number of typical binary mixtures. Most of the substances chosen

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[1] *J. Chem. Soc.*, 39, 526 (1881).

[2] *Loc. cit*

for the study had been investigated isothermally by Zawidzki. The new measurements, however, were carried out, not at constant temperature, as Zawidzki's, but under the constant pressure of 760 millimeters of mercury. In the first place, it seemed desirable to thus deepen the existing knowledge of a few well selected substances. Secondly, the measurement of vapor composition under normal atmospheric pressure promised results that would stand closely related to the phenomena of ordinary isopiestic distillation. And finally, equilibria observed under constant external pressure, and hence with the temperature varying from point to point, had never been closely considered from the theoretical standpoint, nor correlated with the corresponding isothermal equilibria. The measurements have suggested and have furnished an experimental basis for the theoretical considerations set forth in the following sections:

2. Theory: Generalization of Raoult's Law.

We start from Kirchhoff's well-known thermodynamic equation,[1]

$$\frac{\partial Q}{\partial y} = -RT^2 \frac{\partial \ln \frac{P_1}{p_1}}{\partial T} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Here, $\partial Q/\partial y$ denotes the heat of dilution, that is, the heat-change involved in adding 1 mol of a liquid to an infinite amount of a mixture containing y mols of that liquid ("the solvent") and 1 mol of some other substance; T is the absolute temperature, R is the gas constant expressed in gram-calories, P_1 is the vapor pressure of the solvent in the isolated state, and p_1 is the partial vapor pressure of the same component in the mixture.

The composition of the mixtures dealt with in the present paper will be uniformly expressed in molar fractions, denoted by x and $1 - x$. If Δy mols of the solvent must be added to the mixture corresponding to the above equation, in order to change the molar fraction x by the amount Δx, then

$$x + \Delta x = \frac{x + \Delta y}{1 + \Delta y},$$

or

$$\Delta y = \frac{\Delta x}{1 - x - \Delta x},$$

and in the limit,

$$dy = dx/1 - x.$$

Substituting in (1) this value of dy, we obtain the Kirchhoff equation in the following form:

$$(1 - x)\frac{\partial Q}{\partial x} = -RT^2 \frac{\partial}{\partial T} \ln \frac{P_1}{p_1},$$

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[1] Poggendorff's *Annalen*, 103, 200, and 104, 615 (1858); see also Nernst, "Theoretische Chemie" (Ed. 5, Stuttgart, 1907), p. 115.

or

$$\frac{\partial}{\partial T}\ln\frac{P_1}{p_1} = -\frac{1-x}{RT^2}\cdot\frac{\partial Q}{\partial x} \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Equation (2) leads immediately to a first important conclusion. When, namely, $x = 1$ (that is, at infinite dilution),

$$\frac{\partial}{\partial T}\ln\frac{P_1}{p_1} = 0.$$

This is nothing else than that part of Raoult's law according to which the relative depression of vapor tension in *infinitely dilute* solutions is independent of the temperature; and it is thus established thermodynamically as a rigorous principle of absolutely general applicability.

Now, in the case of binary mixtures of most organic substances, this important principle can be extended to include, not only ideal "infinitely dilute" solutions, but *actual mixtures of all possible concentrations.*

Consider the typical case of toluene and carbon disulphide. Linebarger[1] has measured the (considerable) heat absorbed when these substances are mixed in various proportions. Linebarger's observations of the heats of mixture, Q, expressed in the form of a parabolic function of the fourth degree in x (molar fraction), lead, by differentiation, to the following values for the heat of dilution $(1-x)\frac{\partial Q}{\partial x}$, as defined above:

x.	$(1-x)\frac{\partial Q}{\partial x}$
0.3	—53.39
0.5	+ 1.29
0.8	+23.32

Assuming $T = 316$ (*i. e.*, about 43° C.) and $R = 2$, the following values of $\frac{\partial}{\partial T}\ln\frac{P_1}{p_1}$ result according to equation (2):

x.	$\frac{\partial}{\partial T}\ln\frac{P_1}{p_1}$
0.3	+0.00027
0.5	—0.0000064
0.8	—0.000117

At this rate, a change of ten degrees in temperature would involve changes in the value of $\ln\frac{P_1}{p_1}$ at the points $x = 0.3, 0.5, 0.8$, amounting to only 0.25, 0.006, and 0.012 per cent., respectively. *For moderate changes of temperature, even for changes of 40 or 50 degrees, the changes of* $\ln P_1/p_1$, *and hence of* P_1/p_1, *will thus be negligible for all ordinary purposes.*

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[1] *Physic. Rev.*, **3**, 428 (1896).

It is thus clear that while in accordance with Raoult's law, at infinite dilution

$$p_1/P_1 = x$$

independently of the temperature, the ratio p_1/P_1 is, in the case of all ordinary organic mixtures, all but independent of the temperature no matter what the concentration, its value depending on nothing but x:

$$p_1/P_1 = f_1(x).$$

On similar grounds,

$$p_2/P_2 = f_2(x).$$

Margules[1] has recommended the following functions of x for representing the partial pressures of binary mixtures determined isothermally:

$$\left.\begin{aligned} p_1 &= P_1 x e^{\frac{\alpha_2}{2}(1-x)^2 + \frac{\alpha_3}{3}(1-x)^3 + \frac{\alpha_4}{4}(1-x)^4} \\ p_2 &= P_2(1-x) e^{\frac{\beta_2}{2}x^2 + \frac{\beta_3}{3}x^3 + \frac{\beta_4}{4}x^4} \end{aligned}\right\} \ldots\ldots\ldots\ldots \quad (3)$$

In accordance with the principle just enunciated, the exponents

$$\frac{\alpha_2}{2}(1-x)^2 + \frac{\alpha_3}{3}(1-x)^3 + \frac{\alpha_4}{4}(1-x)^4$$

and

$$\frac{\beta_2}{2}x^2 + \frac{\beta_3}{3}x^3 + \frac{\beta_4}{4}x^4,$$

and hence the coefficients α_2, α_3, α_4, β_2, β_3, β_4 must be independent of the temperature. Therefore, Margules's functions ought to represent partial pressures measured isopiestically as well as they represent isothermal measurements.

In order that these expressions should satisfy the Duhem-Margules equation,

$$d\ln p_1/d\ln p_2 = d\ln x/d\ln(1-x),$$

the following relations must exist between the two sets of coefficients:

$$\beta_2 = \alpha_2 + \alpha_3 + \alpha_4; \quad \beta_3 = -\alpha_3 - 2\alpha_4; \quad \beta_4 = \alpha_4.$$

Margules himself,[2] and later Zawidzki,[3] carried the exponents only to the third powers of $1-x$ and x. The results of the present communication will show that it is necessary (and sufficient) to add the fourth powers, with the corresponding constants α_4 and β_4.

To obtain the really *optimum* values of the constants involved, we combine the pair of Margules functions into one:

$$\ln\frac{p_1(1-x)}{p_2 x} = \ln\frac{P_1}{P_2} + \alpha_2\left[(1-x)+\frac{1}{2}\right] - \frac{\alpha_3}{2}\left[(1-x)^2 - \frac{1}{3}\right] + \frac{\alpha_4}{3}\left[(1-x)^3 - \frac{1}{4}\right] \ldots\ldots\ldots (4)$$

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[1] *Sitzungsbericht der Wiener Akademie*, **104**, 1243 (1895).

[2] *Loc. cit.*

[3] *Z. physik. Chem.*, **35**, 165 (1901).

and then find, on the basis of the measurements, the numerical values of the coefficients, including that of ln P_1/P_2, by the method of least squares. The value of ln P_1/P_2 yielded by the method of least squares is that corresponding approximately to the mean temperature involved. Thus, for the pair carbon disulphide (boiling point, 46.3°) and carbon tetrachloride (boiling point, 76.7°) the mean boiling temperature is 61.5°. For this temperature Regnault's data lead to the value, ln $P_1/P_2 = +0.948$. On the other hand, on the basis of the partial-pressure measurements, the method of least squares yields the value ln $P_1/P_2 = +0.94356$.

The agreement between the observed and calculated values of the partial pressures, as may be seen from the tables and figures in later sections of this communication, is all but perfect. This agreement attests the uniformity of the results yielded by the new experimental method, and on the other hand, endorses our theoretical representation of those results.

In this connection attention may be called to the fact that *all partial-pressure curves reproduced in this paper were first carefully drawn on the basis of our calculations, then the actual results of the measurements were introduced in the form of dots, independently, so that the diagrams present faithful pictures of the agreement between calculation and experiment.*

3. Some Applications.

The generalization of Raoult's law proposed above will prove useful in connection with a variety of theoretical and experimental problems. A few such applications require discussion in the present paper in view of their intimate connection with its main theme.

I. Practically nothing has hitherto been known concerning the variation of the vapor from a given binary mixture with the temperature. In Roozeboom's monograph on heterogeneous equilibria there is nothing on this subject except a brief remark in connection with Brown's work on carbon disulphide and carbon tetrachloride.[1]

On the basis of the working principle adopted above,

$$\left.\begin{aligned} \frac{p_1}{p_2} &= \frac{P_1}{P_2} f(x), \\ \text{where} \quad f(x) &= \frac{x}{1-x} e^{\alpha_2[(1-x)-1/2] + \frac{\alpha_3}{2}[(1-x)^2-1/3] + \frac{\alpha_4}{3}[(1-x)^3-1/4]} \end{aligned}\right\} \cdots\cdots\cdots\cdots (5)$$

For any given value of x the variation of vapor composition will thus be proportional to the variation of the ratio, P_1/P_2, of the vapor pressures of the components in the free state. In those cases in which, through moderate ranges of temperature, P_1/P_2 varies but slightly, the composition of the vapor, too, will not change much. Generally the use of

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[1] "Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre" (Braunschweig, 1904), Vol. II, Part 1, p. 66.

our principle in connection with questions of vapor composition will yield the better results the more rapidly P_1/P_2 varies with the temperature and the smaller the heat of dilution.

Not only can the variation of vapor composition be predicted qualitatively, but the composition itself corresponding to almost any desired temperature can be readily computed if $f(x)$ for the given pair of substances, and the vapor pressure curves of those substances in the free state, are known. The function $f(x)$ may be obtained by computing the numerical values of α_2, α_3, α_4 in Margules's expressions, on the basis of a few observations made either isothermally or isopiestically. On this principle, using the values of the constants based on our own isopiestic measurements, we have computed the vapor compositions corresponding to the temperatures at which Zawidzki studied the same pairs isothermally. The results of these calculations, given in subsequent sections, will be found to be in good agreement with Zawidzki's actual observations.

