ON THE VAPOR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.

BY C. E. LINEBARGER.

[*Continued from page 652*]

TABLE VII.

Vapor-Tensions of Mixtures of Toluene and Chloroform at 34.8°.

Vapor-Tension of Toluene at 34.8° is 46.8 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_7H_8 in vapor.	Tension of $CHCl_3$ in mm.	Tension of C_7H_8 in mm.	Volume of air in cc.	Barometer in mm.	Internal pressure in mm.
28.74	65.29	0.4856	0.1994	64.7	34.4	1040	747	24
60.43	89.20	1.3578	0.1270	160.9	19.5	1031	754	23

TABLE VIII.

Vapor-Tensions of Mixtures of Benzene and Carbon Tetrachloride at 34.8°.

Vapor-Tension of Benzene at 34.8° is 145.4 mm. of Mercury.

Vapor-Tension of Carbon Tetrachloride at 34.8° is 169.4 mm. of Mercury.

Molecules CCl_4 in 100 molecules of liquid mixture.	Molecules CCl_4 in 100 molecules of gaseous mixture	Grams CCl_4 in vapor.	Grams C_6H_6 in vapor.	Tension of CCl_4 in mm	Tension of C_6H_6 in mm.	Volume of air in cc.	Barometer in mm.	Internal pressure in mm.
7.21	9.66	0.1741	0.8260	14.5	135.4	1205	762	18
18.68	20.54	0.3931	0.7561	32.5	125.5	1205	758	20
28.00	35.71	0.6267	0.5730	60.0	105.0	1016	756	12
50.19	55.03	1.1231	0.4666	91.3	75.6	1201	762	19
63.88	65.27	1.2699	0.3431	103.1	54.5	1219	760	27
77.89	83.01	1.5321	0.1669	117.6	31.8	1034	754	26

TABLE IX.

Vapor-Tensions of Mixtures of Toluene and Carbon Tetrachloride at 34.8°.

Vapor-Tension of Toluene at 34.8° is 46.8 mm. of Mercury.

Vapor-Tension of Carbon Tetrachloride at 34.8° is 169.4 mm. of Mercury.

Molecules CCl_4 in 100 molecules of liquid mixture.	Molecules CCl_4 in 100 molecules of gaseous mixture.	Grams CCl_4 in vapor.	Grams C_7H_8 in vapor.	Tension of CCl_4 in mm.	Tension of C_7H_8 in mm.	Volume of air in cc.	Barometer in mm.	Internal pressure in mm.
30.69	58.19	0.4754	1.2046	51.5	37.0	1016	756	12
53.85	67.86	0.9305	0.1260	78.3	22.3	1022	758	17
60.00	83.67	0.9624	0.1126	99.1	19.4	1020	759	14
91.87	97.22	1.6063	0.0281	155.1	4.5	1017	756	13

TABLE X.

Vapor-Tensions of Mixtures of Nitrobenzene and Carbon Tetrachloride at 34.8°.

Vapor-Tension of Nitrobenzene at 34.8° is 1.16 mm. of Mercury.

Vapor-Tension of Carbon Tetrachloride at 34.8° is 169.4 mm. of Mercury.

Molecules CCl_4 in 100 molecules of liquid mixture.	Molecules CCl_4 in 100 molecules of gaseous mixture.	Grams CCl_4 in vapor.	Grams $C_6H_5NO_2$ in vapor.	Tension of CCl_4 in mm.	Tension of $C_6H_5NO_2$ in mm.	Volume of air in cc.	Barometer in mm.	Internal pressure in mm.
5.37	93.51	0.3095	0.0175	18.9	1.3	1973	760	20
50.73	94.47	1.1111	0.0489	113.9	6.2	1020	756	12
73.54	96.09	1.4420	0.0471	141.5	5.6	1022	753	18
95.21	98.61	1.7798	0.0190	167.6	2.3	1022	753	18

10. INFLUENCE OF TEMPERATURE ON THE VAPOR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.

It is a well-known fact that the higher the temperature the greater the vapor-tension; this is true of mixtures of liquids as well as of the liquids themselves. It may be, now, that the vapor-tensions of mixtures of volatile liquids exhibit a deportment varying with the temperature; but if it can be shown that change of temperature is without influence upon the nature of the phenomenon presented by the vapor-tensions of such mixtures, the experimental investigation of the subject is much simplified, for theoretic conclusions based on data found at a certain temperature can be at once applied to other temperatures, so that the investigation of the vapor-tensions of mixtures of various concentrations at one temperature suffices for the discussion and elucidation of the entire problem. Material which furnishes an answer to the question as to whether temperature has an influence upon the vapor-tensions of mixtures of volatile liquids can be found in the papers of Regnault (*loc. cit.*), Raoult (*loc. cit.*), and Brown (*loc. cit.*).

