$$
\begin{array}{ll}
1 \ldots\ldots\ldots\ldots\ldots\ldots & 0.1464 \text{ gram.} \\
2 \ldots\ldots\ldots\ldots\ldots\ldots & 0.1464 \quad `` \\
3 \ldots\ldots\ldots\ldots\ldots\ldots & 0.1460 \quad `` \\
4 \ldots\ldots\ldots\ldots\ldots\ldots & 0.1464 \quad `` \\
\end{array}
$$

The separation of silver from copper and from cadmium is just as rapid and complete as these last separations.

The deposits of mercury, gold, and silver, were carefully ex· amined in the quantitative way for the various metals with which they had been associated; in every instance they showed them· selves perfectly pure, so that these methods can be relied upon and trusted where accurate and rapid work is required.

The metallic deposits were washed and dried in the manner described in previous articles.

During the progress of the preceding experiments behaviors were observed pointing toward the separation of silver from gold, and mercury from gold and from silver in cyanide solution, but thus far expectations in these directions have not been realized. When conditions apparently favorable were obtained, traces of one or the other metal would be discovered in the metallic de· posit, so that, at this moment, trustworthy and definite data cannot be given.

UNIVERSITY OF PENNSYLVANIA.

ON THE VAPOR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.

By C. E. LINEBARGER.

CONTENTS.

I. INTRODUCTORY.

THE investigation of the elastic forces or tensions of vapors emitted by a solution of a fixed substance in a volatile liquid has received much attention, especially within recent years.   The impetus for investigations of this kind is, in a great measure, due to the new notions that have been introduced into science in regard to the nature of solutions.   The possibility of ascertaining the molecular mass of a substance from a determination of the amount of the depression of the vapor-tension of a liquid, occasioned by its being dissolved therein in known proportions, has induced chemists to study carefully this field of scientific inquiry, which it may truly be said, has been gone over very elaborately.

In the greater part of the work that has been done, both theoretical and experimental, it has been assumed that the dissolved substance is not appreciably present in the gaseous state, and but sparingly present in the liquid state; in other words, the dissolved substance is supposed to be involatile, and the solutions are made dilute.

Now, absolute involatility in any body whatsoever cannot be affirmed; there must always be, at every temperature, some degree of power of assuming the gaseous state, although it may be so slight as to be imperceptible to our senses.   Still, for all practical purposes, the assumption of non-volatility in many substances can be admitted, as our means of experimentation are not sufficiently delicate to detect any small amount of volatility.

Although so much has been done on the vapor-tensions of solutions of fixed substances in volatile liquids, comparatively little attention has been paid to the study of the vapor-tensions of mixtures of the volatile liquids; yet this is the general case, of which the restriction that the dissolved substance be fixed

makes only a special application.   It must, indeed, be allowed
that the consideration of a mixture of vapors, instead of a single
one, introduces certain complications into the problem; and this
is, perhaps, just the reason so little work has been done on this
part of the subject; still difficulties of this sort are probably not
unsurmountable.

The limitations of work on vapor-tensions to dilute or, at
most, moderately concentrated solutions cannot be said to be
satisfactory.   True, the theory of solutions has been developed
on the hypothesis that dissolved matter, in analogy with gas-
eous matter, is in a state of considerable dilution; and experi-
mental confirmations of theoretical predictions can be expected
only when such a state of affairs is realized.   Notwithstanding
that circumstance, it seems of importance to extend our line of
operations and attack the problems presented by concentrated
solutions; perhaps they will be found to exhibit fewer anomalies
than has been supposed.

There are two circumstances which render work that has
hitherto been done on the vapor-tensions of mixtures of volatile
liquids of all concentrations unsatisfactory; they are to be found
in the choice of the liquids investigated, and the kinds of vapor-
tension measured.   The liquids chosen were almost invariably
those which are now recognized to be made up of associated
molecules; they are just those which exhibit the greatest
abnormalities in respect to most of their properties, and it
cannot be expected that simple relations, if they exist at all,
will be discovered when such liquids are used as material of
investigation.   All investigators also, almost without exception,
have measured only the total pressure of the mixtures of liquids
examined, which is the sum of the partial pressures, these,
however, being entirely unknown.   But more important is it to
know the share which each vapor has in the exerting of the
total pressure, and only when this is learned can our knowledge
of the matter be said to be in any adequate measure complete.

This paper seeks to fill in some degree this gap in the subject
of vapor-tensions.   The method employed is such as to permit of
the specification of the partial pressures of a mixture's compo-
nents, and also of their concentrations in the gaseous phase.   The

choice of the liquids has been made with an eye towards employ-
ing those which have been found to be most "normal," so that
in the examination of more complex liquids, that is, those con-
sisting of associated molecules, the simplicity to be expected in
the phenomena of the former may aid us in getting some light on
the possible intricacies of the latter.   All the mixtures examined
are freely soluble in one another so that no disturbing influence
from layer·formation can take place.

In reality, we have before us a case of equilibrium; the equi-
librating system consists of two substances, each present in two
phases, the liquid and gaseous.   We have to ascertain at the
points of equilibrium the temperature, the partial pressures of the
two substances in gaseous phase, and their concentration in both
liquid and gaseous phase.

2. HISTORICAL.

The first paper that I know of which treats of the vapor·ten·
sions of mixtures of liquids soluble in every proportion in one
another is by Gustav Magnus,[1] who states that, when to a volatile
liquid, such as ether, contained in a barometric vacuum,
another less volatile liquid, such as alcohol, be added, the ten·
sion of the vapors of both liquids is less than that of the ether
alone ;   the cause of this behavior Magnus seeks in a certain
reciprocal attraction on the part of the two liquids.   Magnus'
paper, being almost the first on the subject, contains, as,
indeed, is generally the case with pioneer papers, some impor·
tant statements, which, through the labors of later investigators,
have become generalized into wide-reaching laws ; but every·
thing in it is purely of a qualitative nature, no reliable quantita·
tive data being given.

Regnault[2] in the course of his extended investigations on the
elastic forces of the vapors given off by liquids, determined at

1 Ueber das Sieden von Gemengen zweier Flüssigkeiten und ueber das Stossen
solcher Gemenge.   *Ann. der Phys. u. Chem. Pogg.*, **38**, 481-492. *1836*.

2 Ueber die Elasticitätskräfte der Dämpfe bei verschiedenen Temperaturen im Vacuo
und in Gasen ; und ueber die Spannung der Dämpfe aus gemengten oder geschichteten
Flüssigkeiten ; *Ann. der Phys. u. Chem. Pogg.*, **93**, 537-579. *1854*. and Mémoires de l'
Academie des Sciences, **26**, *1862*.   Quatrième Partie : Forces Élastiques des Vapeurs qui
sont Émises par les Liquids volatiles. Melangées par Dissolution reciproque on super-
posés.   Troisième Classes : Mélanges binaires des Liquides qui se dissolvent mutuelle·
ment en toutes Proportions, 724 and 743.

different temperatures by the static as well as dynamic method, the vapor-tensions of several mixtures of various liquids. Regnault did not pay much attention to the composition and analysis of the mixtures investigated, his object being merely to get a general idea of the relations of the vapor-tensions of the mixtures to those of the compotent liquids. Still there is but a little doubt that the composition of the mixtures is specified with sufficient accuracy to admit of his data being regarded as reliable enough for theoretical considerations and confirmations. In a later section are given his results so rearranged as to furnish some indications of the nature of the phenomenon which they represent. Regnault states in the papers printed in the Mémoires de l' Acadimie that his experiments lead to the same conclusions as those of Magnus; but in the German translation (*loc. cit.*) from the Comptes rendus, he does not seem to have given Magnus this credit, which induced the latter in a paper[1] immediately following that by Regnault, to call attention to his results published some eighteen years before (*loc. cit*). In this last paper by Magnus nothing new is communicated, a considerable part of it being occupied with quotations from his former paper.

Plücker[2] determined by means of Geissler's "Vaporimeter" the composition of the liquid and gaseous phases, as well as the total pressure of the latter, of a system consisting of a mixture of alcohol and water; the work has the stamp of having been done with great care, and the accuracy of the results—rather meager, it must be said—can probably be relied upon.

Bussy and Buignet[3] in the course of their researches on the physical properties of mixtures of hydrocyanic acid and water, made determinations according to the static method of the vapor-tensions of seven mixtures of the above two liquids (page 245 of their memoir). The work, which was carried out at 13.25° is fairly accurate, but the range of concentrations is not extensive enough to permit of utilization of their results.

[1] Ueber die Spannkraft der Dämpfe von Mischungen zweier Flüssigkeiten ; *Ann. der Phys. u. Chem. Pogg.*, 93, 579–582, 1852.

[2] Untersuchungen über Dämpfe und Dämpfgemenge ; *Ann. der Phys. u. Chem. Pogg.*, 92, 193-220, 1854 : A continuation of this article was promised by the author, but I have been unable to find it and regard its appearance as very doubtful.

[3] Recherches sur l'acide cyauhydrique : *Ann. Chim. Phys.*, [4] 3, 231–263, 1864.