The above considerations furnish a valuable hint in connection with fractional distillation. The question, at what temperature the fractional distillation of a binary mixture may be carried out most advantageously, may be answered by ascertaining whether the expression

$$\ln\frac{P_1}{P_2}+\alpha_2\left[(1-x)-\frac{1}{2}\right]+\frac{\alpha_3}{2}\left[(1-x)^2-\frac{1}{3}\right]+\frac{\alpha_4}{3}\left[(1-x)^3-\frac{1}{4}\right]$$

has a value farther removed from zero at higher temperatures (atmospheric pressure) or at lower temperatures (vacuum distillation). What is needed in a given case, then, is a knowledge of P_1/P_2 for a series of temperatures and of the characteristic constants α_2, α_3, α_4.

II. The question as to the influence of temperature on the position of the maximum or minimum of a total-pressure curve has been the subject of much theoretical and some experimental study, with very little agreement between theory and experiment.[1] The practical constancy of α_2, α_3, α_4 under varying temperature answers this question, too, not only qualitatively, but quantitatively.

A maximum, or a minimum, occurs when

$$\frac{p_1/p_2}{x/(1-x)}=\frac{P_1}{P_2}e^{\alpha_2[(1-x)-1/2]+\frac{\alpha_3}{2}[(1-x)^2-1/3]+\frac{\alpha_4}{3}[(1-x)^3-1/4]}$$

or

$$\xi=e^{\alpha_2[(1-\ )-1/2]+\frac{\alpha_3}{2}[(1-x)^2-1/3]+\frac{\alpha_4}{3}[(1-x)^3-1/4]}=P_2/P_1\ldots\quad(6)$$

Computing the values of the left-hand member, which will be denoted below by the symbol ξ, for several values of x, and on the other hand finding from tables the values of P_2/P_1 corresponding to several different

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[1] For literature references see Roozeboom, *Loc. cit.*, pp. 91ff.

temperatures, and comparing the two sets of results, it will be easy to see whether a rise of temperature requires an increase or a diminution of x in accordance with equation (6).

The actual position of the maximum or minimum at any given temperature may be readily obtained by substituting the corresponding value of P_1/P_2 in the cubic equation

$$\ln\frac{P_1}{P_2} + \alpha_2\left[(1-x)-\frac{1}{2}\right] + \frac{\alpha_3}{2}\left[(1-x)^2-\frac{1}{3}\right] + \frac{\alpha_4}{3}\left[(1-x)^3-\frac{1}{4}\right] = 0 \quad \ldots\ldots(7)$$

and solving for x. As an example, a set of constants based on our own isopiestic measurements in the case of the pair carbon disulphide and acetone show that at the temperature of 35°, at which Zawidzki has measured the total pressures for this pair, the maximum should be expected to lie at $x = 0.6686$. Interpolation of Zawidzki's actual results points to the value $x = 0.6680$.

III. The relation between the shape of the boiling-point curve and the vapor composition for a given pair of substances has hitherto been imperfectly understood. In fact, all that is definitely known is that for a mixture of maximum or minimum boiling point the composition of the vapor is identical with that of the liquid phase. Knowing now that the constants α_2, α_3, α_4 are all but independent of the temperature, we can *calculate boiling-point curves* on the basis of a few partial-pressure determinations carried out either isothermally or isopiestically.

Having, namely, determined the constants for a given pair of substances, and having calculated by means of them the partial pressure p_1 and p_2 corresponding to some uniform total pressure, say 760 millimeters, we obtain from the Margules functions (equations 3 above) values of either P_1 or P_2 corresponding to a number of values of x. From the temperature-pressure data for the chosen component (in the free state), we then find, by interpolation, the temperature corresponding to each calculated value of P_1 or P_2. For each value of x we thus find a temperature value which may be taken as the boiling point corresponding to that value of x. Owing to the unavoidable difference of substances purified and studied by different observers, one cannot expect such boiling-point calculations to lead to results of very high precision. Still, the tables in further sections of this paper give calculated boiling points that agree with the actually observed ones mostly within a fraction of a degree.

4. The Apparatus.

The apparatus (Fig. 1) may be considered as consisting of six parts:

1. A chamber A in which the vapor of constant composition comes into equilibrium with the liquid mixture and from which a portion of the latter is withdrawn for analysis.

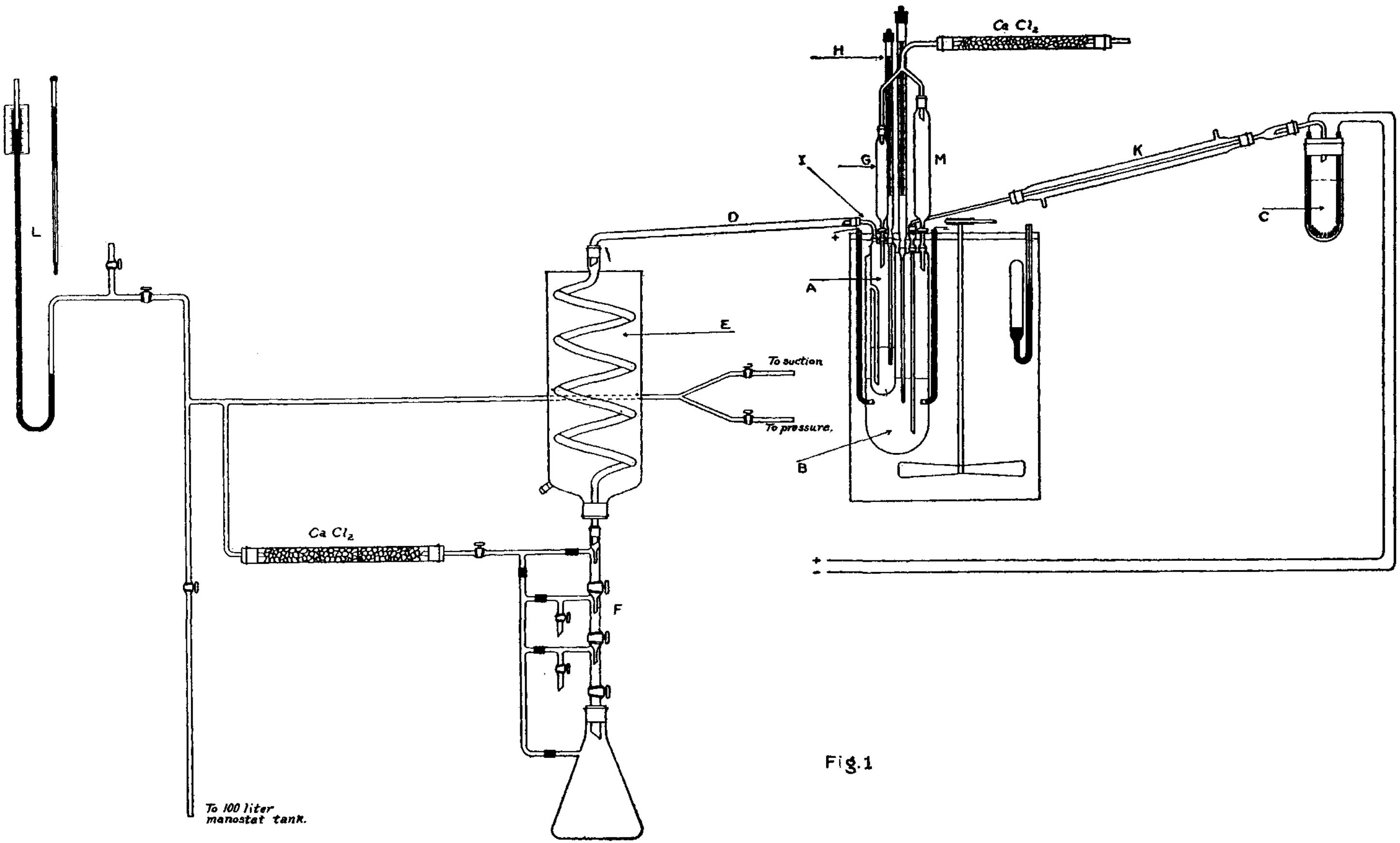
Ca Cl₂
H
I
G
M
K
C
D
L
A
E
To suction
To pressure,
B
Ca Cl₂
+
-
F
To 100 liter manostat tank.

Fig.1

2. A vessel *B* in which the vapor of constant composition is produced.

3. A vessel *C* out of which the more volatile component is introduced into *B* in such quantities as to maintain the composition of the liquid in *B* constant.

4. An air condenser *D* followed by a worm condenser *E* placed in a freezing mixture.

5. A receiver *F* with three compartments, two of which can be used for collecting two separate samples of the condensed vapor.

6. An apparatus for regulating and measuring the total pressure within the apparatus.

The details of the construction of the several parts are as follows:

1. *The Equilibrium Chamber A.*—This is a glass vessel somewhat similar to the boiling chamber in the Beckmann apparatus[1] for boiling-point determinations by the Landsberger method.[2] The vessel is 18 centimeters in length, 2.5 centimeters in diameter, and has a tube 3 millimeters in diameter fused into its side and running nearly to the bottom. The top of the equilibrium chamber has three openings in the form of protruding, ground-glass shoulders into which are fitted: (*a*) A 25 cubic centimeter glass dropping funnel *G* for introducing the liquid mixture and, when necessary, for changing its composition by the addition of one or the other of the ingredients. (*b*) A thermometer *H* whose bulb reaches considerably below the level of the liquid and which permits of temperature readings with certainty to 0.01°, possibly even to 0.005°. The thermometers employed were accurately ground to fit the shoulder. Each thermometer had a range of 20°, the scale being 26 centimeters long and graduated into twentieths of a degree. All the thermometers used in this investigation were calibrated by the U. S. Bureau of Standards at Washington, and the proper corrections were applied to the readings. Finally, (*c*) a delivery tube *I* ground into the third opening of the vessel and constructed somewhat on Georg Kahlbaum's idea, as shown in the accompanying diagram (Fig. 2).

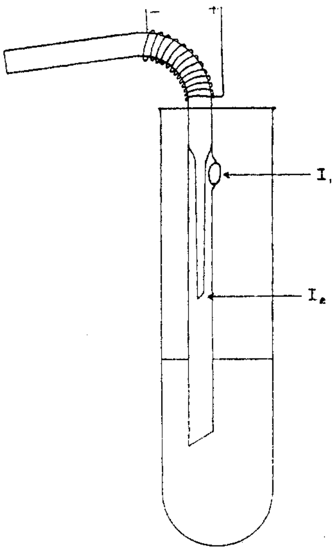

Fig. 2.

The vapor enters the tube at I_1 and passes downward and out through the inner concentric tube I_2, liquid particles being thus presumably eliminated from

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[1] *Z. physik. Chem.*, **40**, 145 (1902).

[2] *Ber.*, **31**, 461 (1898). See also Sakurai, *J. Chem. Soc.*, **61**, 994 (1892).

the vapor. The bottom part of the delivery tube dips well below the surface of the liquid. To prevent reflux condensation, the upper part of the delivery tube, which protrudes above the apparatus, is surrounded by an electrically heated platinum wire 0.1 millimeter in diameter, wound over a thin sheet of asbestos paper and covered with a paste of shredded asbestos and sodium silicate. The current is so regulated that a temperature of about 125° prevails within the short part where reflux condensation is possible. The superheating of the vapor in this part of the apparatus is obviously harmless. A polished sheet of nickel placed between this platinum heater and the neighboring thermometer prevents the heating of the stem of the latter by radiation.