Regnault's determinations were made through a considerable range of temperature, and, although, at most only three different concentrations were examined, it is possible by rearranging them to get an answer to our query. The mixtures which can be utilized are five in number,—two mixtures of carbon bisulphide and ethyl oxide, whose vapor-tensions were determined by the static method, and one mixture of the same liquids, the vapor-tension of which was determined by the dynamical method; and two mixtures of carbon bisulphide and carbon tetrachloride of which the vapor-tensions were investigated by the static method.

The first mixture of carbon bisulphide and ether was made up of sixty-two volumes of the first liquid and thirty-eight volumes of the second, ("Mélange de 62 sulphure de carbone et 38 d'éther, en volumes"), and eleven determinations of its vapor-tension were made in the temperature interval 4.72° to 39.44°. If we put the specific gravity of Regnault's carbon bisulphide at 1.27, and that of his ether at 0.78, the mixture contained by weight 27.35 per cent. of ether, and 72.65 per cent. of carbon bisulphide; or a hundred molecules of the mixture contained 27.20 molecules of ether and 72.80 molecules of carbon bisulphide. The second mixture was prepared by mixing fifty-six volumes of ether and forty-one volumes of carbon bisulphide ("Mélanges de 56 éther et de 41 sulphure de carbone en volumes"). Thirteen determinations were made of the vapor-tensions of this mixture at temperatures varying from 8.01° to 38.18°. One hundred parts by weight contained then 45.61 parts of ether and 54.39 parts of carbon bisulphide; and one hundred molecules of the mixture contains 46.29 molecules of ether and 53.71 molecules of carbon bisulphide.

The third mixture of carbon bisulphide and ether was made up of equal volumes of each; ("Mélange, a volume éguax, de sulphure de carbon et d'éther") about twenty-five measurements were made in the temperature interval from 20.81° to 121.48° The percentage composition of the mixture is 61.95 per cent. of carbon bisulphide and 38.05 per cent. of ether, and the molecular percentage composition is 61.32 molecules of carbon bisulphide and 38.68 molecules of ether.

The first mixture of carbon tetrachloride and carbon bisulphide contained equal volumes of the two liquids; ("Mélange de volumes égaux de chlorure de carbone et de sulphure de carbone") ten determinations of its vapor-tension were made at temperatures varying from 8.75° to 48.43°. If we put the specific gravity of Regnault's carbon tetrachloride as equal to 1.62, and that of his carbon bisulphide as equal to 1.27, the percentage composition by weight of the mixture is 56.06 per cent. of carbon tetrachloride and 43.94 per cent. of carbon bisulphide; and one hundred molecules of the mixture contain 61.2 molecules of the first-named liquid and 38.8 molecules of the last-named.

In indicating the composition of the second mixtures Regnault uses the following words: "Mélange de 60 parties sulphure de carbone et de 145 chlorure de carbone." There is doubt here as to whether Regnault means by "parties," parts by weight or by volume. This is the only place where this form of expression is used, and in the other cases, it is expressly stated that the units of measure are volumes. I take it, then, that in this case parts by weight are to be understood, and in the sequel it will be seen that the regularity of the data as represented graphically renders this understanding of the matter warranted. At any rate, the difference between the results of calculations with volumes or weights as bases is not very great, so that there is not much danger of committing any very gross error. By weight the percentage composition of this mixture is 70.73 per cent. of carbon tetrachloride and 29.27 per cent. of carbon bisulphide, while one hundred molecules of it contain 65.47 molecules of carbon tetrachloride and 34.53 molecules of carbon bisulphide. I give also the percentage molecular composition on the assumption that Regnault's "parties" means parts by volume; one hundred molecules of the mixture contain 54.47 molecules of carbon tetrachloride and 45.53 molecules of carbon bisulphide.