While the preceding scientists for the most part endeavored to find relations between the tensions of vapors emitted by a mixture, and those given off by its components in a state of purity, Duclaux[1] set himself about to get a knowledge of the relations of the composition of the liquid mixture to that of the vapors emitted. His method consisted in distilling a large quantity (1100 cc.) of a mixture of known composition and collecting several distillates, the composition of which was determined through their surface tensions by means of the " Drop-method." Duclaux, believing, for reasons which he does not state, that simpler relations are to be discovered, if the proportions of the liquids in a mixture be expressed in volumes rather than in weights, communicates results and data, which, as he neglects to give any accurate indications as to the temperature at which and the pressure under which the mixtures investigated by him entered into ebullition, and as to the amount and direction of the change of temperature as the boiling proceeded, it is impossible to put into a shape permitting of comparison with others ; the mixtures studied consisted of water and the series of alcohols up to caprylic alcohol, and of water with formic, acetic, and butyric acids.

Wüllner[2] determined according to the static method[3] the vapor-tension of five different mixtures of ethyl alcohol and water at temperature intervals of about 10° from 11.8° to 84.6°; also of two mixtures of sulphuric ether and alcohol at temperature intervals of about 3° from 7.2° to a little over 30°. Wüllner had especially in mind in his work the determination of the variation of constancy of the ratio of the tension of the mixture of vapors to the sums of the tensions of each vapor alone with the temperature; no mention is made of experimental details and of the purity of the liquids experimented upon.

It may be well for the sake of completeness to make mention

1 Sur les Forces Elastiques Emmises par les Mélanges de deux Liquides : *Ann. Chim. Phys.*, [5] 14, 305-345, 1878.

2 "Ueber die Spannkraft der Dämpfe von Flüssigkeitsgemischen": *Ann. der Phys. u. Chem. Pogg.*, 129, 353-366. 1866.

3 *Ann. der Phys. u. Chem. Pogg.*, 103, 534-542.

here of Alluard's,[1] Berthelot's,[2] and Brown's[3] work on the boil·
ing points of mixtures of liquids, although little is to be found
therein which bears directly upon our subject.

An important experimental as well as theoretical investigation
on the subject in question has been made by Konowalow.[4]   The
method employed was the static, so arranged, however, that the
error arising from the change of composition of a liquid mixture
due to the evaporation of its components was reduced to a mini·
mum.   The determinations were made with mixtures of water
with each of the first four members of the series of alcohols,
$C_n H_{2n+2} O$, and of the series of acids $C_n H_{2n+2} O_2$ at several different
temperatures; the work of Konowalow may be looked upon as
very accurate.

Among Raoult's numerous and important publications on the
vapor·tensions of solutions, there is one which deserves mention
in the history of the vapor·tensions of mixtures of volatile liquids,
even if one component of the binary mixtures investigated by him
has but a feeble tension of vapor.   The paper referred to[5] treats
of the vapor·tensions of solutions of turpentine, nitrobenzene, an·
iline, methyl salicylate, and ethyl benzoate, all almost non·volatile
liquids, in ether ; the determinations were made at ordinary tem·
peratures by the static method, and are to be considered as re·
markably exact.   In a later section, the data will be given in a
modified form.

In the last five or six years papers by Planck, by LeChatelier,
and by Nernst, treating of the theoretical side of the question,
have appeared ; from their importance as well as for convenience
of reference, their co..tents will be quite fully reproduced.

Max Planck[6] enunciated certain relations between the differ·

1 " Experiences sur la Temperature d' Ebullition de quelques Mélanges binaires de
Liquides que se dissolvent mutuellement en tous Proportions." : *Ann. Chim. Phys.*, [4] 1,
384-392. *1894*.

2 "Sur la Distillation des Liquides Mélanges." *Compt. rend.*, 57, 430 *(1863); Ann. Chim.
Phys.*, [4] 1, 384-392. *1864*.

3 " On the Distillation of Mixtures of Carbon Disulphide and Carbon Tetrachloride" :
Transactions of the Chemical Society of London. 39, 304. *1881*.

4 "Ueber die Dampfspannungen der Flüssigkeitgemischen." : *Ann. der Phys.
Wied.*, 14, 219, *1881*.

5 "Ueber die Dampfdrucke Atherischer Losungen." : *Ztschr. phys. Chem.*, 2, 353-5;3.
1888.

6 "Ueber die Dampfspannung von verdünnuten Losungen flüchtiger Stoffe." : *Ztschr.
phys. Chem.*, 2, 405-414, *1888*.

ence of concentrations of mixtures of two volatile substances in
equilibrating gaseous and liquid phases, and the depression of
the vapor-tension, which permit of experimental verification.
Planck assumes the applicability of the law of Raoult-van't Hoff
and that of Henry to the case of the vapor-tensions of mixtures
of volatile substances (liquids); that is, there must be direct
proportionality between lowering of vapor-tension and molecu-
lar concentration, and also between concentration in liquid phase
and partial pressure in gaseous phase; furthermore he states
expressly that his deductions are made for the case of dilute
solutions only, and that the substances in all phases of a system
consist of normal molecules.

Such a system made up of a liquid and gaseous mixture in
contact may be represented by the symbol:

$$nm, \; n_1 m_1 + n'm', \; n_1'm_1',$$

where n and n_1 represent numbers of molecules, and m and m_1
molecular masses; the accented letters refer to the vapor, and the
unaccented to the liquid; those written with the subscript have
reference to the dissolved substance, those without subscript to
the solvent; n and n' are large in comparison with n_1 and n_1'.
The numerical concentrations of the individual substances are:

$$c = \frac{n}{n + n_1}; \; c_1 = \frac{n_1}{n + n_1}; \; c' = \frac{n'}{n' + n_1}; \; c_1' = \frac{n_1'}{n' + n_1'}.$$

If a reaction supervenes occasioning the following changes in
the numbers of the molecules:

$$\delta n : \delta n_1 : \delta n' : \delta n_1' = \gamma : \gamma_1 : \gamma' : \gamma_1',$$

equilibrium occurs, in case this condition,

$$\gamma \log c + \gamma_1 \log c_1 + \gamma' \log c' + \gamma_1' \log c_1' = \log K,$$

is fulfilled[1]; K is a function of pressure and temperature. In the
case before us, we have two different reactions to consider: the
vaporization of the solvent and that of the dissolved substance.
Accordingly:

1. $\gamma = -1$ $\gamma_1 = 0$ $\gamma' = 1$ $\gamma_1' = 0$
2. $\gamma = 0$ $\gamma_1 = 1$ $\gamma' = 0$ $\gamma_1' = 1$

The necessary conditions for equilibrium are:

[1] See M. Planck. Ueber die Vermehrung der Entropie. *Ann. der Phys. Wied.,* **32,** 489. *1887.*)

$$- \log c + \log c' = \log K$$
$$- \log c_1 + \log c_1' = \log K_1,$$

or, if it be taken into consideration that c and c' differ but little from unity, and if members of higher degrees be neglected:

$$c_1 - c_1' = \log K,$$
$$\text{and} \qquad \log \frac{c_1'}{c_1} = \log K_1.$$

Only the first of these relations can be gotten into a form ex-perimentally verifiable in the present state of our knowledge, and, accordingly, it alone will be treated of in this review.

K is not a directly known function of temperature and pres-sure, and in order to get its expression in terms of those energy-factors, use must be made of the thermodynamic differential equation:

$$\frac{\delta (\log K)}{\delta p} = -\frac{V}{T}.$$

V being the change of volume occasioned by the reaction at the temperature T, $\log K$ developed in a series according to powers of $(p - p_0)$ becomes:

$$\log K = \log K_0 + (p - p_0)\left(\frac{\delta \log K}{\delta p}\right)_0 + \cdots\cdots\cdots$$

The subscript ($_0$) indicates that for p the value p_0 is to be placed; on account of the great dilution, $(p - p_0)$ must be small, and hence all terms in the series can be neglected after the first power. If the term $\frac{V_0}{T}$ be substituted for the differential quo-tient, the equation

$$c_1 - c_1' = \log K_0 - (p - p_0)\frac{V_0}{T}$$

is obtained.

V_0 is the change of volume of the system, when, at the tem-perature T and under the pressure p_0, a gram molecule of the solvent vaporizes; accordingly we can put for it the molecular volume of the vapor, which is equal to $\frac{T}{p}$ by Boyle's and Gay-Lussac's laws; we then obtain

$$c_1 - c_1' = \log K_0 - \frac{p - p_0}{p_0}.$$

K_0 depends only on the temperature and remains constant during isothermal changes of pressure. If we take $p=p_0$, we have to do with the pure solvent, and c_1 and c_1' must be equal to zero, as well as log K also; and generally we may put

$$c_1 - c_1' = \frac{p_0 - p}{p_0}$$

In words this relation runs thus: " The relative depression of the vapor-tension is equal to the difference between the concen-trations of the dissolved substance in the liquid and in the vapor."

Planck also got another expression for the differences between the concentrations $(c_1 - c_1')$ in the following manner: If the equa-tion $c_1 - c_1' = $ log K be developed in a series according to the powers of $T - T_0$, the series

$$\log K = \log K_0 + (T - T_0) \left(\frac{\delta \log K}{\delta T} \right)_0 + \cdots \cdots$$

is obtained. Treating this equation in a way similar to that taken in the previous case, and making use of the thermodynamic re-lation,

$$\frac{\delta (\log K)}{\delta T} = \frac{Q}{T^2},$$

we obtain the expression

$$c_1 - c_1' = (T - T_0) \frac{Q}{T_0^2}$$

where Q is the heat which is derived from the exterior, when a gram-molecule of the solvent vaporizes at the temperature T_0 and under the pressure p. Planck accordingly enunciates this law : " The difference in the concentrations of the dissolved substance in the liquid and in the vapor is equal to the rise in the boiling point, divided by the square of the boiling point and multiplied by the molecular heat of vaporization of the solvent."