2. *The Outside Vessel B.*—This is a glass tube 6 centimeters in diameter and 25 centimeters in length, closed at the bottom and provided with four openings in its top as follows: (*a*) A large opening to hold, by means of a ground-glass joint, the equilibrium vessel described in the preceding paragraphs. (*b*) Into a second opening is ground a thermometer similar in every respect to the one in the equilibrium chamber. The bulb of this thermometer, too, dips below the surface of the liquid. (*c*) A 60 cc. dropping funnel ground into the third opening serves to introduce either the required liquid mixture, or one of the components, into the vessel at any time. Finally, (*d*) the fourth opening serves for the gradual introduction of the more volatile component, which is necessary in order to maintain the composition of the boiling liquid in the vessel, and therefore of the vapor given off by it, constant. If the component in question were introduced in the form of vapor, more or less of it would bubble through the liquid unabsorbed and the vapor composition would vary continually. This component must reach the boiling liquid in the form of liquid drops. To prevent vaporization of the drops before the surface of the boiling liquid is reached, the component in question is introduced through a double-walled Dewar tube extending almost to the bottom of the vessel. In those cases in which the boiling points of the two components are far apart, this tube answers its purpose very well. It frequently happens, however, that even the slight amount of vapor necessary to keep the boiling liquid from rising within this tube is condensed; then it is necessary to promote vaporization by moderating the cooling of the more volatile component in the condenser leading to the vessel *B*.

The mixture in vessel *B* was heated by a 0.1 mm. platinum wire about 1.5 meters long. Artificial stirring being impracticable, the bubbles arising from the electric heater served the purpose of keeping the components thoroughly mingled. The importance of this, especially in the case of mixtures whose components differ widely in density and interdiffuse slowly, is very great. The heating wire is well distributed throughout the volume of the liquid mixture by being wound on a glass rod bent in the form of a conical spiral whose apex extends almost to the bottom of the vessel (Fig. 3). The spiral is joined at its two ends to narrow glass tubes passing through the sides of the vessel *B* and filled with mercury, by means of which the platinum heater can be connected with the terminals of a battery. On the basis of an extensive experience, this form of the electric heater may be recommended as an extremely convenient improvement on those described heretofore. The Dewar tube mentioned above terminates within the spiral of the heater. The component entering through that tube is thus generally distributed with sufficient rapidity by the bubbles from the wire.

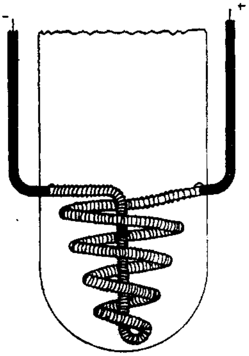

Fig. 3.

Vessel *B* is immersed totally, save the shoulders in the top of the inner vessel *A*, in a thermostat kept, by means of an Ostwald regulator with electric break, at a temperature about half a degree above that of the boiling mixture in *B*. The liquid of the bath was in most cases a clear paraffin oil. The use of water might have resulted in traces of moisture getting into the substances experimented upon while they were being introduced or withdrawn. An efficient stirrer was driven by an electric motor. The front part of the thermostat is provided with a large window of glass, through which it is possible to observe the operation constantly.

3. *The Vessel C.*—In a number of preliminary experiments, the more volatile component was introduced into the boiling mixture simply from a dropping funnel with a stop-cock, the necessity of supplying more or less of that component being indicated by the rise or fall of the temperature in *B*. While such regulation is by no means impossible, it proved difficult at times to control the flow of liquid through the narrow opening in the stopcock: at certain moments the liquid would refuse to flow altogether, while at other times the flow would unexpectedly become excessive. It was therefore decided to avoid the use of a stopcock, and supply the necessary liquid by distillation, the rapidity of which could be varied at pleasure. A quantity of the more volatile component was placed in the vessel *C* and heated internally by an electric wire 0.1 mm. in diameter and 1 meter in length, wound on a flat spiral of glass tubing. The intensity of the current was controlled by means of a slide-resistance placed within easy reach of the operator. The rate of supply of the distillate to the boiling mixture in vessel *B* was thus at all times under complete control. As already stated, the more volatile component had to be supplied in liquid form. The vapor from vessel *C* was therefore condensed by an ordinary Liebig cooler

(*K* in Fig. 1), the regularity of the supply being further promoted by the vessel *C* being thoroughly insulated.

4. *The Condenser.*—The condensing apparatus consists, as already stated, of an ordinary air condenser *D* (Fig. 1) and an efficient spiral condenser of wide glass tubing 1 meter in length, which requires no detailed description.

5. *The Receiver.*—The receiving apparatus consists of a glass tube *F* joined below, by means of a rubber stopper, to a suction flask and constructed as shown in Fig. 1. The side tubes of *F* connect the entire apparatus with the pressure regulator and the manometer. The three compartments of *F* permit of collecting consecutive samples of the condensed vapor, and of isolating them from one another, without changing the pressure in any part of the apparatus. The tube *F* is 37 cm. long and its lower two compartments have a capacity each of approximately 8 cubic centimeters. The narrow tubes within the compartments prevent the spattering of the distillate and contamination of the samples finally collected.

6. *The Pressure Apparatus.*—This consists essentially of two parts: a manometer *L* (Fig. 1) for measuring the total pressure within the apparatus and a tank of about 100 liters capacity connected with the rest of the apparatus and permitting of keeping the total pressure all but absolutely constant with the aid of a suction pump and a blast pump, which, however, had to be employed but seldom after the required pressure had once been established within the apparatus.

The 100 liter tank, totally immersed in a very large quantity of water, was kept in a room below the working laboratory, the temperature in that room being subject to but slight variations. Not the slightest variation of pressure within the apparatus was ever noticed during the course of an experiment. The manometer was of the siphon form, the glass tube having an internal diameter of 0.8 cm. The manometer was provided with two stopcocks, of which one connected it with the rest of the apparatus, the other with the atmosphere. These stopcocks were used for the purpose of preventing the mercury from "sticking" within the manometer tube. The pressure of 760 mm. within the apparatus was generally different from that of the atmosphere outside. By shutting out the apparatus and opening the atmosphere stopcock for an instant, then shutting out the atmosphere and re-connecting the manometer with the apparatus, the mercury column was thrown into motion within the manometer. The volume of air between the mercury and the stopcock is relatively so small that the change of total pressure brought about by the procedure just described was entirely negligible. The height of the mercury column was read off when after several oscillations the mercury had attained its position of rest. The process was repeated, and again repeated, three readings being taken every time the total pressure was to be determined. The extreme variation of the readings from the mean was in no case greater than 0.1 mm. All the connecting tubes of the apparatus were wide (approximately 1 centimeter in diameter) and permitted of instant equalization of pressure in the several parts of the apparatus.

The manometer scale was rigidly fixed to the wooden stand holding the manometer and was divided into fifths of a millimeter. The observations were made by means of a cathetometer which was conveniently placed at a distance of about two meters from the manometer. The scale was illuminated by means of a Nernst lamp filament placed just over the polished top face of the glass plate on which the scale was etched. The light thus entered the body of the plate from above and was totally reflected from the scale etchings. The illumination was perfect. The point on the scale showing the required pressure of 760 mm. was found with the aid of a standard normal barometer.

5. Mode of Manipulation.

About 350 cubic centimeters of the liquid mixture whose partial pressures are to be determined are introduced into vessel *B* through the funnel *M*. A small amount of a similar mixture is introduced into vessel *A* through the funnel *G*. Then the liquids in *B* and *C* are set boiling, and the pressure within the whole apparatus is brought to about 760 mm. The distillation from *C* is regulated so that the composition in *B* should remain as constant as possible. There is no trouble in maintaining the temperature in *B* constant within 0.02°. The thermometer in *A* is observed from time to time. The temperature in *A* will either rise or fall, as the case may be, till equilibrium is attained. During this process the distillate is allowed to run into the suction flask under the receiver tube *F*. When constancy of temperature in *A* is finally attained, a new pressure observation is made. The pressure is generally found to be somewhat different from 760 mm. It is regulated by means of the blast or suction, as the case may be, until it approaches the value of 760 mm. within a small fraction of a millimeter. The thermometer in *A* still remains constant, although, owing to the slight change of pressure, the temperature differs somewhat from that previously established. Now the lowest stopcock in the receiving apparatus is closed and a sample collects in the lower compartment. Then the next higher stopcock is closed and another sample collects in the compartment above, and finally this compartment, too, is isolated, by shutting the uppermost stopcock. While the samples are being collected, the temperature in *A* is closely watched, the constancy of the thermometer *H* being relied upon to show that equilibrium has been attained. If, as sometimes happens, the thermometer in *A* shows variation of temperature during the collection of the samples, the stopcocks of the receiving tube *F* are opened, the distillates are allowed to run into the suction flask below, and a new attempt is made to obtain equilibrium distillates.

After two satisfactory samples of the distillate have been collected, the boiling in vessels *B* and *C* is interrupted by turning off the currents, the apparatus is isolated from the tank, and a sample of the liquid in *A* is collected by removing the funnel *G* and sucking out approximately 15 cubic centimeters of the mixture in *A* by means of a straight thin-walled pipette.

This pipette consisted of a glass tube 30 cm. long and of approximately 1 cm. bore, bent downward at the top, and attached there by means of rubber hose to a small rubber bulb. On the lower end of this tube was fused a very narrow glass tube about 18 cm. long and bearing a cork which exactly fitted the funnel opening of the vessel *A*. The wider part of the pipette was cooled by a freezing mixture of snow and hydrochloric acid contained in a very long surrounding tube of glass. This device for collecting the required sample of the hot liquid is very efficient, the boiling solution being reduced to nearly 0° in a very short time and escape of vapor from *A* being possible only during the few seconds between the removal of the funnel and the insertion of the pipette. The simple and not unwieldly piece of apparatus is described in detail because of the obvious importance of collecting the mixture totally unchanged in composition.

The sample of the liquid from *A* is allowed to remain for a short time in the pipette and assume a temperature near that of the freezing mixture in the surrounding tube; then two or three cubic centimeters are rejected and the rest is allowed to run rapidly into a small bottle provided with a perfect ground-glass stopper. The bottle is allowed to remain in a thermostat at the temperature at which the index of refraction is to be determined for analytical purposes. Finally, the two samples of the distillate isolated in the compartments of the receiving apparatus *F* are allowed to run separately into two small bottles and placed in the thermostat with the sample from *A*.