In order to transform Regnault's data, the following procedure was gone through with: In a system of coordinates with temperatures as abscissas and vapor-tensions as ordinates, his measurements were plotted on a large scale; as might be expected of any of Regnault's experimental work, the points fell very close to a regular curve. At points at this curve corresponding to 0°, 10°, 20°, 30°, etc., the value of the ordinates was carefully taken. that is, the vapor-tensions for each of the above temperatures. In this way data were obtained by means of which isothermal curves were drawn in a system of coordinates with concentrations as abcissas and vapor-tensions as ordinates.

An inspection of the isothermal curves shows that no appreciable influence of temperature manifests itself; the vapor-tension of the more volatile component of the mixture increases, indeed, more rapidly than that of the less volatile, but this does not affect the contour of the curve, its inclination alone being somewhat altered.

Raoult[1] made a special study of the possible influence of temperature upon the vapor-tensions of mixtures of ether with each of the following liquids almost nonvolatile at low temperatures: turpentine, aniline, perchlorethane, and benzoic acid, the temperature interval being from 0° to 22°. The results of his experiments permitted him to draw the definite conclusion that in the above temperature interval the vapor-tension is quite independent of the temperature.

The experiments of Brown[2] on the boiling-points of carbon bisulphide and carbon tetrachloride may be brought forward as evidence that the influence of the temperature on the vapor-tensions of mixtures of normal liquids is very slight; he found the curves, sketched with percentage composition on the axis of abscissas, and boiling-points on the axis of ordinates, for the pressures 747 to 760, and 430 to 432 mm. to be practically parallel.

From the above considerations, we may conclude that temperature has but a vanishing influence upon the vapor-tensions of mixtures of normal liquids; that is to say, although the higher the temperature, the greater the vapor-tension, the regularities found and the laws deduced from observations made at any one temperature are, without question, applicable to any other temperature, which, however, be it remarked as a caution, should probably not be too different from that of the observations.

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[1] *Loc. cit.*

[2] *Loc. cit.*

XI. RELATIONS BETWEEN THE VAPOR-TENSIONS, PARTIAL AND TOTAL, AND THE CONCENTRATION OF THE LIQUID PHASES.

We remark first, that the tension of the mixed vapor emitted by any of the mixtures of volatile liquids examined is always greater than the tension of the less volatile liquid and always less than that of the more volatile liquid; also, that the partial tension or pressure of either component, of any mixture, is always less than the vapor-tension of the component in a state of purity;[1] these two properties belong to all the mixtures investigated. In the discussion of the other properties, we shall find it convenient to divide the mixtures into classes. In the first class we put the mixtures of benzene and toluene with monochlor- and monobrombenzene; in the second, the mixtures of chloroform with benzene, and with toluene; in the third, the mixtures of carbon tetrachloride with toluene, and with benzene; and in the fourth and last, the mixture of nitrobenzene and carbon tetrachloride.

Now the mixtures of the first class are made up of liquids which are very similar in their chemical constitution, and it is natural to expect that they will exhibit the very simplest phenomena when mixed with one another. And, indeed, this expectation is realized, for the vapor-tensions of their mixtures are seen to be linear functions of the concentration: in the graphic representations (abscissas = molecular percentages; ordinates = vapor-tensions) of the determinations, these fall upon or very close to the straight lines connecting the points on the axes of ordinates corresponding to the vapor-tensions of each of the pure liquids. In order to find the vapor-tension of any mixture of these liquids, all that is necessary to do is to connect on the axis of ordinates, the points representing the vapor-tensions of the two liquids in a state of purity, by a straight line, and where the perpendicular to the axis of abscissas cuts this line, the value of the ordinate corresponding to the point of intersection gives

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[1] This observation does not seem to be confirmed in the case of the partial pressure of nitrobenzene in its mixture with carbon tetrachloride. This exception, however, I am inclined to attribute to experimental errors, which made themselves particularly felt in the investigation of mixtures of these two liquids. Indeed, if the allowance be made for the degree of accuracy which we have decided the method capable of yielding, it will be seen that the discrepancy can be made to disappear almost entirely.

the vapor-tension of the chosen concentration; of course, partial tensions can be found in a similar way. Also, by the application of the "rule of mixtures," it is easy to calculate the total or partial tensions. It may be worth while to remark, in passing, that these four liquids, which we have put in a class by themselves, are just those which verify by far the best the generalizations of van der Waals; undoubtedly, these liquids are to be reckoned as in the highest degree "normal," as their behavior approaches most nearly that theoretically predicted.