From experiments by Konowalow (loc. cit.) on mixtures of for-mic acid and water and of isobutyl alcohol and water, Planck calculated, according to his two formulas just given, the concen-tration in the gaseous phase, a satisfactory correspondence be-tween the two sets of data being found.

Le Chatelier[1], in his remarkable paper on chemical equilib-

1 Recherches Expérimentales et Théoriques sur les Equilibres Chimiques : Extrait des Annales des Mines de Mars-Avril, 1888, 281.

rium, devotes a section to the theoretical treatment of the vapor-tension of a mixture of liquids. The expression finally arrived at is quite complicated, and, although important results may be probably obtained by its applications, it is not expedient to enter into its development here.

A. Winkelmann[1], in seeking experimental proof of the rela-tions established by Planck (*loc. cit.*) between the composition of liquid mixtures and their vapors, condensed some of the va-pors arising from a solution and ascertained the composition of the condensed vapors, or liquid by measuring its index of refrac-tion. The experiments were made with mixtures of water and propyl alcohol ; there is undoubtedly a correspondence between his experiments and Planck's theory, but it cannot be said to be very close.

Nernst[2] also has found an expression for the concentration of a volatile dissolved substance in the gaseous phase in terms of vapor-tensions. If n be the number of molecules of dissolved substance contained in N molecules of a solvent, k a factor of proportionality corresponding to the absorption coefficient of the dissolved substance, and p the partial pressure of the vapor of the dissolved substance in the saturated vapors over the solution, by Henry's law, the equation

$$Kp = \frac{n}{n+N}$$

may be formed. The vapor-tension of the solvent P is

$$P = P_0 \frac{N}{N+n}$$

where P_0 is the vapor-tension of the pure solvent at the tempera-ture in question.

According to Dalton's law, the total pressure of the saturated vapor π of the solution is

$$\pi = P + p$$

[1] Ueber die Zusammensetzung des Dampfes aus Flüssigkeitgemischen : *Ann. der Phys. Wied.*, **39**, 1-15, *1890*.

[2] Vertheilung eines Stoffes zwischen zwei Lösungsmittel und zwischen Lösungsmit-tel und Dampfraum : Dampfspannungen verdünnter Lösungen flüchtiger Stoffe *Ztschr. phys. Chem.*, **8**, 124, *1891*.

and the composition of the vapor may be shown to be

$$K \frac{n'}{N' + n'} = \frac{p}{P + p}.$$

Where N' and n' have the same significance for the vapor as N and n have for the liquid mixture.

Nernst gives in a little table a comparison of the data calcula· ted by his formula with those obtained by the use of Planck's formula, both in turn being compared with the results of Win· kelmann's experiments.

TABLE I.

Mixture of 6.2 grams propyl alcohol and 93.8 grams water.

| | | | | | | Per cent alcohol in vapor. | | |
t	P_0ı	π	P	p	$\frac{n}{N' + n'}$	Winkel-mann.	Nernst.	Planck.
17.65	15.0	20.8	14.7	6.1	0.293	....	58.0	64.2
31.5	31.3	....	30.7	....	....	52.3	59.4	66.0
40.3	55.7	79.4	54.6	24.8	0.312	57.4	60.2	67.2
51.0	96.7	138.7	94.8	43.9	0.316	60.8	61.9	67.7

It is apparent that Nernst's calculated data correspond better with the data observed than do those calculated by Planck's for· mula, although the correspondence in no case can be reckoned very close; it must be kept in mind. however, that Winkelmann's method is not very exact, and that the vapor·tensions and com· position of distillates have been measured on chemical prepara· tions from different sources.   A difference, which may be called an advantage, between Nernst's and Planck's formulas, is that the former is not, like the latter, restricted to the consideration of dilute solutions only.

Nernst has also developed certain views in regard to the vapor· tensions of binary mixtures of volatile liquids.

Taking as base of his considerations the empirical law: the vapor·tension of a liquid is lowered when a foreign fixed sub· stance is dissolved in it; he states that this law is applicable also to solutions of volatile substance, only, in this case, the superin· cumbent vapor consists not of that of the solvent alone, but of a mixture of those of the dissolved liquid and of the solvent; the gaseous phase of the system contains both components of the so-

[1] *Theor. Chem.* 97, *1893*, aud Siede und Schmelzpuukt, 6?, *1894*.

lution, and according as the partial pressure of one component is greater or less than the diminution of the vapor-tension of the other which it causes by its presence, the total tension of the solution is greater or less. If now a small quantity of a liquid, A, be added to a liquid, B, the vapor-tension of B will be diminished proportionally to the quantity of A added; but the total pressure of the resulting solution will be increased, inasmuch as A as well as B gives off vapors, and the partial pressure of A is so much the greater as the solubility of the vapor A in the solution is smaller. According as the first or the second influence preponderates, the vapor-tension of the solution will be smaller or greater than that of the liquid B in a state of purity. Since the properties of such a mixture must vary continuously with the composition, the influence of the proportions of the two liquids upon the vapor-tension of the mixture may be considered under three cases.

1. The vapors of both A and of B are easily soluble in each other. If we add ever-increasing quantities of A to B the vapor-tension of the mixture will at first sink to a minimum and then rise, until, when a very great quantity of A has been added, it will approximate to that of the liquid A in a state of purity.

2. The vapors of A and of B are but slightly soluble in each other. If constantly increasing quantities of A be added to B, the vapor-tension increases, reaches a maximum, and decreases when a large excess of A has been added, to that of the pure liquid A.

3. The vapor of A is easily soluble in B, while the vapor of B is but slightly soluble in A. The addition of constantly increasing quantities of one liquid to the other causes the vapor-tension of the resultant mixture to pass without maximum or minimum from the vapor-tension of the second liquid to that of the first. But it is perhaps possible that the vapor of B in A is so difficultly soluble that the addition of a small portion of B to A elevates the vapor-tension, while at the same time the vapor of A is so easily soluble in B that by addition of A to B the vapor-tension is lowered. In that case, when B is added to A the vapor-tension increases at first, passes through a maximum, decreases to pass through a minimum, finally rising and approximating, when great excess of B is present, to that of the pure liquid B.

Recently, George U. A. Kahlbaum[1] and his assistants have de-
termined according to the dynamic method the vapor-tensions at
different temperatures of mixtures of water with formic and with
acetic acid; also of mixtures of various acids of the fatty series.
The determinations, which are very numerous, have been made
by a method and with material undoubtedly capable of giving
the best of results; it is to be regretted, however, that associa-
ted, instead of normal, liquids were taken.

It is seen in the foregoing historical sketch that only in the
rarest cases have mixtures of normal liquids been investigated
as to their vapor-tensions, and the partial pressures of the consti-
tuents of the vapor been determined. Now, as already stated
on page 617, in order to get a full knowledge of the phenomena
of vaporization of mixtures of volatile liquids, we must learn
what the partial pressures of each is, when converted into vapor
in equilibrium with the liquid phase ; and we are the more
likely to get clear ideas by investigating the simplest mixtures
first, that is, mixtures made up of simple normal molecules.
Having by considerations similar to these been led to take nor-
mal liquids to form the mixtures, the vapor-tensions of which
are to be determined, my first task was to devise some experi-
mental method, which furnishes a means of measuring the par-
tial tensions of the vaporous members of a system of bodies.   In
order to do this, it is almost indispensable that the composition
of the vapor be known, for, that being the case, it is easy to de-
termine what part of the total pressure is to be attributed to each
of its components.   The problem then reduces itself to one of a
simple analysis ; but the difficulty is to get the vapor away from
the liquid with which it is in equilibrium without its composi-
tion becoming changed during the operation.   If the so-called
static method of determination of vapor-tensions be adopted, it
is possible by enlargement of the barometric vacuum to be filled
by the vapor, and, after equilibrium has been attained, by sepa-
ration of the liquid from the vapor by means of a stop-cock or
other arrangement, to get enough of vapor to permit of its analy-
sis.   But a small amount can be obtained, however, and there is

1 Studien über Dampfkraftmessungen. Basel, 1893.

great danger that the composition of the liquid mixture becomes considerably changed.

It is possible to collect some of the condensed vapor given off by a boiling mixture of liquids, and determine its composition, as did Duclaux in the paper cited above (page 620). Here, although it is easy to get a sufficient quantity of the condensed mixture of vapor to permit of quite accurate analysis,—provided that a method of analysis of the two liquids in question had been elaborated,—the change of concentration of the solution during the boiling as well as the concurrent change of temperature, together with the other disturbing circumstances, render the accuracy of such work rather illusory.

Accordingly, another means of determination of vapor-tensions had to be found for the purpose of this investigation : and, indeed, the method founded upon the determination of the quantity of a volatile liquid carried off by a definite volume of an inert gas made to pass through it, and the direct subsequent analysis of the gaseous mixture, either by passing it through appropriate liquid absorbents, such as an alkali, where one of the components of the gaseous mixture is an acid, or over decomposing agents, such as red-hot lime, etc., in case one of the components contains sulphur or a halogen, has been adopted ; the method, be it said right here, has been found to meet the requirements of the investigation in a satisfactory manner. It is, indeed, true that the variety of the liquids which can be subjected to investigation is limited, for one member of a mixture must needs be a liquid containing a halogen or sulphur atom, or an acid. Still it is possible to find enough such liquids of differing functions that the results obtained by them can without question be transferred to mixtures made up of any normal liquids whatsoever, and any conclusions drawn, become general.