6. Critique of the Experimental Method.

Not to speak of the analytical errors, which are slight when the proper precautions are taken, there is a source of some error inherent in the method itself, or rather in the apparatus described above. The vapor passing out of the vessel *B* and bubbling through the liquid in the equilibrium chamber *A* has to overcome in the latter the pressure of a liquid column several centimeters in height. This keeps the temperature in *B* somewhat above that in *A*. The difference varies from case to case, depending, as it obviously must, upon the density of the liquid and the height of the liquid column in *A*. Usually the difference amounts to about one-half a degree. The disturbance brought about by this difference is remotely analogous to the disturbing effect first pointed out by Nernst and Abegg,[1] of external supercooling in freezing point determinations. In view of this, an effort was made to maintain the liquid in *A* at about the same level in all the experiments. The error involved, however, can in most cases be but slight.[2]

Another source of error lies in the fact that during the collection of the two samples of vapor the thermometer may remain practically constant (apparently testifying to perfect equilibrium between liquid and vapor), while, as a matter of fact, both liquid and vapor may still be appreciably changing in composition. This may easily occur in the case of mixtures whose boiling points vary but slightly with the composition. For instance, let the mixture experimented upon consist of benzene and carbon tetrachloride—substances whose boiling points differ by scarcely five degrees. And let, while the samples are being collected, the temperature in the equilibrium chamber rise or fall through an interval of 0.005°. Such a change could hardly be observed with a thermometer divided into twentieths of a degree. Yet it would correspond to the appreciable change of about 0.1 per cent. in the composition of the mixture. Near maxima or minima of total-pressure curves, where the variation of temperature with the composition is still smaller, the change in composition corresponding to inappreciable changes of temperature may obviously be still greater. It seems hardly possible to remedy this. However, it must be pointed out that in all such cases the two separate samples of vapor collected will necessarily differ in composition, showing that something has gone wrong. Furthermore, the results of the present research, which are completely stated in this communication, seem in no case to have suffered badly from this source of error.

7. The Analytical Method.

The analyses of the liquid mixtures were carried out by the refractometric method, with the aid of an excellent Pulfrich instrument (*Neuconstruction*). The refractometer parts were maintained at the desired constant temperature by a stream of water from the same thermostat in which the mixtures to be analyzed were kept. In working with volatile organic mixtures, it is extremely important to prevent evaporation in the refractometer cup. For this purpose the felt washer over the cap was replaced by a material prepared by heating agar-agar with glycerol. After being applied to the cap the mass was coated over with a collodion

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[1] *Z. physik. Chem.*, 15, 681 (1894).

[2] It was realized too late that this source of error might have been all but completely removed by cutting off the inlet tube of vessel *A* (see Fig. 1) to end only about 1 cm. below the surface of the liquid. If this is done, equilibrium would probably be attained more slowly, but the results would be more nearly perfect.

preparation, and this was treated with ammonium sulphide, in order to denitrate(?) and render it impervious to the vapors of all ordinary organic liquids, and to impart to it greater elasticity. A coating thus prepared is quite elastic and permits of closing the refractometer cup perfectly without exerting appreciable pressure upon it. The cap of the refractometer was connected with the constant temperature barrel passing through it by means of a piece of rubber hose tightly wired on to both cap and barrel and thus the narrow annular space through which evaporation might take place was effectively closed. With this arrangement it was possible to keep in the refractometer even the most volatile mixtures for some fifteen minutes without the slightest change taking place in the index of refraction. The time actually allowed for the mixture in the refractometer to assume the desired temperature was generally five minutes.

TABLE I.—CARBON TETRACHLORIDE AND BENZENE. TEMP. 25.2°.

The index of C_6H_6 is 1.49779. That of CCl_4 is 1.45732.

Ideal molar per cent. CCl_4.	Correction.
0	0
10	+0.15
20	+0.28
30	+0.37
40	+0.44
50	+0.48
60	+0.45
70	+0.37
80	+0.27
90	+0.14
100	0

TABLE II.—CARBON DISULPHIDE AND ACETONE. TEMP. 25.4°.

The index of $(CH_3)_2CO$ is 1.35607. That of CS_2 is 1.62309 (Dufet's value, corrected for temperature.)

Ideal molar per cent. CS_2.	Correction.
0	0
10	+4.18
20	+6.93
30	+8.60
40	+9.27
50	+9.21
60	+8.56
70	+7.22
80	+5.14
90	+2.80
100	0

The percentage composition of the mixtures was found by comparing their refraction indices with those of a set of mixtures of known composition and index of refraction. The interpolation method employed was half analytical, half graphic, as recommended by Ostwald and used by Zawidzki in his well-known study of binary mixtures.[1] A number of mixtures of known composition were made up by ourselves and their indices determined. In order to add to the reliability of the method we took into account also the refractometric measurements published by Zawidzki. We then calculated the composition of the mixtures that would have these indices if the latter obeyed the rule of additivity. Those ideal percentages formed a series of abscissae, while the "corrections" which must be algebraically added to them to obtain the true percentages

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[1] *Z. physik. Chem.*, **35**, 129 (1901).

formed the corresponding ordinates, and thus correction curves were obtained for our several cases. The figures given in the tables show corrections read off from our curves at equal intervals. With the aid of the tables it is easy to reproduce the correction curves themselves. In making practical use of these data, one calculates, on the basis of the index observed in the given case, and of those of the isolated components, the molar percentage composition that the given mixture would have if its index obeyed the rule of additivity. Algebraic addition of the correction corresponding to that molar percentage according to the curve gives the true molar percentage, and finally, division by 100 gives the "molar fraction" (x) for the given mixture.

TABLE III.—CHLOROFORM AND ACETONE. TEMP. 25.4°.

The index of $(CH_3)_2CO$ is 1.35605. That of $CHCl_3$ is 1.44288.

Ideal molar per cent. $CHCl_3$.	Correction.
0	0
10	—0.64
20	—1.25
30	—1.80
40	—2.30
50	—2.76
60	—3.04
70	—2.98
80	—2.28
90	—1.30
100	0

TABLE IV.—ETHYLENE CHLORIDE AND BENZENE. TEMP. 25.2°.

The index of C_6H_6 is 1.49779. That of $C_2H_4Cl_2$ is 1.44218.

Ideal molar per cent. $C_2H_4Cl_2$.	Correction.
0	0
10	—0.62
20	—1.19
30	—1.57
40	—1.69
50	—1.59
60	—1.39
70	—1.10
80	—0.77
90	—0.40
100	0

TABLE V.—CARBON DISULPHIDE AND CARBON TETRACHLORIDE. TEMP. 25.2.°

The index of CCl_4 is 1.45730. That of CS_2 is 1.62325.

Ideal molar per cent. CS_2.	Correction.
0	0
10	+6.60
20	+11.08
30	+13.56
40	+14.50
50	+14.20
60	+12.80
70	+10.66
80	+7.60
90	+4.04
100	0

TABLE VI.—ACETIC ACID AND BENZENE TEMP. 25.2°.

The index of C_6H_6 is 1.49762. That of $C_2H_4O_2$ is 1.37043.

Ideal molar per cent. $C_2H_4O_2$.	Correction.
0	0
10	—3.64
20	—6.72
30	—9.11
40	—11.02
50	—12.08
60	—12.18
70	—11.27
80	—9.05
90	—5.32
100	0

8. Carbon Tetrachloride and Benzene.

Purification of the Substances.—A sample of Kahlbaum's carbon tetrachloride was allowed to stand over lime for the purpose of eliminating traces of sulphur. When subsequently distilled, it was found to pass over within less than 0.1°. Another sample was simply dried with calcium chloride and distilled. The two samples had identically the same index of refraction and boiled at the same temperature. The treatment with lime having thus proved to be superfluous, the bulk of the carbon tetrachloride was simply dried with calcium chloride and distilled, the first and last fractions being rejected.

Kahlbaum's thiophene-free benzene was dried over calcium chloride and distilled. The bulk of the liquid passed over within less than 0.1°.

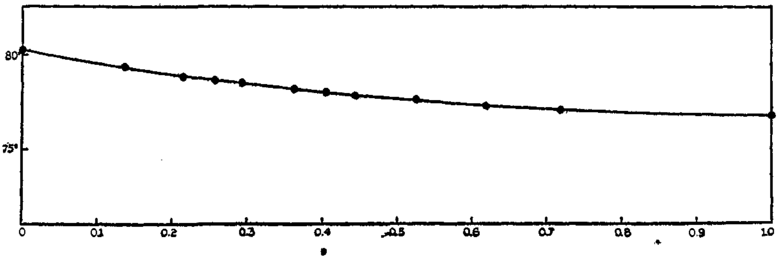

Fig. 4.—Carbon tetrachloride and benzene. Boiling-points.

Numerical Results.—Table VII gives the results of experiment and of theoretical calculation. The first column gives the observed boiling points (corrected), which are also represented graphically in Fig 4. The calculated boiling points in the second column were obtained by means of equations (3), with the numerical constants given below. The third column gives the composition of the boiling mixtures in vessel *A*. The fourth and seventh columns (under p_1 and p_2 obs.) give the observed composition of the vapor expressed in terms of partial pressures, the sum being, of course, 760 millimeters throughout. The fifth and eighth

TABLE VII.

1. B.p. obs.	2. B.p. calc.[1]	3. x. CCl_4 in liquid.	4. p_1 obs.	5. p_1 calc.	6. Diff. per cent.	7. p_2 obs.	8. p_2 calc.	9. Diff. per cent.
80.23°	80.3°	0	0	0	0	760.0	760.0	0
79.36	79.3	0.1364	120.2	120.0	—0.03	639.8	640.0	+0.03
78.82	78.8	0.2157	183.9	184.1	+0.03	576.1	575.9	—0.03
78.62	78.6	0.2573	218.7	216.6	—0.28	541.3	543.4	+0.28
78.48	78.5	0.2944	244.1	245.1	+0.14	515.9	514.9	—0.14
78.15	78.2	0.3634	297.7	297.1	—0.08	462.3	462.9	+0.08
77.97	78.0	0.4057	330.6	328.5	—0.28	429.4	431.5	+0.28
77.57	77.6	0.5269	416.8	416.9	+0.01	343.2	343.1	—0.01
77.23	77.4	0.6202	485.0	484.1	—0.12	275.0	275.9	+0.12
77.07	77.2	0.7223	556.9	557.2	+0.04	203.1	202.8	—0.04
76.69	....	1.0000	760.0	760.0	0	0	0	0

[1] The boiling points in this case were calculated on the basis of Young's vapor-pressure curve for pure benzene (P_2): *J. Chem. Soc.*, **55**, 486 (1889).

columns (under p_1 and p_2 calc.) give the corresponding partial pressures calculated by means of equation (4), with the observed values of x and the numerical constants given below. Finally, the sixth and ninth columns give the percentage differences (referred to the total pressure of 760) between the calculated and the observed values of p_1 and p_2, respectively.

The numerical values of the constants in this case are as follows: $\ln P_1/P_2 = +0.097291$, $\alpha_2 = +0.22284$, $\alpha_3 = -0.31950$, $\alpha_4 = +0.44650$.