In the second of our classes we find a different behavior. When chloroform is added to benzene or to toluene, the total vapor tension is less than that resulting from the calculation by the rule of mixtures; the variation reaches a maximum when 100 molecules of the mixture contain from fifty to sixty molecules of chloroform; the curve then tends to approach the straight line connecting the points on the axis of ordinates representing the vapor-tensions of the pure liquids, practically coinciding with it when the number of chloroform molecules has passed eighty. The depression of the vapor-tension of chloroform, caused by the addition of either benzene or toluene, is linearly proportional to the concentration only in solutions containing less than twenty molecules of either hydrocarbon to 100 molecules of the mixture.

When we consider the partial tensions of these mixtures, we see that the same regularity as was observed in the first class of liquids is found here, but only for toluene and benzene; the partial tension curve for chloroform resembles closely in its contour that for the total tension of the mixture. The departure of chloroform from the straight line is not, however, very marked.

In the third class of mixtures, we meet with a different behavior. When benzene or toluene is added to carbon tetrachloride, we observe that the curve of total tension follows closely the line connecting the points corresponding to the vapor-tensions of the mixed liquids until towards the abscissas value of eighty; the curve then commences to fall, only to rise again, and pass above the straight line, when, finally, it changes its direction to fall upon the axis of ordinates at the point standing for the vapor-tension of the pure hydrocarbon, benzene, or toluene, as the case may be. As is seen, the curve has three turning points. The curve of the partial tension of the carbon tetrachloride resembles in every detail, in each mixture, that of the total tension; but once more it is observed that the partial pressure curve for the hydrocarbons is, so to say, a straight line. It is truly a remarkable result that in the mixtures which have such different total tension curves, the curve for these two liquids should turn out so simple. There is but little doubt that the above instances are sufficient to render very probable the assumption that this behavior is general, and that in all binary mixtures made up of benzene or toluene, with any other volatile liquid whatsoever, the same normality in the behavior as regards partial vapor-tension of these two hydrocarbons will be found. It is even possible to go a step farther, and claim that, inasmuch as in the mixtures of the first class, normality of the partial pressure was found in the case of each component of the mixture, this normality will persist in mixtures of the halogen compounds of benzene with any other liquids.

The fact that benzene and toluene possess "straight line" partial pressure curves will enable us to get reliable and important information as to the partial pressures of other liquids mixed with either of the hydrocarbons, from a knowledge of the total pressure of the mixtures; for all that is necessary to do is to draw, in the coordinate system adopted in this paper, the total pressure curve and a straight line from the point, representing, on the axis of ordinates, the vapor-tension of benzene at the temperature at which the determination has been made, to the foot of the opposite ordinate; the value of any ordinate comprised between these two curves gives, then, the partial pressure, to a very close approximation, of the other component of the mixture.

Furthermore, it is apparent that the partial tensions of either chloroform or carbon tetrachloride is the same when mixed in the same proportions with either benzene or toluene; the simplicity of the behavior of the latter liquids permits of the free exhibition of the peculiarities in that of the former.

The fourth class of mixtures, of which the only representative here is the mixture of nitrobenzene and carbon tetrachloride, does not, in reality, belong to our subject of investigation, which is to study mixtures of volatile liquids only, and not those of a volatile with an almost involatile one. Still it was thought advisable to find out what the partial tensions of mixtures of such liquids would be, inasmuch as Raoult[1] has made an elaborate study of the total vapor-tension of mixtures of ether and several almost non-volatile liquids. As is seen in the curve, the partial pressure of the carbon tetrachloride and the total pressure of the mixture are almost identical, just as would naturally be expected. The curves are, if we regard the right-hand ordinate first, at the beginning parallel with the straight line connecting the points representing the vapor-tensions of the pure liquids; they then turn upwards, reach a maximum distance from the straight line at about the abscissas value of fifty, and then gradually turn downwards towards the origin. I was curious to see if this behavior was characteristic of the mixtures of liquids investigated by Raoult.

Accordingly, I have recalculated his data so as to get them into a form comparable with mine. These recalculated data are given in the following small tables:

TABLE A.