3. DESCRIPTION OF APPARATUS.

It is of prime importance in the determination of vapor-tensions that the temperature be kept uniform ; accordingly I describe, first of all, the apparatus employed for that purpose.

Thermostat.—This consisted of a cylindrical copper vessel holding nearly forty liters of water. It was heated by means of

a ring burner; the pressure of the gas was kept constant by means of a pressure-regulator, and a thermo-regulator as described by Ostwald,[1] controlled the combustion of the gas.   To insure uniformity of temperature in all parts of the bath, the water was kept in constant agitation by means of a number of fine streams of air blown up through it, the laboratory being provided with air under pressure.   Such a means of agitation gives very satisfactory results: it takes up but very little room, and permits of the examination of the pieces of apparatus plunged in the water by shutting off for a few seconds the flow of the air.

The temperature of the bath remained constant to within $0.05°$ during an experiment; the thermometer employed was one graduated to tenths of degrees, and had recently been tested by the " Physikalische Reichsanstalt " of Berlin.

The apparatus consisted of three principal parts, each made up from material easily found in almost every chemical laboratory.   The first part consists of those pieces required to measure a definite volume of air, to compress it enough to force it through the apparatus, and to dry it thoroughly; the second part is the contrivance for saturating the volume of air with the vapor of the liquid under examination; and the third is the arrangement for the analysis of the gaseous mixture.

First Principal Part of Apparatus.—This consists of a measuring vessel, a vessel for regulating the internal pressure, a manometer, and a system of drying-tubes.   I pass to the description of each.

The Measuring Vessel consists of an ordinary bottle of a capacity varying from one to three liters, according as it is required to employ a larger or a smaller volume of air; the height of the bottle should be such that only the neck is above the water; in its neck is fitted a good rubber stopper through which passes one branch of a ⊤ tube.   This branch of the ⊤ tube is made of tubing of about a quarter inch bore, and is about eight inches long, while the other branch has only half this bore, with a length of about three inches.   The wider branch of the tube is

[1] *Ztschr. phys. Chem.*, **2**, 565, 1888.

pushed through the stopper so that its lower edge is just flush with that of the rubber, and care is taken that this adjustment is in every experiment maintained, as well as that the stopper is always inserted to the same distance in the neck of the measuring vessel. In the upper end of the wider branch of the T tube is inserted (an air-tight joint being assured by the use of rubber tubing) a tube somewhat drawn out and narrowed at its lower end, and provided with a stop-cock at its upper end. The end of the lower part must be about a half inch above level of the stop of the measuring vessel, and the upper end is put, by means of a piece of rubber tubing, in communication with a water supply at constant level about a yard above the thermostat. If the stop-cock be opened, water will flow into the vessel, and displace the air therein contained which escapes through the side branch, which, being in the middle of the vertical branch, is an inch or so above the orifice of the tube introducing the water.

Sufficient mercury is poured into the vessel to make it sit firmly on the floor of the thermostat. The residual volume of the vessel is carefully determined by pouring into it from graduated vessels, enough water to fill it up to the level with the upper surface of the stopper. If the adjustment of the stopper and the tubes be always the same, duplicate determinations of the capacity do not differ by more than one-half cc. If the same volume of mercury always be taken, the volume of water will represent the volume of air passed through a liquid or mixture of liquids undergoing investigation in all determinations.

It is superfluous to make corrections for the expansion of the mercury and the glass when determinations of vapor-tensions are made at higher temperatures, as the error of the estimation of the capacity exceeds the amount of the corrections.

The Pressure Regulator consists of a bottle of any convenient size, provided with enough mercury to make it stand steadily under water, and fitted with a twice perforated rubber stopper. Through one of the holes of the stopper passes a tube nearly to the level of the mercury and furnished with a stop-cock at its upper end ; this tube is connected by means of rubber tubing with the same water source as the measuring vessel. In the other hole is fitted a T tube, of which one of the horizontal

branches is connected by means of a bit of stout rubber with the
narrower branch of the ⊤ tube belonging to the measuring ves·
sel, while the other is attached by rubber tubing to the other
parts of the apparatus.   If water be run into the bottle serving
as pressure regulator, the air in it is compressed until it can
force itself through the liquid with the vapor of which it is to be
saturated.

The Manometer is intended to measure the amount of this
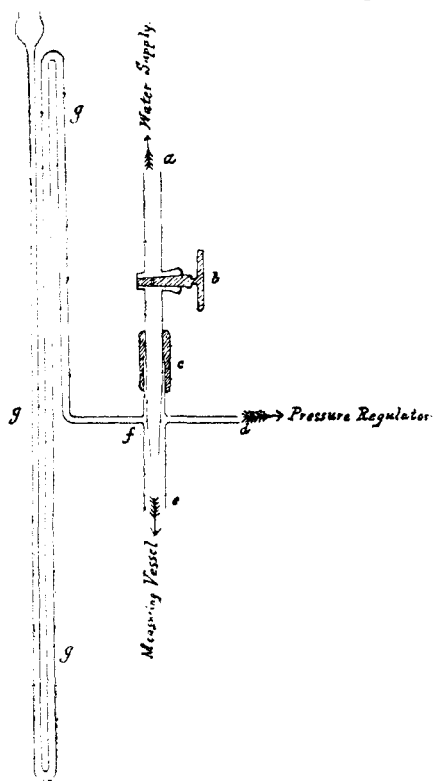compression or the internal pressure; it is made of ordinary
glass tubing bent into ∪
shape, with the branches
about two feet long. It may
be put between the meas·
uring vessel and the pres·
sure-regulator, or between
the drying tubes and the
latter; 1 have found it most
convenient, however, to
melt it into the vertical
branch of the ⊤ tube of the
measuring vessel just oppo·
site the horizontal branch,
as shown in Fig. 1.   The
manometric liquid is water,
and the differences of the
heights of the liquid col·
umns of the two branches,
is read to a millimeter by
means of a metric rule; the
readings are then easily
exact to a tenth mm. of
mercury.

The Drying Tubes can, of
course, be of various shapes

FIG. 1.

and filled with various drying agents.   Liquids, such as strong
sulphuric acid, must be rejected, however, as they increase the
internal pressure, and often cause an irregularity in the flow of
the gas.   I found ∪ tubes to be the best shape, and grains of

pumice stone, soaked in concentrated sulphuric acid, the best drying agent; a length of at least sixty centimeters is to be taken, and the pumice must be changed often. When it be· comes necessary, in work on acid solutions, to remove the carbon dioxide from the air, an additional tube filled with soda lime is taken. At the end of the last ∪ tube, a mercury valve is attached to prevent the backward diffusion of the vapors; this is of the smallest size convenient, and the delivery-tube dipping into the mercury of capillary dimensions.

Second Principal Part of Apparatus. This is the absorption vessel, which may consist of a simple potash bulb according to Mohr. I found it better, however, to add two more bulbs, making five small and two large ones. As liquids which dissolve rubber somewhat were often introduced into the apparatus, and as it was necessary to let it stand sometime before weighing, the outlet and inlet tubes were provided with tiny ground glass stoppers. At first the bulbs were shut up in a copper case set in the ther· mostat; the case had holes in its sides, below the surface of the water, for the conduction and abduction of air, platinum capil· laries and ground glass caps being employed to make the connections. This arrangement was not, however, found satisfac· tory, since one was never sure, air being such a bad conductor of heat, that the contents of the bulbs had the same temperature as that of the bath. Also, the platinum tubes proved to be very delicate, breaking readily if bent often, which was inevitable. It was accordingly found best to plunge the absorption vessel directly into the water of the bath, connection with the system of drying tubes being made with a bit of stout rubber tubing of small bore. When the vessel was removed from the water it was carefully wiped dry and set in the balance case, the atmos· phere of which was kept dry by means of concentrated sulphuric acid.

Third Principal Part of Apparatus.—In order to analyze the mixture of vapors issuing from the absorption vessel two modifications of this part of the apparatus are required—one to be employed when the gaseous mixture contains a halogen compound of carbon, and the other when it contains an acid. In the first, the compound was decomposed by heated lime, and, in the sec-

ond, the acid was absorbed by a solution of potash or baryta. In the following lines a description of each is given:

(1) The outlet tube of the absorption apparatus is fitted by means of a good cork into one branch of a ∪ tube of rather thick glass; this branch is bent at right angles at about the middle of its length, while the other branch is left straight. The latter branch is held clamped to a heavy and hence steady retort-stand set beside the thermostat, and is connected by means of a narrow lead tube to a tube of hard glass placed in the gutter of a combustion furnace. In the further end of the hard glass tube, a Maquenne absorption apparatus, containing a little dilute nitric acid, is inserted, the connection being made with a rubber stopper; this outlet of the absorption apparatus is in communication with a suction pump, and in the rubber tube making this connection a T tube is interposed, over the open end of which is slipped a piece of rubber tubing long enough to reach to the thermostat. When this tube is open, the interior of the apparatus, up to the liquid in the absorption vessel, is under atmospheric pressure; if it be pinched together a little so as to prevent enough air to feed the suction pump from entering, the pressure in the apparatus may be made less than that of the atmosphere; by this little device it is possible to regulate the pressure with great nicety.