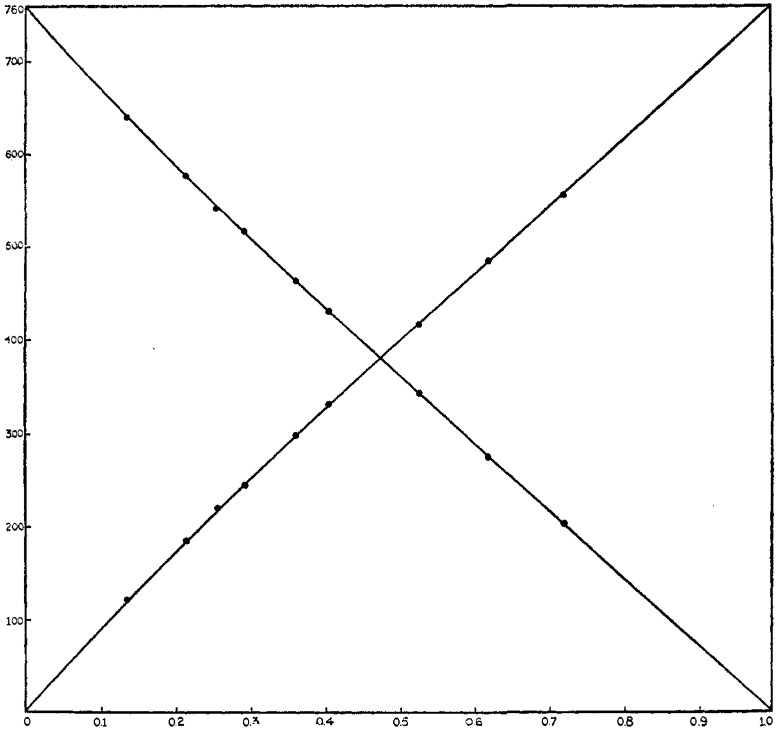

Fig. 5.—Carbon tetrachloride and benzene. Partial pressures.

Fig. 5 represents the observed and the calculated partial pressures. Assuming that the calculated pressures, represented by the curves of Fig. 5, are free from error, the percentage differences given in Table VII show that *the probable total error of the measurements in this case was ±0.11 per cent.*

Change of Vapor with the Temperature.—The dependence of the composition of the vapors given off by different mixtures of carbon tetrachloride and benzene on the temperature may be determined on the basis of equation (5). Since the ratio P_1/P_2 of the vapor pressures of the pure substances decreases with rising temperature, it follows that as the temperature rises the ratio corresponding to any given composition of the liquid phase will likewise decrease. In other words, as the temperature rises the vapor will become richer in benzene. For the temperature 49.99°, at which Zawidzki studied the partial pressures of the substances in question,

$$\ln P_1/P_2 = +0.13915.$$

Combining this with the values of α_2, α_3 and α_4, based on our own experiments at temperatures ranging between 76.7° and 80.2°, we have calculated, with the aid of equation (4), the molar percentages (*i. e.*, p_1 for $p_1 + p_2 = 100$) of carbon tetrachloride in the vapor, which ought to be observed at 49.99°, on the theory that the values of α_2, α_3, and α_4 are independent of the temperature. The first column of Table VIII gives the composition of several boiling mixtures studied by Zawidzki. The next column gives the molar per cent. of carbon tetrachloride in the vapor, as calculated by us for those mixtures. The third column gives the composition of the vapor as found by Zawidzki.

Table VIII.

Mol. per cent. CCl_4 in liquid.	Mol. per cent. CCl_4 in vapor calc. R. and E.	Mol. per cent. CCl_4 in vapor found Z.
5.07	6.4	6.82
11.70	14.2	14.57
17.72	20.9	21.26
25.25	28.9	29.22
29.47	33.2	33.65
39.59	43.3	43.85
56.00	59.0	58.60
67.37	69.6	69.26
76.58	78.1	77.83

The differences between the calculated and Zawidzki's experimental values are insignificant. Their systematic run, however, may be taken as possibly indicating that Zawidzki's dynamic method and the one employed by us will generally give slightly different results.

9. Carbon Disulphide and Acetone.

Purification of the Substances.—An excellent commercial carbon disulphide was further purified by shaking with lime, allowing to stand over mercury, then carefully drying and distilling. The bulk of the preparation passed over well within 0.2°, and the initial and final fractions that had to be rejected were small. The product had the pleasant ethereal odor of pure carbon disulphide.

The acetone was prepared as follows: A good commercial product was boiled for several hours with potassium permanganate,[1] distilled off from the permanganate, dried over potassium carbonate, and dis-

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[1] See Sachs and Whittaker, *Ber.*, **34**, 501 (1901).

tilled, a large middle portion only being kept. To control the purity of the product, a sample of Kahlbaum's best acetone made from the bisulphite compound was dried and redistilled. This highly reliable sample boiled at the same temperature and had the same index of refraction as the main product. The two were mixed together for use.

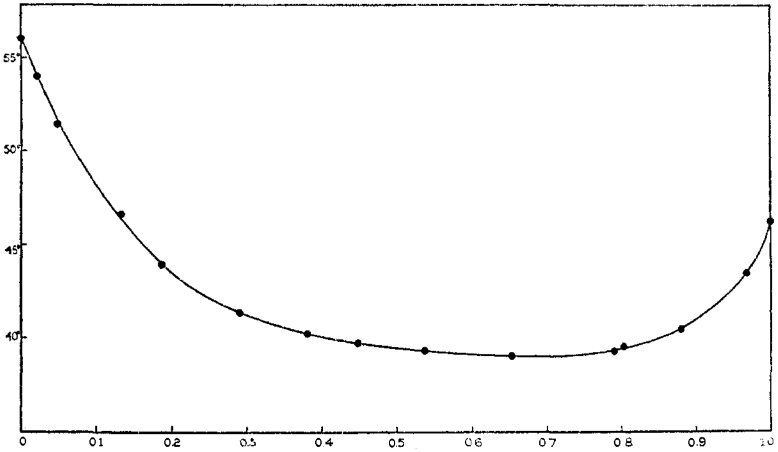

Fig. 6.—Carbon disulphide and acetone. Boiling points.

Numerical Results.—Fig. 6 represents the boiling-point curve for this case. The numerical results of experiment and of theoretical calculations are given by Table IX, in which the symbols have the same meaning as in Table VII.

TABLE IX.

1. B. p. obs.	2. B.p. calc.[1]	3. x CS_2 in liquid.	4. p_1 obs.	5. p_1 calc.	6. Diff per cent.	7. p_2 obs.	8. p_2 calc.	9. Diff. per cent.
56.19°	....	0	0	0	0	760.0	760.0	0
54.00	55.2°	0.0190	63.2	63.3	+0.01	696.8	696.7	—0.01
51.40	52.6	0.0476	140.6	140.0	—0.08	619.4	620.0	+0.08
46.64	46.9	0.1340	(267.1)	285.6	(+2.43)	(492.9)	474.4	(—2.43)
43.98	44.6	0.1858	336.7	336.8	+0.01	423.3	423.2	—0.01
41.36	41.8	0.2912	401.4	401.1	—0.04	358.6	358.9	+0.04
40.25	40.7	0.3798	436.7	434.4	—0.30	323.3	325.6	+0.30
39.78	40.2	0.4477	454.5	454.0	—0.07	305.5	306.0	+0.07
39.34	39.8	0.5360	475.6	476.1	+0.07	284.4	283.9	—0.07
39.06	39.6	0.6530	502.4	502.2	—0.03	257.6	257.8	+0.03
39.29	40.0	0.7894	536.3	539.3	+0.39	223.7	220.7	—0.39
39.59	40.1	0.8023	541.8	543.5	+0.22	218.2	216.5	—0.22
40.45	40.9	0.8799	577.5	577.9	+0.05	182.5	182.1	—0.05
43.46	43.7	0.9683	673.4	674.6	+0.16	86.6	85.4	—0.16
46.34	....	1.0000	760.0	760.0	0	0	0	0

[1] The boiling points in this case were calculated on the basis of Regnault's vapor-pressure curve for pure carbon disulphide (P_1): *Mém. de l'Acad.*, **26**, 339 (1862). Landolt-Börnstein *Tabellen* (Ed. 3, Berlin, 1905), p. 135.

In computing the values given in this table, two distinct sets of constants were employed. The case of carbon disulphide and acetone was the first to be computed. We had not yet realized that a three term equation was incapable of reproducing the results of experiment with precision, and employed throughout the following numerical constants:

$$\ln P_1/P_2 = +0.36248,\ \alpha_2 = +4.4426,\ \alpha_3 = -3.1308.$$

The calculated boiling points in Table IX are based on these constants, and no rash conclusions should be drawn from the somewhat considerable differences between calculation and experiment. Later the partial pressures given in columns 5 and 8 were computed on the basis, not of a four-term equation, which would have been sufficient, but of a five-term equation with the following numerical values of the constants:[1]

$$\ln P_1/P_2 = +0.35418,\ \alpha_2 = +7.3601,\ \alpha_3 = -22.963,\ \alpha_4 = +37.445,\ \alpha_5 = -20.879.$$

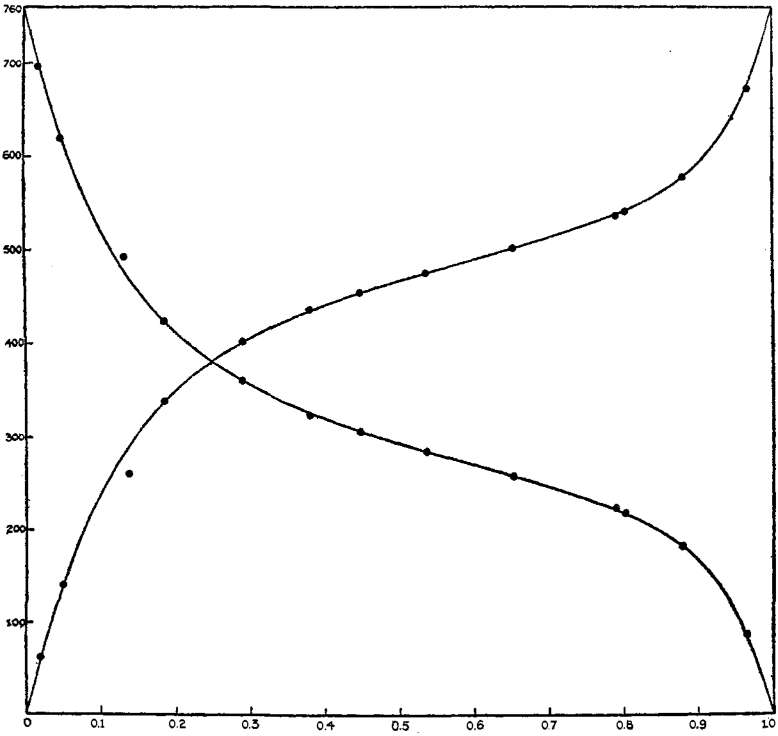

Fig. 7.—Carbon disulphide and acetone. Partial pressures.