Vapor-Tensions of Solutions of Turpentine in Ether at 16.2°.
Vapor-Tension of Turpentine at 16.2° is four mm. of Mercury.
Vapor-Tension of Ether at 16.2° is 377 mm. of Mercury.

Molecules of turpentine in 100 molecules of solution.	Vapor-tension in mm. of mercury.	Molecules of turpentine in 100 molecules of solutions.	Vapor-tension in mm. of mercury.
5.9	354	35.5	255
12.1	332	47.9	212
23.4	294	64.5	159

TABLE B.

Vapor-Tension of Solutions of Nitrobenzene in Ether at 16.0°.
Vapor-Tension of Nitrobenzene at 16.0° is four mm. of Mercury.
Vapor-Tension of Ether at 16.0° is 374 mm. of Mercury.

Molecules of nitrobenzene in 100 molecules of solution.	Vapor-tension in mm. of mercury.	Molecules of nitrobenzene in 100 molecules in solution.	Vapor-tension in mm. of mercury.
6.0	353	56.2	232
17.9	321	75.9	166
35.5	278	84.0	132

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[1] *Loc. cit.*

TABLE C.

Vapor-Tensions of Solutions of Aniline in Ether at 15.3°.
Vapor-Tension of Aniline at 15.3° is four mm. of Mercury.
Vapor-Tension of Ether at 15.3° is 364 mm. of Mercury.

Molecules of Aniline in 100 molecules of solution.	Vapor-tension in mm. of mercury.	Molecules of Aniline in 100 molecules of solution.	Vapor-tension in mm. of mercury.
3.8	349	20.5	292
7.7	335	49.6	210
14.8	308	68.7	147

TABLE D.

Vapor-Tension of Solutions of Methyl Salicylate in Ether at 14.2°.
Vapor-Tension of Methyl Salicylate at 14.2° is four mm. of Mercury.
Vapor-Tension of Ether at 14.2° is 306 mm. of Mercury.

Molecules of methyl salicylate in 100 molecules of solution.	Vapor-tension in mm. of mercury.	Molecules of methyl salicylate in 100 molecules of solution.	Vapor-tension in mm. of mercury.
1.1	344.6	23.2	281
2.1	343.6	49.0	208
4.8	332.0	77.0	125
9.2	316.0	85.0	101
15.1	301.0	....	....

TABLE E.

Vapor-Tensions of Solutions of Ethyl Benzoate in Ether at 11.7°.
Vapor-Tension of Ethyl Benzoate at 11.7° is three mm. of Mercury.
Vapor-Tension of Ether at 11.7° is 313 mm. of Mercury.

Molecules of ethyl benzoate in 100 molecules of solution.	Vapor-tension in mm. of mercury.	Molecules of ethyl benzoate in 100 molecules of solution.	Vapor-tension in mm. of mercury.
4.9	296	53.0	167
9.6	286	75.5	94
27.1	235	94.4	39

If these results be plotted in a system of coordinates, the curves will be found to have a close resemblance to the one which I have found for the mixture of nitrobenzene and carbon tetrachloride. It seems likely that this form of curve is the general one for the total tension of mixtures of a volatile with an almost fixed liquid.

XII. RELATIONS BETWEEN THE CONCENTRATIONS IN THE GASEOUS AND LIQUID PHASES.

The relations between the concentration in the gaseous and liquid phases is clearly shown by curves drawn in a system of coordinates, of which the axis of abscissas is taken for the representation of the molecular percentage composition of the liquid phase, and the axis of ordinates for that of the gaseous phase. In Fig. V are drawn these curves, the data being taken from the first two columns of tables.

As is seen, the curves prove to be very regular, and group themselves on either side of the diagonal of the square, according as the component chosen to increase from left to right in the diagram is more or less volatile than the other; as this was taken to be the component containing a halogen, the curve is below the straight line when the halogen-containing liquid is less volatile than the other, and above, when it is more volatile.