(2) This analyzing apparatus consists simply of a potash bulb, according to Liebig, made of thick glass; one branch is flared out to receive the outlet tube of the absorption vessel, and the other is straight so as to glide up and down in a clamp of a retort stand.

The pieces of apparatus just mentioned will receive complementary description in the directions for performing experiments.

Performance of an Experiment when the Mixture Contains an Organic Halogen or Sulphur Compound.—The hard glass tube (about eighty cm. long) is filled with lime or sodium carbonate just as in a determination of halogens in organic analysis, joined to the lead tubing which establishes communication with the ∪ tubes held in a clamp just above the surface of the water in the thermostat, and placed in the furnace. The gas is now lighted and the tube with its contents heated up to a red heat, while a

current of dried air is passed through it to remove all moisture.

The measuring vessel, the pressure-regulator, and the system of drying-tubes are joined air-tight together, and so set in the thermostat that as much room as possible is left for the absorption vessel.

The absorption vessel is filled with the liquid or solution under examination, a few bubbles of air drawn through so as to get the liquid beforehand in the right position, and carefully weighed. It is then connected with the ∪ tube (of course, no air is now being passed through the analyzing tube), and after a couple of minutes of half submersion in the bath, it is attached to the system of drying tubes. It is now wholly submerged in the bath and air is made to pass through it as follows :

The stop-cock of the pressure-bottle is opened so that water may be run in slowly and, by compression of the air, gradually increase the internal pressure. As soon as bubbles of air commence to pass out of the absorption vessel, the stop-cock of the pressure-regulator is closed, and that of the measuring vessel opened. The water issues in drops or a fine stream in full sight of the operator, and its rapidity of flow can be very easily regulated. Experience has taught me that about a liter an hour was about the best rate; after a brief acquaintance with the apparatus, it is possible to judge very closely from the rate of the flow how long it will take for the measuring vessel to become filled. While the operation is proceeding, the height of the manometric column is read off at several different times; if the rate of flow is constant this does not vary by more than one or two mm. of water, or less than one-tenth mm. of mercury.

The barometer is also read off at the beginning and at the end of the experiment : in all my determinations, the difference of the two readings was less than one mm. of mercury.

A minute or so before the measuring vessel is full, the absorption bulbs are lifted out of the water enough to bring the end tubes about two inches above the surface, and there, together with the joining tube on one side and the cork and end of ∪ tube on the other, are carefully dried with filter-paper. When the water in the measuring flask has reached the mark on the ⊤ tube (level of cork), the absorption vessel is detached from the dry-

ing tubes, and the little glass stopper fitted into its inlet tube. Immediately after this operation, the connection between the absorption vessel and the ⊔ tube is broken, and as soon as this is done a perforated cork, through which passes a narrow glass tube so bent at right angles that a long vertical branch is obtained is fitted into the ⊔ tube, its object being to prevent the escape by diffusion of any portion of vapor contained in the ⊔ tube. A current of air is now drawn through the tubes, slow at first to avoid causing too much vapor to pass over upon the heated lime all at once, as, if there be a deficit of air, the combustion is incomplete, and free carbon collects in the cooler portion of the tubes ; in a well conducted experiment, the lime should remain perfectly white. Towards the end of the determination, a more rapid stream of air is drawn through the apparatus, so that one may be sure that all the halogen compound has been brought into contact in the decomposing agent. If any free carbon collects in the tube or if the dilute nitric acid in the Maquenne absorption bulb shows on the addition of silver nitrate the slightest trace of cloudiness, the determination ought to be rejected as untrustworthy.

The absorption vessel, as soon as possible after its removal from the water in the thermostat, should be closed with the second tiny stopper, wiped dry, and set in the balance case, where it takes on the temperature of the room. When this is thought to have taken place, it is weighed, and the loss of weight set down as the evaporated quantity of solution. When the furnace has cooled down, the lime tube is removed and its contents washed out with water and nitric acid into a flask, which is set over a flame and boiled until complete solution ensues, more nitric acid being added, if necessary. If more than a half gram of the halogen compound has evaporated, the solution is brought to a certain volume and an aliquot portion of it taken for analysis.

Most of the analyses were made by the gravimetric method of determination of halogens by precipitation with silver nitrate ; some, also, were analyzed volumetrically, Volhard's method being employed.

Performance of an Experiment when the Mixture contains an Acid.—The absorption vessel is filled with the mixture being

investigated, and weighed as described above. It is then joined by means of a good cork to the analyzing apparatus, into which are run from a pipette ten cc. of a stock solution of potash or baryta; the pipette being provided with a straight calcium chloride tube filled with soda lime, all contamination from the carbonic acid of the breath is avoided. The alkaline liquor is of such strength that it is more than sufficient to neutralize the vaporized acid. The further end of the analyzing arrangement is closed with a ∐ tube filled with soda lime so that the alkaline solution may be in contact with an atmosphere free from carbon dioxide.

The two pieces of apparatus thus filled and joined together are submerged in the water of the thermostat, the whole being held in place with a clamp embracing the upright tube of the analyzing contrivance and attached to a heavy retort stand. The other end of the absorption vessel is then placed in com·munication with the drying tubes, etc., by means of a short bit of stout rubber tubing.

The internal pressure is regulated and the air passed just as described in the preceding section, note being taken of the amount of internal pressure, the volume of the air and the barometric height. A slight correction has to be made to the barometric reading for the following reason : after the air passes the liquid contained in the absorption vessel and comes into the analyzing tube, it is under a pressure equal to that of the atmosphere plus that due to the weight of a column of liquid corres·ponding to the difference of level between the two surfaces of the alkaline solution ; this, in my apparatus, was determined to be equal to one mm. of mercury, which was added to all barometric readings.

When the measured volume of air has passed through the apparatus, the stop·cock, through which water enters into the measuring vessel, is closed, the absorption and analyzing vessels are lifted nearly out of water, and after the joint between the absorption vessel and the system of drying tubes has been wiped dry, it is broken. Both the pieces of apparatus are wiped dry with bibulous paper, and agitated somewhat so that any acid vapors in the bulbs may be brought in contact with and absorbed by the alkaline liquor.

The pieces are then disconnected, the absorption vessel stop·
pered and set in the balance-case, while the contents of the
analyzing vessel are poured into a beaker, rinsing being done
with water free from carbon dioxide. Without delay, the excess
of alkali is estimated by titration against deci·normal acid solu·
tion, and by a simple calculation, the quantity of evaporated acid
is obtained.

4. CALCULATION OF RESULTS.

In the calculations it is assumed that the laws of perfect or
ideal gases may be applied to the mixtures of vapors; that is,
the laws of Boyle, Gay Lussac, and Dalton. Where not too
much vapor is present in the gaseous mixture the legitimacy of
this assumption is unquestionable; and even though this condi-
tion be not fulfilled, the approximation to accuracy may be
sufficient (see section 6).

Calculation of Volume of Air Passed Through a Mixture.—In
order to force the air in the measuring vessel through the liquid
in the absorption vessel, it is necessary that it be brought under
a pressure equal to that of the atmosphere plus that required to
vertically displace the liquid contained in the bulbs, the latter
pressure varying with the density and amount of the mixture.
The volume of the air under atmospheric pressure may be obtained
then as follows:

Let P represent the pressure of the atmosphere. Let P' repre·
sent the pressure which forces the air through the liquid. Let
V' represent the volume of air under the pressure $P + P'$. Let
V represent the volume of air under the pressure P.

According to Boyle's law, and inasmuch as the temperature
remains constant,

$$V = \frac{(P + P')\, V''}{P}$$

Calculation of Composition of·Mixture of Liquid Vaporized.—
As this calculation is simply one of quantitative analysis, it is
not necessary to treat of its details.

Calculation of Partial Volumes of Mixtures of Vapors.—Let m
represent the quantity of one component in the gaseous mixture.
Let M represent its molecular mass. Let 22.32 represent the
volume in liters of a gram·molecule of hydrogen at the tem·

perature $0°$ and under the pressure 760 mm. Let α represent the coefficient of expansion. Let v_1 represent the volume of vapor at the temperature of the determination t and under the atmospheric pressure p. We then have

$$v_1 = 22.32 \, \frac{m}{M} \times 7 \frac{60(1 + \alpha t)}{p}$$

Calculations of Partial Pressures of Components of Vapor Mix·ture.—Let v_1 represent partial volume of one component. Let v_2 represent partial volume of the other. Let v represent partial volume of air. Let p_1 represent partial pressure of one com·ponent. Let p_2 represent partial pressure of the other. Let p represent the atmospheric pressure.

In accordance with Dalton's law,

$$p_1 = p \, \frac{v_1}{(v + v_1 + v_2)}$$

and

$$p_2 = p \, \frac{v_2}{(v + v_1 + v_2)}$$

5. DISCUSSION OF SOURCES OF ERROR IN APPARATUS.

In order to make a just estimate of the degree of accuracy attainable by the above described apparatus, it is necessary to consider somewhat in detail the possible sources of error that may accompany a determination of the vapor·tension of a liquid made by it.