Fig. 7 represents the observed and the calculated partial pressures. Assuming the calculated pressures to be absolutely correct, and leaving

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[1] The large value of α_5 is due to x being fractional.

out of account the grossly erroneous observation for the fourth point, *the probable total error of the measurements in this case is ±0.12 per cent.*

Change of Vapor with the Temperature.—While the heat of dilution in this case is by no means inconsiderable, the variation of the ratio P_1/P_2 with the temperature is quite rapid, and therefore our theory may be applied to this case with hope for very good results.

Qualitatively, since the ratio P_1/P_2 decreases with rising temperature it must be expected that the ratio p_1/p_2 will likewise decrease. In other words, as the temperature rises the vapor ought to become poorer in carbon disulphide and richer in acetone.

The first quantitative corroboration of the correctness of the theory may be seen in the fact that the constants α_2 and α_3 which were computed on the basis of the isopiestic data are nearly the same as those obtained by Zawidzki from his isothermal measurements:

Our constants:	Zawidzki's constants:
$\alpha_2 = +4.4426$	$\alpha_2 = +4.82$
$\alpha_3 = -3.1308$	$\alpha_3 = -3.12$

That the difference in the two values of α_2 is due, not to the influence of temperature, but to an error involved in Zawidzki's graphic method of determining his constants, is proved in a striking manner by Table X, which shows that our constants reproduce Zawidzki's observations better than his own.

TABLE X.

Mol. per cent. CS_2 in liquid.	Mol. per cent. CS_2 in vapor, calc. R. and E.	Mol. per cent. CS_2 in vapor, obs. Z.	Mol. per cent. CS_2 in vapor, calc. Z.
18.57	45.0	46.66	48.5
28.15	53.7	54.27	56.7
35.26	57.8	57.77	60.1
45.02	61.5	61.18	62.7
57.16	64.6	64.37	64.4
67.13	66.9	66.81	65.7
72.08	68.3	68.31	66.6
82.80	72.4	72.07	70.3
92.16	81.8	80.09	78.2

The differences between our calculations and Zawidzki's experiments at the two ends is due, as already stated, to a three-term equation being incapable of reproducing the results of experiment perfectly.

Temperature and Maximum Vapor Pressure.—Equation (6) permits of predicting the influence of temperature on the position of the maximum of the vapor pressure curve. Table XI gives, on the one hand, the values of the ratio P_2/P_1 corresponding to a number of temperatures according to Regnault's measurements. On the other hand, it gives a number of values of ξ (see equation 6) corresponding to a number of values of of x.

TABLE XI.

Temp.	$\frac{P_2}{P_1}$	x.	ξ.
20°	0.6027	0.1	2.8034
30	0.6465	0.2	2.3461
40	0.6804	0.3	1.9028
50	0.7034	0.4	1.4956
60	0.7389	0.5	1.1393
70	0.7663	0.6	0.84124
80	0.7926	0.7	0.60195
90	0.8177	0.8	0.41745
100	0.8412	0.9	0.30065

Since a maximum occurs when $\frac{P_2}{P_1} = \xi$, the table shows that at temperatures from 20° to 100° the maximum will lie between $x = 0.6$ and $x = 0.7$, and will shift slowly in the direction of decreasing x (*i. e.*, of liquids poorer in carbon disulphide) as the temperature rises.

Quantitatively, the minimum of our own boiling-point curve lies, by graphic interpolation, at $x = 0.6650$. At the lower temperature at which Zawidzki worked, equation (6) predicts that the maximum vapor pressure must correspond to a *slightly greater* value of x. Equation (7) requires that the maximum shall be at $x = 0.6686$; and, as a matter of fact, interpolation of Zawidzki's results shows that the maximum lies at $x = 0.6680$.

10. Chloroform and Acetone.

Purification of the Substances.—A quantity of Kahlbaum's chloroform was shaken with dilute sulphuric acid, then with caustic potash solution, washed with water, dried, and distilled. The large middle fraction which passed over within 0.3° was kept for use. The purification of the acetone is described in Sec. 9.

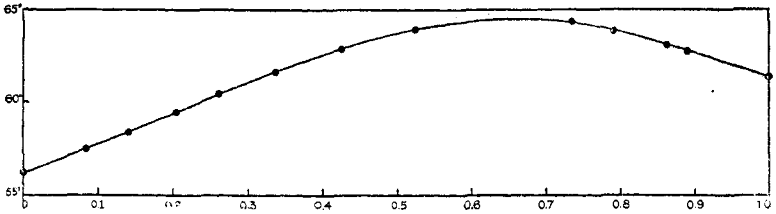

Fig. 8.—Chloroform and acetone. Boiling points.

Numerical Results.—Fig. 8 and the first column in Table XII reproduce the observed boiling points. The observed and calculated values of the partial pressures are arranged as in the previous tables.

TABLE XII.

1. B.p. obs.	2. B.p. calc.[1]	3. x. $CHCl_3$ in liquid.	4. p_1 obs.	5. p_1 calc.	6. Diff., per cent.	7. p_2 obs.	8. p_2 calc.	9. Diff., per cent.
56.20°	56.1°	0	0	0	0	760.0	760.0	0
57.49	57.4	0.0855	36.3	36.3	0	723.7	723.7	0
58.34	58.3	0.1410	63.4	63.4	0	696.6	696.6	0
59.44	59.3	0.2045	99.7	98.8	—0.12	660.3	661.2	+0.12
60.42	60.3	0.2612	134.1	135.1	+0.13	625.9	624.9	—0.13
61.60	61.5	0.3367	189.6	191.0	+0.18	570.4	569.0	—0.18
62.84	62.7	0.4250	267.4	267.5	+0.01	492.6	492.5	—0.01
63.91	63.8	0.5229	367.1	364.2	—0.38	392.9	395.8	+0.38
64.36	63.9	0.7340	580.0	579.5	—0.07	180.0	180.6	+0.07
63.84	63.5	0.7892	626.1	628.3	+0.29	133.9	131.7	—0.29
63.08	62.7	0.8625	684.7	684.3	—0.05	75.3	75.7	+0.05
62.77	62.3	0.8892	702.0	702.3	—0.03	57.8	58.0	+0.03
61.32	....	1.0000	760.0	760.0	0	0	0	0

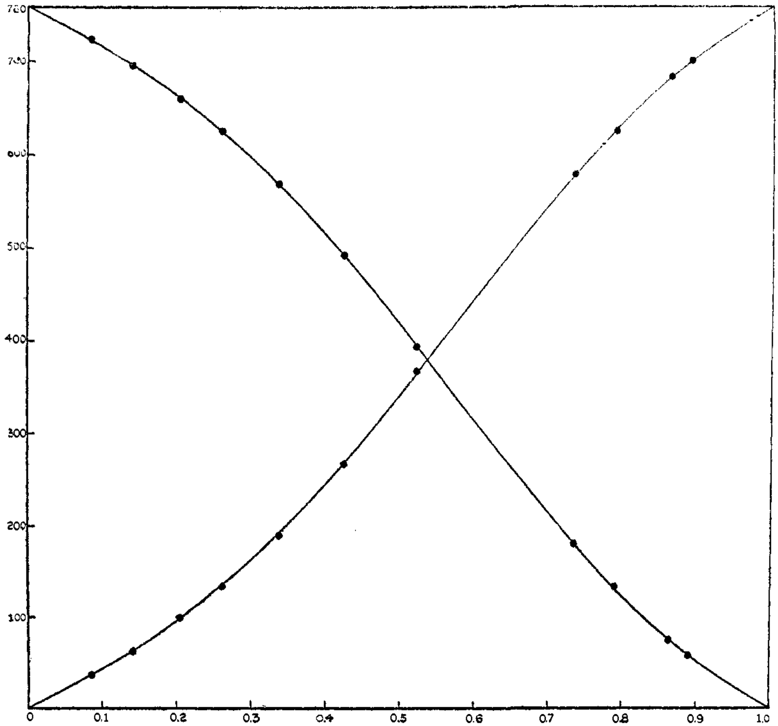

Fig. 9.—Chloroform and acetone. Partial pressures.

Fig. 9 represents the relation between the results of calculation and

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[1] Calculated by linear interpolation of Regnault's data for the vapor pressure (P_2) of pure acetone, *viz.*, 602.86 mm. at 50°, 860.48 at 60°, and 1139.38 (corrected) at 70°.

experiment graphically. Assuming, as before, the calculated results to be free from error, *the probable total error of the measurements in this case was ±0.12 per cent.*

The numerical values of the constants on which the calculations of Table XII and the curves of Fig. 9 are based were kindly computed by Professor William Edward Story, of this University. They are as follows:

$$\ln P_1/P_2 = -0.14773,\quad \alpha_2 = -1.6860,\quad \alpha_3 = -0.26970,\quad \alpha_4 = +1.7022.$$

To test the idea that a four-term equation can represent partial-pressure measurements with sufficient precision, and that a fifth term is superfluous, Professor Story undertook to compute the numerical constants of a five-term equation. He reported the following optimum constants:

$$\ln P_1/P_2 = -0.14462,\quad \alpha_2 = -2.1569,\quad \alpha_3 = +3.3480,\quad \alpha_4 = -6.2122,\quad \alpha_5 = +5.1637.$$

This more extensive set of constants, however, scarcely brought the results of calculation and experiment nearer together, the probable error being reduced from ±0.12 per cent. to ±0.11 per cent. Seeing that chloroform and acetone form a typical case of large deviations from additivity, this result may be taken as proving that a four-term equation is sufficient quite generally.

Change of Vapor with the Temperature.—Chloroform and acetone mixtures present an excellent example of a case in which our theory should *not* be used to answer questions concerning changes of vapor composition with the temperature. On the one hand, the ratio P_1/P_2 of the vapor pressures of the pure substances changes but very slightly with the temperature, and, on the other hand, the heat of dilution is quite large. For this reason we refrain from saying anything about the relation between Zawidzki's and our own results and about the influence of temperature on the composition of the minimum of the total-pressure curve.

11. Ethylene Chloride and Benzene.

Purification of the Substances.—Kahlbaum's ethylene chloride was purified by washing with caustic alkali solution and with water, drying with calcium chloride, and distilling. The fraction used for the measurements distilled within 0.3°. The purification of the benzene was mentioned in Sec. 8.

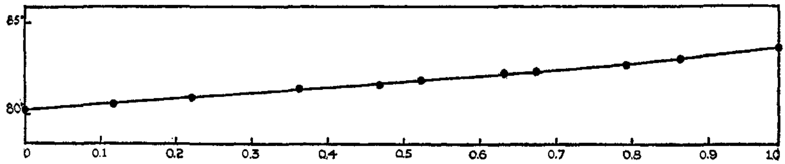

Fig. 10.—Ethylene chloride and benzene. Boiling points.

Numerical Results.—Table XIII gives the results of experiment and of theoretical calculation, as before. The percentage differences between the calculated and observed values are again referred, of course, to the total pressure of 760 millimeters.

TABLE XIII.