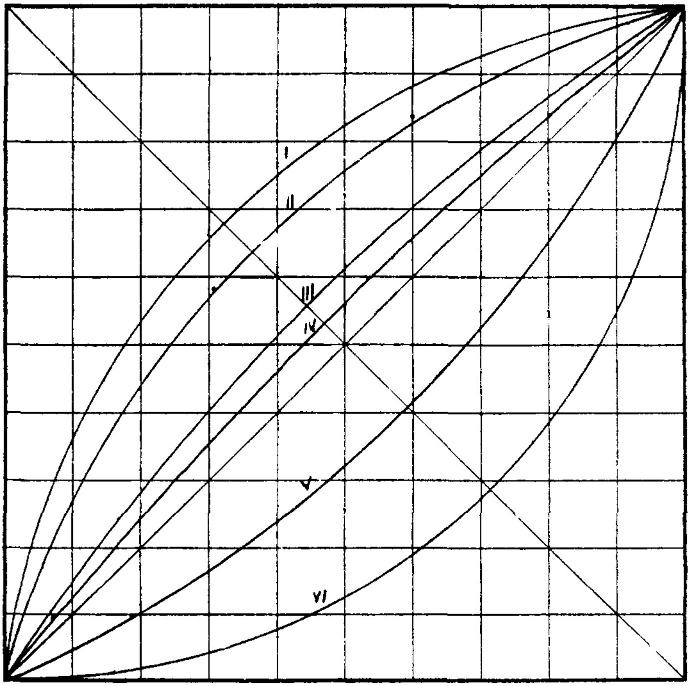

FIG. 5.—RELATIONS BETWEEN THE CONCENTRATIONS IN LIQUID AND GASEOUS PHASES.

Abscissas = molecules of one liquid in 100 molecules of mixture of liquids.
Ordinates = molecules of one vapor in 100 molecules of mixture of vapors.

Curve I	Toluene-chloroform.
" II	Toluene-carbon tetrachloride.
" III	Benzene-chloroform.
" IV	Benzene-carbon tetrachloride.
" V	Toluene-monochlorbenzene.
" VI	Benzene-monochlorbenzene.

Furthermore, the greater the difference in the volatility of the two liquids in the mixture the greater the curvature. It is very probable that mixtures of two normal liquids with the same vapor tension would give off vapors with identical composition in both liquid and gaseous state.

XIV. HEAT OF DILUTION AND SOLUTION. IDEAL CONCENTRATED SOLUTIONS.

Kirchoff[1] developed by thermodynamic considerations an equation showing a relation betweenthe heat of dilution of a solution and its vapor-tension. If we designate by dQ the heat brought into play when the small quantity dm of water is added to the solution, and if p' represent the vapor-tension of the solution and p that of the pure solvent, while T is the temperature and R the gas constant measured in units of heat, he found that

$$\text{(A)} \qquad \frac{dQ}{dm} = RT^2 \frac{k \log \frac{p'}{p}}{dT}$$

This equation was more particularly developed for the case of solutions of fixed substances, and has in fact been compared with the experiments done on the vapor-tensions and heat of dilution of sulphuric acid dissolved in water. Recently, however, three quite similar formulas have been obtained which apply directly to the heat given out or taken in when two liquids are mixed, and the corresponding changes of the elastic forces of the vapors. LeChatelier[2] developed for the case of a mixture of two liquids the formula

$$\text{(B)} \qquad n\frac{dp}{p} + n'\frac{dp'}{p'} - 500\,\frac{nL_1 + n'L_2 + \lambda}{T^2}\,dT = 0$$

wherein p and p' are vapor-tensions, L_1 and L_2 latent heats of vaporization, λ the heat disengaged on mixing $n + n'$ molecules of two liquids, and T is the temperature. As is readily seen, this formula is a special adaptation of Kirchoff's formula; in reality, they may be considered as expressing similar relations.

Nernst[3] by carrying out a closed cycle in the thermodynamic

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[1] Ueber einen Satz der Mechanischen Wärmetheorie und einige Anwendungen desselben : *Ann. der Phys. Pogg.*, 103, 177, *1885*.

[2] *Loc. cit.*, 281.

[3] Theor. Chem., 102-105.

sense of the term, in which semi-permeable membranes play a conspicuous rôle, has arrived at this equation :

$$\text{(C)} \qquad Q_{(x)} = -R\,T^2 \frac{d}{dT}\left(ln\,\frac{p_0}{p} + x\,ln\,\frac{P_0}{P} \right)$$

in which $Q_{(x)}$ is the heat of mixture,—equal to the decrease of the internal energy,— R and T have the same signification as in formula (A), p_0 and P_0 are the vapor-tensions of the pure liquids, and p and P the vapor-tensions at the moment of mixing, and x the number of molecules of one component to one molecule of the other. As is evident, this formula is quite similar to that of Kirchoff, which, Nernst claims, is but a special case of his more general one.