Error in Measurement of Volume of Air Passed Through the Absorption Vessel.—At the beginning of an experiment, both surfaces of the liquid under examination are under atmospheric pressure: by compression of the air in the reservoirs and drying tubes it is forced through the system of bulbs of the absorption apparatus. If, in all experiments, the same volume of liquid be taken, the amount displaced will be the same, and the internal pressure will be greater or less, according as the liquid employed is more or less dense. The internal pressure in some determinations varies slightly during their performance; the variation, however, never exceeds a millimeter or so of mercury. The use of a column of water to measure the internal pressure renders its determination very exact. The atmospheric pressure was found

to remain practically constant during an experiment, which sel-
dom lasted more than an hour and a half. The error arising
from the determination of the pressure to which the air in the
interior of the apparatus is subjected, can accordingly be reck-
oned so slight as to be entirely negligible.

The mercury filled into the measuring vessel for the ballast,
as well as the volume of water used to calibrate the same, can
be measured to within a half cc., and as from 100 to 300 cc. of
mercury and 1,000 to 3,000 cc. of water were taken, the error
committed cannot be more than a thousandth of volume of air,
and, in most cases, is probably less.

The air is, from the way it is forced from the measuring ves-
sel, always measured when saturated with aqueous vapor. The
drying tubes are always to be so filled with the drying reagents
as to leave as little room as possible; I found, however, by spe-
cial experiments, that the shape and size of the drying tubes
exercise no appreciable influence upon the quantity of liquid
carried off by the air; the only requisite seems to be that they
dry the air thoroughly.

All the parts of the apparatus employed in measuring the vol-
ume of air being completely submerged in the water of the ther-
mostat, there is no possibility of error arising from non-uniformity
of temperature. The temperature of the water which expelled
the air was, in most of my experiments, about 20° lower than
that of the thermostat, but it entered the measuring vessel so
slowly that it took on the temperature of the bath without dis-
turbing, to any appreciable degree, the prevailing thermal con-
ditions. That the water introduced took on rapidly the tempera-
ture of the bath was proven by the circumstance that, when, at
the end of a determination, the flow of the water was stopped, and
the level of the letter was flush with the guage-mark, if the
measuring vessel, which in this condition might be said to be a
rude but still quite delicate thermometer, was allowed to stand
undisturbed for some time, no expansion or, at most, but very
slight expansion of the water occurred.

Error from Change of Concentration of Mixture.—A source of
error is to be found in a possible change of the concentration
caused by one or the other of the components of the mixture

being carried off by the air in such quantity that the composition
of the residual mixture is not the same as at the beginning of an
experiment; I think, however, that the error introduced in this
manner is so slight as to be practically negligible, and for the
following reasons :

1. The shape of the absorption vessel is such as to form five
chambers almost entirely independent of one another as far
as their contents are concerned.   The stream of air becomes
saturated in passing through the first two or three bulbs, and
passes through the last two without changing, to an appreciable
degree, the composition of the mixture contained in them.
That saturation is complete after the air has been passed through
the first three bulbs, I assured myself by special experiments;
that is, I filled only the three first bulbs, and found, on passing
a certain volume of air through them, that the evaporated quan·
tity of liquid was the same as when the same volume of air
under similar conditions was passed with all the bulbs filled
with the liquid.

2. As from forty to eighty grams of solution were taken in a
determination, and as the quantity evaporated rarely exceeded
two grams, it is evident that, even if, towards the last of the
experiment, the concentration of the first bulb had altered some·
what, the composition of the mixture in the fifth bulb would
remain practically unchanged.

3. Most of the mixtures examined were made up of liquids
possessing not greatly different vapor·tensions, so that the vapors
of both liquids passed off in about the same proportions.

Error in Analysis of Mixture of Vapors.—The mixture of
vapors on escaping from the absorption vessel passes into the ⋃
tube, and thence through the lead tube into the analyzing tube.
In order that no vapor may condense in the end of the ⋃ tube
flared out for the reception of the cork through which passes the
outlet tube of the bulb apparatus, the latter tube is ground into
the horizontal branch which is somewhat constricted for that
purpose ; the cork is employed to give solidity and stiffness to
the juncture.   It is believed that by this means all the vapor
passes into the horizontal branch of the ⋃ tube where it is
directly exposed to the action of the entering current of air.

Necessarily, the outer branch of the ∐ tube has to project a little out of the water of the bath in order that the lead tube may pass over the side of the thermostat; hence, as the upper part and the lead tube are generally at lower temperature than the water of the bath, some condensation of the vapors occurs; the condensed vapor runs down the tube to collect at the bottom. In order to vaporize this liquid and cause it to pass over the glowing lime, it is necessary to pass a current of air through the tubes to complete the determination. In this operation, two sources of error may be encountered: First, when the connection between the absorption vessel and the ∐ tube is broken, some of the vapor with which the tubes are filled may diffuse out and be lost; and second, the vapor may be carried along too rapidly with the air to permit of its complete decomposition by the heated lime. There seems to be no simple means of avoiding slight loss of vapor; still, by careful manipulation and rapid operation, the loss may be rendered insensible.

My mode of operation was as follows: Holding between the thumb and first finger of my right hand the little stopper of the absorption vessel, and between the thumb and the first finger of my left hand the cork and tube to be fitted into the horizontal branch of the ∐ tube, I withdrew the cork, and at once inserted in the ∐ tube the cork and tube. The time that the ends of the pieces of apparatus were open was less than two seconds, so that the loss must have been minimal.

A circumstance which aids in the prevention of loss by diffusion is, that the heated lime tube causes a slight draft towards it when the ∐ tube is open. It is certainly legitimate to conclude that the error from this source is exceedingly slight.

In regard to the second source of error the greatest precautions must be taken to prevent its assuming disturbing proportions. As soon as the connection between the absorption vessel and the ∐ tube has been secured, the pinch-cock on the end of the rubber tubing (see page 633) is closed a* little so that air is drawn in a slow stream through the tubes at first, and faster afterwards (see page 634). The amount of error due to this source is best determined by special experiments in which a weighed quantity of a pure halogen compound is introduced

into the absorption vessel, a certain volume of air passed through it, all the usual precautions in determining a vapor·tension being observed, and a comparison made between the loss by vaporization and the amount of the compound calcu· lated from the quantity of halogen found in the lime ; naturally the loss should, in case no error of experimentation has occurred, be equal to the quantity of liquid corresponding to the halogen found by analysis.   Two experiments were carried out, one with carbon tetrachloride, and the other with chloroform.   The dif· ference between the weights and the liquids before and after the passing of the air was for chloroform 1.9014 grams, and for car· bon tetrachloride 2.0178 grams; the results of analysis gave the amount of chloroform to be 1.9022 grams and that of carbon tetrachloride 2.0167 grams.   As is seen, the differences between the two sets of results are not more than those due to the errors of analysis, and it seems that the error due to the analysis of the mixture of the vapors is very slight.

When an acid is in the mixture whose vapor·tension is being determined, the error attendant upon the determination of the amount vaporized cannot be more than that incurred in a titra· tion, since there is no chance for the acid to escape, so quickly and directly is it brought in contact with the absorbing alkaline liquor.   In a special experiment, the loss of acid from the absorption vessel was 0.2908 grams, while a titration of the solution of baryta gave as the amount of acid 0.2896 grams.

While the errors of the experimental method here described seem to be slight, there is an error that may have been commit· ted in the assumption which lies at the basis of our calculations; when the volume of a vaporized liquid is large in comparison with the total gaseous volume, it is very probable that the vapor cannot be likened even approximately to an ideal gas.   This point will be discussed in the following section.

6. COMPARISON OF THE VAPOR·TENSIONS OBTAINED BY THE
   METHOD HEREIN DESCRIBED AND THOSE OBTAINED BY
   OTHER METHODS.

Probably the best way to judge of the accuracy of the results

obtained in the determination of the vapor·tensions of liquids ac·
cording to the method described in this paper is to compare them
with the results obtained by other investigators working by other
methods.   Also a criterion of accuracy is to be found in the more
or less close concordance of duplicate experiments.   In the fol·
lowing table are given the necessary data of my experiments to·
gether with the results obtained by others.   It was in some cases
necessary to interpolate the results of others inasmuch as my re·
sults referred to a limited number of temperatures; the interpo·
lations were made on a large scale, so as to avoid any slight in·
accuracy.   The original papers of Young and Regnault I am now
unable to consult, and have to take their data as given in Landolt
and Börnsteins "Physikalisch·Chemische Tabellen" or other re·
productions.

TABLE II.[1]

Vapor Tensions of Pure Liquids.