1. B.p. obs.	2. B.p. calc.[1]	3. x. $C_2H_4Cl_2$ in liquid.	4. p_1 obs.	5. p_1 calc.	6. Diff., per cent.	7. p_2 obs.	8. p_2 calc.	9. Diff., per cent.
80.24°	80.2°	0	0	0	0	760.0	760.0	0
80.55	80.9	0.1197	83.9	84.5	+0.08	676.1	675.5	—0.08
80.90	81.3	0.2239	163.2	162.9	—0.04	596.8	597.1	+0.04
81.41	81.6	0.3663	269.4	271.0	+0.08	490.6	489.0	—0.08
81.59	81.8	0.4736	350.1	351.6	+0.20	409.9	408.4	—0.20
81.86	82.0	0.5280	393.2	392.2	—0.13	366.8	367.8	+0.13
82.23	82.3	0.6377	476.1	474.3	—0.24	283.9	285.7	+0.24
82.33	82.4	0.6805	504.7	506.7	+0.26	255.3	253.3	—0.26
82.70	82.8	0.7979	596.8	597.3	+0.07	163.2	162.7	—0.07
83.04	83.0	0.8708	655.0	655.2	+0.03	105.0	104.8	—0.03
83.66	....	1.0000	760.0	760.0	0	0	0	0

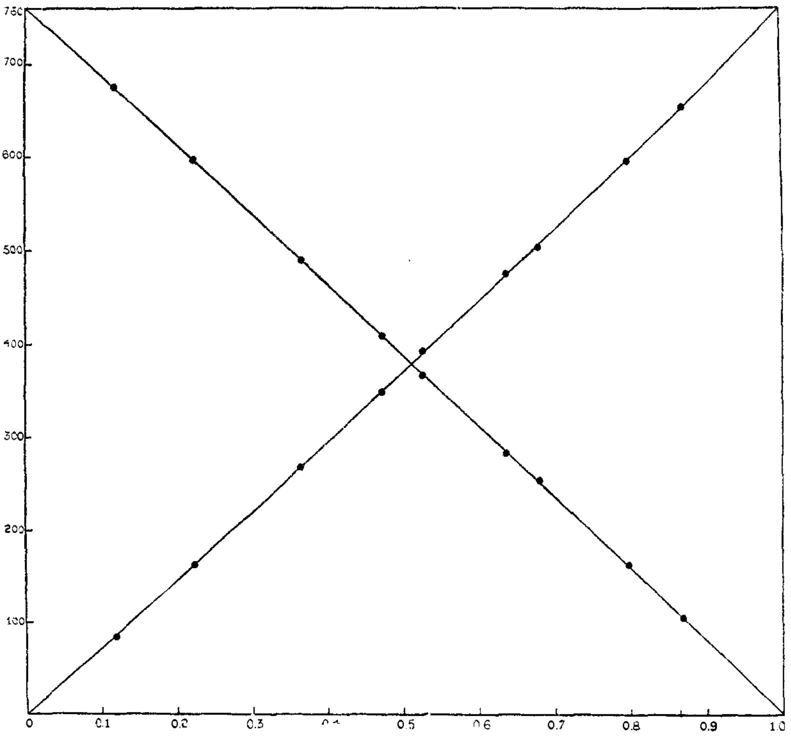

Fig. 11.—Ethylene chloride and benzene. Partial pressures.

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[1] Calculated by linear interpolation of Ramsay and Young's data for benzene. Castell-Evans, "Physico-chemical Tables," Vol. I (London, 1902), p. 507.

The numerical values of the constants, again in this case computed by Professor Story, are as follows:

$$\ln P_1/P_2 = -0.068541, \ \alpha_2 = -0.066679, \ \alpha_3 = +1.0587, \ \alpha_4 = -1.5598.$$

The observed and calculated partial pressures are represented graphically in Fig. 11. Again assuming the calculated values to be free from error, *the probable total error of the measurements in this case was ±0.11 per cent.*

Change of Vapor with the Temperature.—The ratio P_1/P_2 increases with the temperature not inconsiderably, and, on the other hand, the heat of dilution in this case is exceedingly slight. Our theory may, therefore, be expected to lead to reliable results. And first of all, the increase of P_1/P_2 with the temperature leads to the prediction that with rising temperature the vapor will grow richer in ethylene chloride and poorer in benzene.

Table XIV compares the vapor composition which Zawidzki should have observed in his isothermal measurements, according to our theory, with his actual observations. The theoretical calculations were carried out in the same manner as in the case of carbon tetrachloride and benzene (Sec. 8 above).

TABLE XIV.

Mol. per cent. $C_2H_4Cl_2$ in liquid.	Mol. per cent. $C_2H_4Cl_2$ in vapor calc. R. and E.	Mol. per cent. $C_2H_4Cl_2$ in vapor obs. Z.	Diff., per cent.
15.00	13.38	11.52	+1.9
15.00	13.38	12.72	+0.7
29.27	27.15	26.38	+0.8
29.27	27.15	27.06	+0.1
29.79	27.66	27.22	+0.4
41.56	39.12	38.72	+0.4
41.65	39.20	38.90	+0.3
52.15	49.48	49.00	+0.5
52.34	49.65	49.42	+0.2
65.66	62.87	62.66	+0.2
65.66	62.87	62.61	+0.3
75.42	72.90	72.96	—0.1
75.42	72.90	73.07	—0.2
92.06	90.95	91.00	—0.1
91.89	90.76	90.72	0
100.00	100.00	100.00	0

The agreement between the calculations and Zawidzki's experimental data is again as good as might be desired.

12. Carbon Disulphide and Carbon Tetrachloride.

The procedure in purifying the two substances has already been mentioned in previous sections.

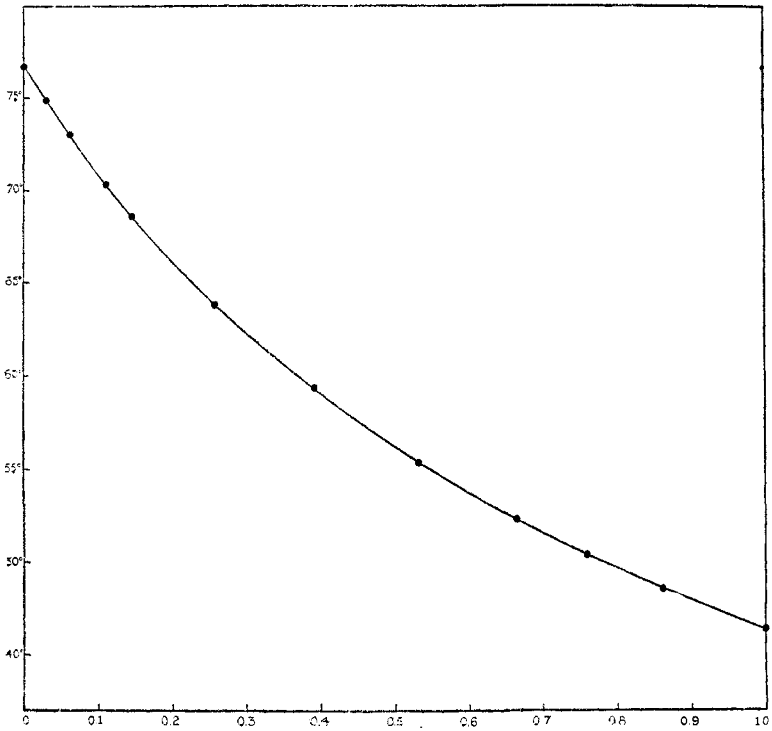

Fig. 12.—Carbon disulphide and carbon tetrachloride. Boiling points.

Numerical Results.—Table XV reproduces, as before, the results of experiment and theoretical calculations.

TABLE XV.

1. B.p. obs.	2. B.p. calc.[1]	3. x CS_2 in liquid.	4. p_1 obs.	5. p_1 calc.	6. Diff., per cent.	7. p_2 obs.	8. p_2 calc.	9. Diff., per cent.
76.69°	....	0	0	0	0	760.0	760.0	0
74.89	76.1°	0.0296	62.5	62.9	+0.05	697.5	697.1	−0.05
73.09	74.0	0.0615	(118.1)	122.9	(+0.63)	(641.9)	637.1	(−0.63)
70.31	71.2	0.1106	202.2	202.4	+0.03	557.8	557.6	−0.03
68.55	69.5	0.1435	(252.9)	248.4	(−0.59)	(507.1)	511.6	(+0.59)
63.78	64.0	0.2585	376.4	377.4	+0.13	383.6	382.6	−0.13
59.32	59.4	0.3908	481.8	483.4	+0.21	278.2	276.6	−0.21
55.33	55.1	0.5318	567.7	567.5	−0.03	192.3	192.5	+0.03
52.25	52.2	0.6630	630.0	629.5	−0.07	130.0	130.5	+0.07
50.35	50.4	0.7574	667.4	668.9	+0.20	92.6	91.1	−0.20
48.52(?)	48.6	0.8604	708.0	708.3	+0.04	52.0	51.7	−0.04
46.34	46.0	1.0000	760.0	760.0	0	0	0	0

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[1] Calculated on the basis of pressure-temperature data for pure carbon disulphide.

The numerical values of the constants on which the calculated values of Table XV are based are as follows:

$$\ln P_1/P_2 = +0.94356,\ \alpha_2 = +0.69682,\ \alpha_3 = -0.90708,\ \alpha_4 = +0.40993.$$

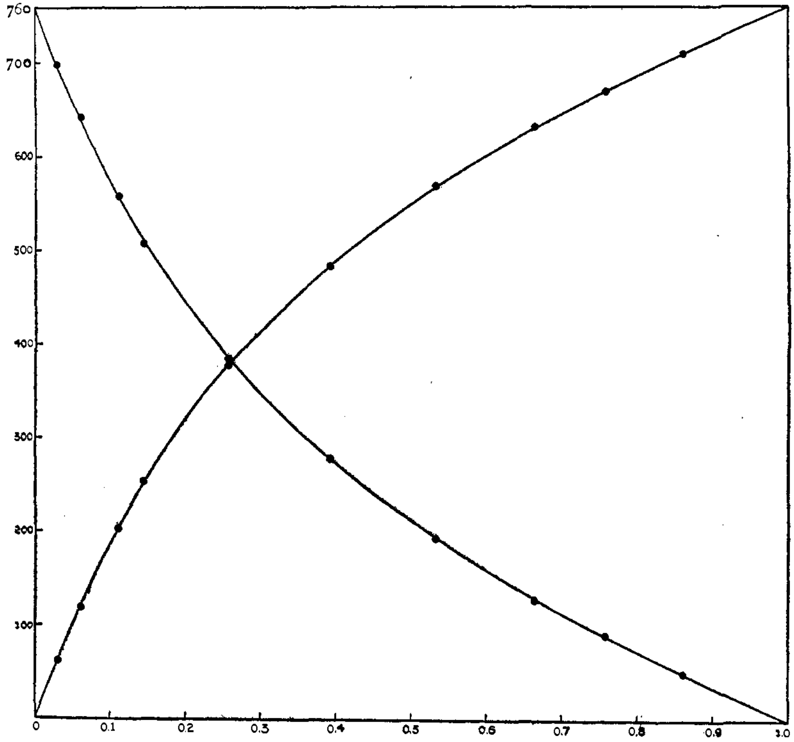

Fig. 13.—Carbon disulphide and carbon tetrachloride. Partial pressures.

Fig. 13 gives a picture of the excellent agreement between theory and experiment. Assuming, again, the calculated curves to represent the true values of the partial pressures, the probable total error of the measurements was ±0.20 per cent. Leaving out of account the two somewhat faulty observations, *the probable total error in this case amounts to only ±0.09 per cent.*

Comparison with Brown's Results.—The present case affords an opportunity to compare the results obtained by the new method with those obtained by Brown,[1] who employed the ordinary dynamic method with external heating. Since both Brown and ourselves carried out the measurements under normal atmospheric pressure, our value for $\ln P_1/P_2$

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[1] *J. Chem. Soc.,* 39, 311 (1881).

could be employed without change. Table XVI gives the results of experiment and calculation, the second column representing percentages that would be yielded by the new method, while the third column gives the corresponding percentages actually observed by Brown.

TABLE XVI.

Mol. per cent. CS_2 in liquid.	Mol. per cent. CS_2 in vapor R. and E.	Mol. per cent. CS_2 in vapor. Brown.	Diff., per cent.
10	24.5	25.4	+0.9
20	41.7	42.4	+0.7
30	54.4	55.5	+1.1
40	64.4	66.2	+1.8
50	72.4	74.2	+1.8
60	79.1	80.4	+1.3
70	85.0	85.8	+0.8
80	90.2	90.6	+0.4
90	95.1	95.2	+0.1

Three conclusions may be drawn from Table XVI. In the first place, the differences between Brown's and our own results are systematic and distinctly greater than the differences between our calculations and Zawidzki's experimental data given in other tables above. Assuming the data yielded by the new method to be entirely reliable, Zawidzki's results (probably owing mainly to his employment of electric heating) appear to be better than Brown's. Secondly, even Brown's results are within one or two per cent. of our own, which indicates that the ordinary dynamic method, even in its simplest forms, is capable of yielding usable results. Thirdly, the great discrepancies between Brown's and Carveth's results[1] in the case of carbon disulphide and benzene, amounting in some cases to eight or nine per cent., point distinctly against the reliability of Carveth's method.

Brown's general statement[2] (based on a very few observations in the case of carbon disulphide and carbon tetrachloride) that "*when a mixture of two liquids is boiled the composition of the vapor evolved is independent of the pressure under which ebullition takes place*" is by no means borne out by our theory. Provided the heat of dilution is sufficiently small (as it is in the case of carbon disulphide and carbon tetrachloride), this principle can only hold in those cases in which the ratio P_1/P_2 does not vary appreciably with the temperature. In the majority of cases it will *not* hold, although usually the variation of vapor composition with the temperature will be rather slow. This subject has already been attacked in these laboratories theoretically and will soon be taken up experimentally, and the results ought to be available for publication before very long.

[1] Carveth, *J. Phys. Chem.*, **3,** 193 (1899). See Young, "Fractional Distillation" (London, 1903), pp. 84–85.

[2] *J. Chem. Soc.*, **39,** 315 (1881).

13. Acetic Acid and Benzene.

Preparation of the Substances.—Kahlbaum's best acetic acid was found to require no further purification and was used directly. The purification of the benzene has already been mentioned.

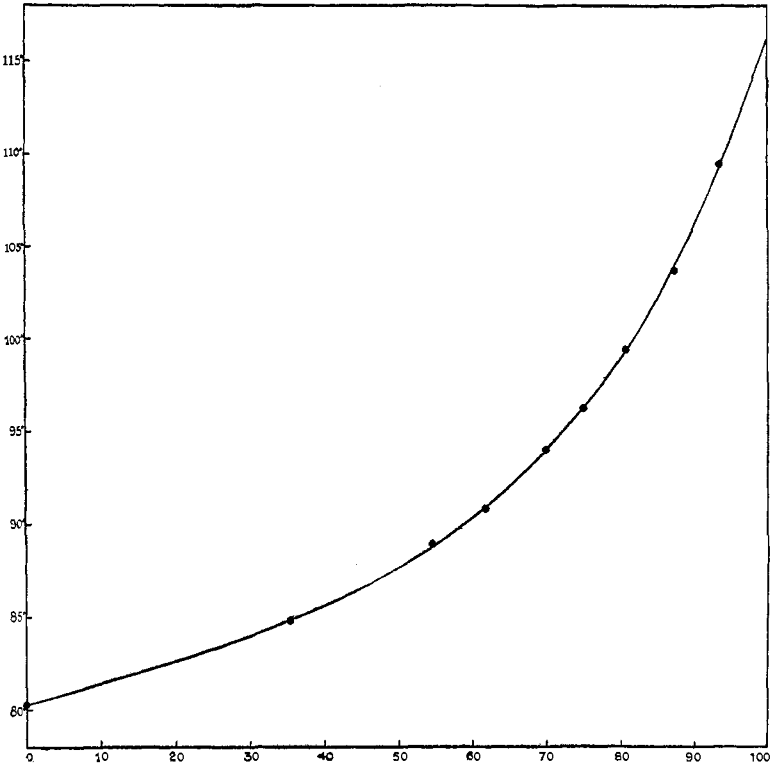

Fig. 14.—Acetic acid and benzene. Boiling points.

Numerical Results.—Owing to the association of acetic acid vapor, the calculation of partial pressures from the composition of the vapor would have been a very laborious task.[1] And as such labor did not seem likely to serve the immediate purposes of the present research, it was decided to express the results in the form of molar percentages, assuming the vapor density of the acid to be normal. Both the observed and the calculated "molar per cents." in Table XVII and in Fig. 15 should therefore be understood as expressing really nothing but the composition of the vapors. The partial pressures remaining for the present unknown, the corresponding values of P_1 and P_2 could obviously not be found, and therefore it was not possible to calculate the boiling points.

[1] See Zawidzki, *Loc. cit.*

TABLE XVII.

B.p. obs.	Mol. per cent. $C_2H_4O_2$ in liquid.	Mol. per cent. $C_2H_4O_2$ in vapor obs.	Mol. per cent. $C_2H_4O_2$ in vapor calc.	Diff., per cent.
80.24°	0	0	0	0
84.72	35.49	14.96	14.97	+0.01
88.96	54.61	22.48	22.20	—0.28
90.85	61.96	25.79	26.04	+0.25
93.99	70.07	31.41	31.36	—0.05
96.23	75.03	35.57	35.61	+0.04
99.44	80.77	42.24	41.97	—0.27
103.71	87.28	52.18	52.39	+0.21
106.82	91.09	61.18	60.83	—0.35
109.51	93.53	68.51	68.49	—0.02
......	100.00	100.00	100.00	0

The calculated percentages in Table XVII are based on the followin constants kindly computed by Professor Story:

$$\ln P_1/P_2 = -1.3093,\ \alpha_2 = +0.98625,\ \alpha_3 = +0.52373,\ \alpha_4 = +0.84538$$

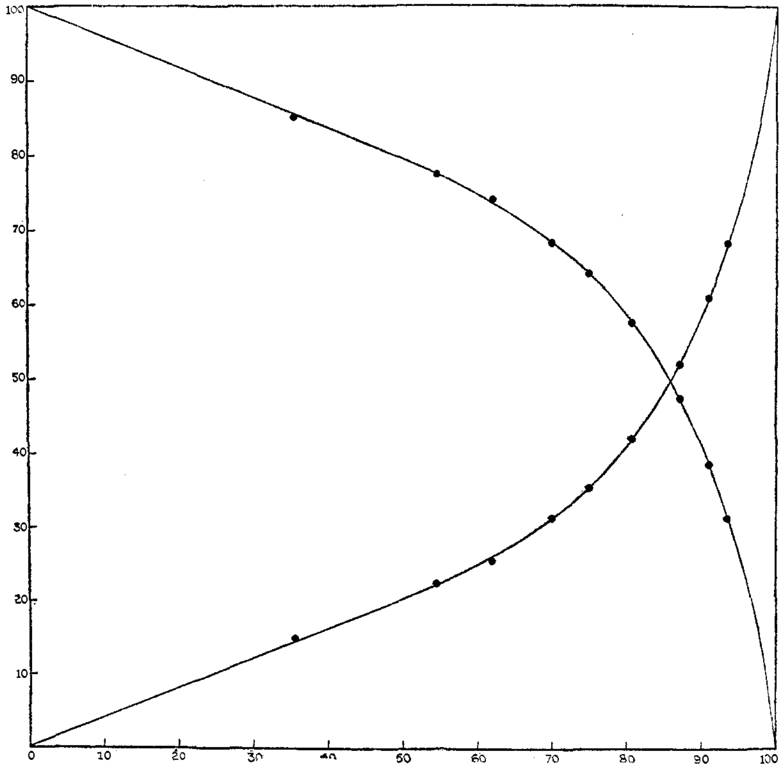

Fig. 15.—Acetic acid and benzene. Molar percentages.

The probable total error involved in the measurements in this case was ±0.15 per cent.

The theoretical principle proposed in Sec. 2 cannot be directly applied to this case for the obvious reason, again, that acetic acid vapor is associated and that its association varies with the temperature. A general theoretical study of cases complicated by phenomena of association or dissociation will be taken up in these laboratories at the earliest opportunity.

CLARK UNIVERSITY, WORCESTER, MASS.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASS. INSTITUTE OF TECHNOLOGY. NO. 43.]

THE CONDUCTIVITY AND IONIZATION OF POLYIONIC SALTS.

BY ARTHUR A. NOYES AND JOHN JOHNSTON.

Received July 14, 1909.

CONTENTS.

1. Outline of the Investigation.

In a previous publication from this laboratory[1] there was described an extended series of investigations on the conductivity and ionization of substances in aqueous solution through a wide range of temperature. The substances studied were, however, of the simpler ionic types, containing only univalent and bivalent ions. The purpose of this research was to extend the measurements to salts with ions of higher valence as well as to study other salts of the uni-bivalent type.

The substances investigated are potassium ferrocyanide, barium ferrocyanide, calcium ferrocyanide, lanthanum nitrate, lanthanum sulphate, potassium oxalate, calcium nitrate, potassium citrate, and potassium nitrate. Their conductivities were measured at various concentrations through a range of temperature extending from 0° to 156°, except in certain cases, when measurements could not be made at the higher temperatures, on account of partial decomposition of the salt. The temperatures employed were 0°, 18°, 25°, 50°, 75°, 100°, 128° and 156°. The concentrations studied were 2, 12.5, 50 and 100 millinormal, and in

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[1] Carnegie Institution of Washington, Publication No. 63 (1907). Briefer accounts of the work have also been given in *J. chim. phys.*, 6, 505–23 (1908); THIS JOURNAL, 30, 335–53 (1908).