Name of liquid.	Temperature.	Loss in grams.	Volume of loss in cc.	Volume of air in cc.	Internal pres·sure in mm.Hg.	Barometer in mm. Hg.	Tension of va·por in mm. Hg.	Tension ac·cording to other obser·vers.	
Benzene············	34.8°	1.3805	443.		1876	5	760	145.4	147.2	(Y)
Monochlorbenzene ··	34.8°	0.2291	5.1	1883	10	757	20.3	20.0	(Y)
Monobrombenzene ··	34.8°	0.1289	2.0	1888	10	757	8.0	8.0	(Y)
Toluene············	34.8°	0.2451	67.6	1014	11	754	46.8		
" ············	34.8°	0.4672	128.9	1949	11	754	46.7		
Metaxylene (not es· pecially purified)··	34.8°	0.1080	25.8	1201	17	757	4.17		
Metaxylene (not es· pecially purified···	34.8°	0.1085	25.9	1201	17	758	4.18		
Nitrobenzene········	34.8°	0.0090	1.85	1210	23	757	1.16		
" ········	34.8°	0.0088	1.83	1207	21	757	1.15		
Carbon tetrachloride·	34.8°	3.3803	5.55	1913	20	758	169.4	172.6	(R)
" "	27.8°	2.4031	3.96	1908	18	756	130.0	130.8	(R)
Chloroform ·········	35.0°	3.0320	64.48	1033	25	755	290.1	301.1	(R)
Ethyl iodide ········	34.8°	4.2091	683.	1913	20	756	199.0	206.0	(R)
" " ········	27.8°	2.9760	483.	1918	22	756	152.2	154.7	(R)
Carbon bisulphide···	20.0°	2.4541	777 4	1206	21	756	296.4	298.1	(R)
Methyl formate ·····	20.0°	5.1090	195.8	1196	16	756	469.4		
Acetic acid ·········	35.0°	0.2900	70.0	1960	20	760	26.3	26.5	(R&Y)

An inspection of the table shows a most excellent correspond·

[1] Bibliographical references to Table II : (Y)=Young ; Chem. Soc. 55, 486, *1889*. (R)= Regnault: Mémoires de l'Academie, 26, 239, *1862*.   (R & Y) = Ramsay & Young, Chem. Soc., 49, 790, *1886*.

ence between my determinations of vapor-tensions and those of others, when the liquid is but slightly volatile, as in the case of the halogen substitution products of benzene.   But when, at the temperature taken for a determination, the elastic force of the vapor exceeds one hundred mm. of mercury, the correspondence becomes less close; and it is at once seen from the data that the greater the volatility of a liquid, the greater the discrepancy. Let us take carbon tetrachloride and ethyl iodide for examples, since determinations of their vapor-tensions were carried out at two different temperatures.   For carbon tetrachloride the differ-ence between Regnault's results and mine is three and two-tenths mm. of mercury at 34.8° and eight-tenths mm. of mercury at 27.8°; for ethyl iodide, the difference at 34.8° is seven and one-tenths mm. of mercury, and at 27.8° one and ` five-tenths mm. of mercury.   Other examples point to the same result.

The cause of this want of concordance between my results and those made by other methods has been hinted at in the last par-agraph of the discussion of the errors to which this method is subject.   The assumption, made in the calculations, that the va-porous mixture may be treated as a mixture of ideal gases, can-not be maintained when the volume of the vaporized liquid forms more than a small fraction of the total volume of the gaseous mixture that leaves the absorption vessel.   The vapor of ethyl iodide that was carried off by the air, occupied more than a fourth of the to-tal volume, and the other volatile liquids also occupied relatively large volumes; the volumes of the vapors of the less volatile liquids, however, were but a small part of the volume of the air passed through the liquid.   And, as has been shown, the less volatile liquids give results perfectly concordant with those ob-tained by others.   Duplicate determinations of the vapor-tensions of some of the liquids, as toluene, nitrobenzene, etc., give almost identical results.

It would not be difficult to apply a correction taking into ac-count the greater volatility of some of the liquids.   This I have not, as yet, done, as in certain details I wish to alter the appa-ratus so as to obtain even more accurate results; thus the use of mercury as the liquid for expelling the air from the measuring

vessel would render the system of drying tubes unnecessary; also ground glass joints are undoubtedly preferable to rubber connections.   Although it is my intention to study and modify the apparatus further, I do not want to seem to "reserve" this subject of investigation; on the contrary I would be most glad to see the apparatus tried and tested by others.

Although the results obtained by the employment of this method do not have in the case of the more volatile liquids the same degree of accuracy attainable by other methods, still they are suited to the requirements of an investigation of the vapor-tensions of mixtures of liquids, since both liquids, if their vapor-tensions be not too different, are affected alike by any weaknesses in the method, and the phenomenon observed permits of the drawing of theoretic conclusions.   Yet I have been careful in the discussion of results to limit myself as much as possible to such as were of the same accuracy as results obtained by others; thus, my method can be counted upon to give results accurate to less than one mm. of mercury when the vapor-tension does not exceed 100 mm. of mercury, and to less than two mm. of mercury when the vapor-tension is less than 150 mm. of mercury; as can at once be seen by a comparison of the data due to Young (*loc. cit.*) and Regnault (*loc. cit.*) in the greater number of cases a closer correspondence than to within two mm. cannot be found. However, the conclusions which I draw from my experiments would still hold if the error in the determination were several times greater than that admitted above, inasmuch as it affects each liquid in the same way, so that, while it may affect the absolute accuracy, its relative effect is but slight.

7. CHOICE AND PURIFICATION OF LIQUIDS.

As stated previously, the liquids employed in the course of this investigation were those recognized to be strictly normal; and of those only such were chosen as can be gotten in a state of great purity.   The only associated liquid taken was acetic acid, whose degree of association as well as whose physical properties are to a certain extent known.

An associated liquid was investigated for the purpose of apply-

ing the regularities and "normalities" discovered in mixture of normal liquids to mixtures of a normal liquid with an associated liquid. Great pains were taken to purify the liquids in the highest possible degree, it being the testimony of all those who have occupied themselves with experimental work on the vapor-tensions of liquids that even very slight impurities have a remarkably disturbing effect upon the accuracy of results; this is especially the case in results obtained by the static method; in the method employed by me, the influence of a slight amount of impurity is not so marked; still, for all that, it has been thought best to employ such material as had been most thoroughly purified.

In order that the readers of this paper may judge for themselves the degree of purity of the liquids examined, a somewhat detailed account of the method of purification of each liquid is given together with a statement of certain characteristic physical properties of each. All of the liquids, it may be stated beforehand were bought as chemically pure from the dealers (Poulenc Frères, Paris, and Billault, Paris), and at least one pound—generally two or three pounds—subjected to the purifying operations.

Benzene.—Nearly three pounds of benzene—labelled chemically pure and free from thiophene—were treated a half dozen times with sulphuric acid to remove last traces of the sulphur compound. The liquid was then repeatedly fractionally crystallized until about a pound was obtained melting at $5.3°$. This purified product when partially solidified showed, no matter what the proportion of liquid and solid was, the same melting point. The whole was then distilled over a few pieces of sodium, no variation from the boiling point $80.1°$ under a pressure of 756 mm. of mercury being observed. Its specific gravity at $25°$ referred to water at the same temperature was found to be 0.876611.

Toluene.—Of the quantity of toluene taken for purification (about two pounds) more than four-fifths distilled at $109.8°$ to $110.1°$, an indication that the commercial article was nearly pure. After a couple of distillations over a little sodium, more than a pound was obtained boiling constantly at $110.1°$ under a pres-

sure of 758 mm. of mercury.   Its density at 25° referred to water at 25.0° was ascertained to be 0.86288.

Monochlorbenzene.—A couple of pounds of monochlorbenzene were repeatedly distilled in fractions until a constant boiling product resulted.   About three·quarters of a pound were obtained, boiling at 131.8° to 131.9° under a pressure of 757 mm. of mercury, and having a density at 25.0° (referred to water at same temperature) of 1.10362.

Monobrombenzene.—Nearly a pound of brombenzene was fractionally distilled until a distillate was obtained boiling between narrow limits.   About 150 grams of the product, boiling at 154.3° to 154.5° under a pressure of 761 mm. of mercury were obtained.   The density at 25° referred to water at 25.0° was 1.49852.

Nitrobenzene.—The commercial article was repeatedly crystallized until an almost colorless liquid was obtained, which when solidified, showed the same temperature during the remelting. It possessed a melting point of 3.6°, and its density was 1.20201, $\left(\dfrac{25°}{25°}\right)$.

Chloroform.—About two pounds of "chloroform anesthétique" of commerce were washed a dozen times with water, dried thoroughly by means of fused calcium chloride, and distilled.   The larger distillate boiled at 60.8° to 61.0° under a pressure of 751 mm. of mercury, and finally nearly a pound was obtained boiling at 60.9° under a pressure of 755 mm. of mercury.

Carbon Tetrachloride.—Two pounds were washed with water, and thoroughly dried by means of concentrated sulphuric acid. The product was then rectified, and nearly a pound boiling throughout the operation at 76.6° under a pressure of 756 mm. of mercury taken for the preparation of the mixtures.   The specific gravity of this product at 25.0° referred to water at the same temperature was 1.58828.

Acetic Acid.—Two pounds of glacial acetic acid were repeatedly fractionally crystallized until a portion melting at 16.7° was obtained.   The bottle containing it as well as the mixtures made

from it were kept under an air·tight bell·jar by the side of very strong sulphuric acid.

8. PREPARATION OF ·THE MIXTURES.

The mixtures were prepared by weighing out to a milligram on a balance turning with a tenth milligram the liquids in a flask ; the córked flask was tared, the less volatile liquid poured in and weighed, and then the more volatile. As from forty to one hundred grams of the mixture were weighed out, the composition of the liquid was thus known to a ten·thousandth at least. The mixtures were preserved in bottles or flasks fitted with the finest corks, and kept in a dry, cool, dark closet. As, almost invariably, the necessary vapor·tensions of a liquid were made immediately after its preparation, no change of concentration occurred even with the most volatile liquids employed.

In the case of some of the mixtures of benzene and carbon tetrachloride, the residues of the investigated mixtures were united, and the amount of chlorine in the resulting mixture determined according to Carius' method.

The mixtures of benzene or toluene with acetic acid had their concentration controlled by an analysis. Five to ten cc. of the mixture were carefully weighed out in a glass·stoppered flask, water was added, which took practically all the acetic acid from the benzene, and then standardized baryta water run in to point of neutralization. In no case did the analysis give results sensibly different from those calculated from the direct weighings.

9. EXPERIMENTAL RESULTS WITH MIXTURES OF NORMAL LIQUIDS.

In the following tables (III to X) are given those data of the experiments necessary for the calculation of the vapor-tensions. The superscriptions over each column of data render any preliminary mention here unnecessary. In some cases, the data have been represented graphically. (Figs. II. to IV.)
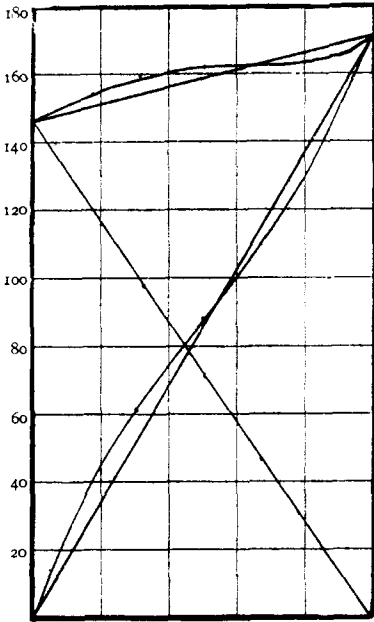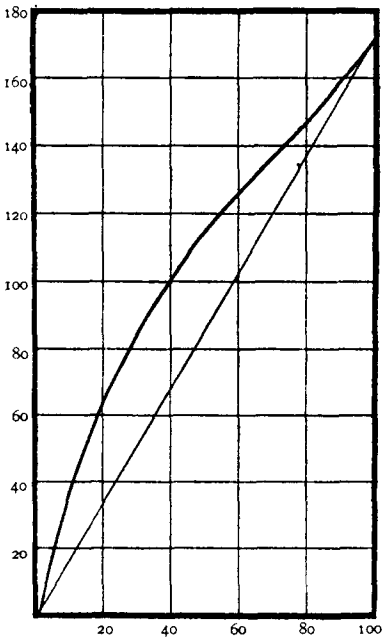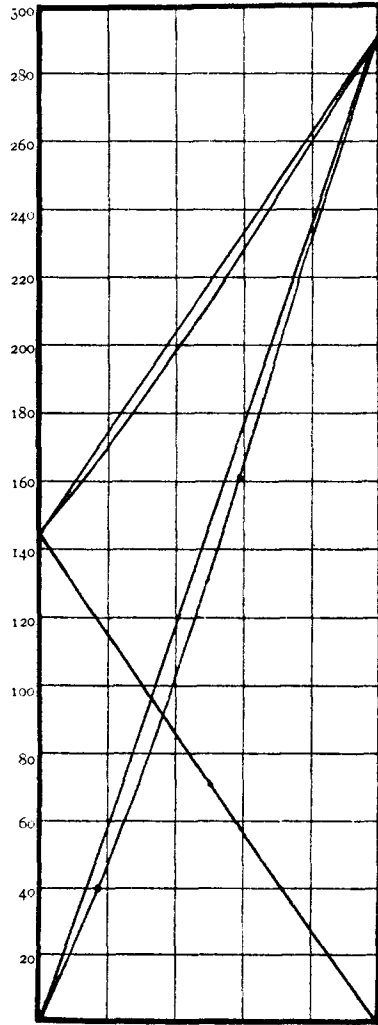
FIG. 2.

FIG. 3.

FIG. 4.

EXPLANATION OF FIGURES.

Fig. 2.—Vapor-tensions, total and partial, of mixtures of benzene and carbon tetrachloride.

Abscissas = molecules of CCl_4 in 100 molecules of mixture.

Ordinates = vapor-tensions in mm. of mercury.

Fig. 3.—Vapor-tensions, total and partial, of mixtures of benzene and carbon tetrachloride.

Abscissas = molecules of $CHCl_3$ in 100 molecules of mixture.

Ordinates = vapor-tensions in mm. of mercury.

Fig. 4.—Vapor-tensions of mixtures of nitrobenzene and carbon tetra-chloride.

Abscissas= molecules of CCl_4 in 100 molecules of mixture.

Ordinates = vapor-tensions in mm. of mercury.

TABLE III.

Vapor-Tensions of Mixtures of Benzene and Monochlorbenzene at 34.8°.
Vapor-Tension of Benzene at 34.8° is 145.4 mm. of Mercury.
Vapor-Tension of Chlorbenzene at 34.8° is 20.3 mm. of Mercury.

Molecules C_6H_5Cl in 100 molecules of liquid mixture.	Molecules C_6H_5Cl in 100 molecules of gaseous mixture.	Grams C_6H_5Cl in vapor.	Grams C_6H_6 in vapor.	Tension of C_6H_5Cl in mm.	Tension of C_6H_6 in mm.	Volume of air in mm.	Barometer in mm.	Internal pressure in mm.
15.18	1.33	0.0454	2.3075	1.7	124.6	3782	763	11
29.08	6.11	0.0857	0.9143	6.6	101.3	1900	757	17
65.06	19.37	0.1800	0.5202	12.3	51.3	2032	758	18
79.21	35.15	0.3572	0.4750	19.1	27.9	3787	756	12

TABLE IV.

Vapor-Tensions of Mixtures of Toluene and Monochlorbenzene at 34.8°.
Vapor-Tension of Toluene at 34.8° is 46.8 mm. of Mercury.
Vapor-Tension of Chlorbenzene at 34.8° is 20.3 mm. of Mercury.

Molecules C_6H_5Cl in 100 molecules of liquid mixture.	Molecules C_6H_5Cl in 100 molecules of gaseous mixture.	Grams C_6H_5Cl in vapor.	Grams C_7H_8 in vapor.	Tension of C_6H_5Cl in mm.	Tension of C_7H_8 in mm.	Volume of air in cc.	Barometer in mm.	Internal pressure in mm.
18.96	9.84	0.0510	0.3821	4.3	38.2	1963	757	17
41.82	22.66	0.0985	0.2754	8.1	27.6	1973	760	21
76.71	67.79	0.2089	0.0821	17.5	8.2	1965	757	18

TABLE V.

Vapor-Tensions of Mixtures of Benzene and Monobrombenzene at 34.8°
Vapor-Tension of Benzene as 34.8° is 145.4 mm. of Mercury.
Vapor-Tension of Brombenzene at 34.8° is 8.0 mm. of Mercury.

Molecules C_6H_5Br in 100 molecules of liquid mixture.	Molecules C_6H_5Br in 100 molecules of gaseous mixture.	Grams C_6H_5Br in vapor.	Grams C_6H_6 in vapor.	Tension of C_6H_5Br in mm.	Tension of C_6H_6 in mm.	Volume of air in cc.	Barometer in mm.	Internal pressure in mm.
30.33	24.30	0.0395	0.4975	2.6	103.1	1018	757	13

TABLE VI.

Vapor-Tensions of Mixtures of Benzene and Chloroform at 34.8 .
Vapor-Tension of Benzene at 34.8 is 145.4 mm. of Mercury.
Vapor-Tension of Chloroform at 34.8 is 289.2 mm. of Mercury.

Molecules $CHCl_3$ in 100 molecules of liquid mixture.	Molecules $CHCl_3$ in 100 molecules of gaseous mixture.	Grams $CHCl_3$ in vapor.	Grams C_6H_6 in vapor.	Tension of $CHCl_3$ in mm.	Tension of C_6H_6 in mm.	Volume of air in cc.	Barometer mm.	Internal pressure in mm.
16.97	24.30	0.3243	0.6607	39.6	123.5	1032	755	25
50.53	63.74	1.1513	0.4187	130.7	74.5	1030	756	25
59.47	73.25	1.4770	0.3531	162.2	59.2	1030	749	25

THE ELECTROLYTIC DETERMINATION OF RUTHENIUM.

BY EDGAR F. SMITH AND HARRY B. HARRIS.
Received April 22, 1895.

FROM time to time efforts have been made in this laboratory to gather information upon the deportment of the metals of the platinum group toward the electric current. Palladium, platinum, and rhodium have been determined quantitatively, and also separated electrolytically from other metals of the group, *e. g.*, palladium from iridium. The purpose of this communication is to present data relating to the electrolysis of ruthenium salt solutions. The literature of electrolysis does not contain any information upon this point.

The salt upon which the experiments were made was the double chloride of potassium and ruthenium. It was prepared by fusing the finely divided metal with potassium nitrate and hydroxide. This fusion was made in a silver crucible. The aqueous extract was acidified with hydrochloric acid, and the solution was then evaporated to crystallization. Much potassium chloride separated at first, but finally the double salt appeared in minute red-colored needles.

The platinum dish in which the electrolytic decomposition was carried out was coated upon its inner surface with a layer of copper. In the first trials the solution of the double salt was mixed with three grams of sodium acetate, and acted upon by a current of N. D.$_{100}$ = 0.01–0.05 ampere. The quantity of the ruthenium salt not being very abundant it was necessary to conduct the determinations with rather small amounts of material.