Duhem[1] has, by the application of the thermodynamic potential, which has proven so fruitful in his hands, developed the following formulas, each of which is applicable to the heat evolved or absorbed when to a solution of two liquids, certain masses of either liquid, δM_1 or δM_2 are added :

$$\text{(D)} \qquad EL_1 = \frac{4\Sigma R}{\alpha_1\ \omega_1}\,T^2\,\frac{d}{dT}\log\frac{p_1\,(x,\,T)}{P_1\,(T)},$$

$$\text{(D bis)} \qquad EL_2 = \frac{4\Sigma R}{\alpha_2\ \omega_2}\,T^2\,\frac{d}{dT}\log\frac{p_2\,(x,\,T)}{P_2\,(T)}\,;$$

in the formulas E is the mechanical equivalent of heat ; L_1 and L_2 heats of solution ; Σ the specific volume of hydrogen in normal conditions of temperature and pressure ; R a constant having the same value for all ideal gases ; α_1 and α_2 atomicities ; ω_1 and ω_2 molecular masses, T the temperature ; p_1 and p_2 the vapor-tensions of the solutions ; and P_1 and P_2 the vapor-tensions of pure liquids. It is at once apparent that this equation, if Duhem's complete, but rather prolix manner of writing be suitably transformed, is identical with the one developed by Kirchoff.

An important conclusion can be drawn from the above equations, in case the heat of solution turns out to be equal to zero ; then, $\frac{d}{dT}\log\frac{p'}{p}$ becomes equal to zero too, and the ratio $\frac{p'}{p}$ is independent of the temperature. That, in reality, to a very close

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[1] Dissolutions et Mélanges ; Troisième Mémoire ; Les Mélanges Doubles ; Travaux et Mémoires des Facultés de Lille, 100, *1894*.

approximation such is the condition of affairs for certain dilute solutions has been known since 1857; and such solutions are said to follow the law of von Babo,[1] which says that the heat of dilution must be zero.

Now we have found that the mixtures of the first class at least, that is, those made up of benzene, toluene, monochlor- and monobrombenzene, have vapor-tensions which are practically independent of the temperature, that is, the fraction $\frac{p'}{p}$ has the same value for all temperatures. It follows then that no thermal change should accompany the act of mixing of the liquids; their heat of solution of dilution is zero. No experiments so far as I know, which can give evidence as to the correctness of this statement, have been performed; but there can be no questioning of the truth of the relation developed and it is not at all probable that the determinations of the vapor-tensions are much in error.

In order to put this prevision of theory to the test of experience, I have made a number of determinations of the thermal effect of mixing liquids, especially those of the first class. Two methods were employed, that requiring the use of a Bunsen's ice-calorimeter, and that depending upon the measurement of the change of temperature.

The ice-calorimeter which was employed was of comparatively large size, the inner tube having an internal bore of twenty mm., and a length of 200 mm. within the outer tube. The calorimeter was filled, set up, and manipulated nearly as recommended by Schuler and Wartha, the amount of mercury absorbed or expelled being weighed.

After the calorimeter had been gotten into normal working condition, it was found that a continuous formation of ice was occurring around the inner tube. The amount was, however, not only slight, but also very constant, so that it was possible to apply an entirely reliable correction for it.

The cooling of the liquids to 0° and their subsequent mixing was accomplished in the following manner: A thin glass tube closed at one end and of such internal diameter as to permit of

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[1] Berichte über die Verhandlungen der Gesellschaft für Beforderung der Naturwisseuschaften au Freiburg in Brisgau. January. 1 57, 282.

its being easily but snugly slipped into the inner tube of the calorimeter was of such length that about an inch of it projected out of the calorimeter. A cylindrical pipette, fitting easily into the glass tube just described, had its lower orifice directly below the bulb, and was closed by means of a glass rod running axially up through the pipette and ground accurately into the orifice; a bit of rubber tubing was slipped over the glass rod, which could be pushed down between the rod and the stem of the pipette, thus closing the latter above. The pipette was held in place in the tube by means of a tightly fitting cork.

A piece of aluminum foil was for about two-thirds of its length cut into in several places along each side nearly to the middle, and the parts thus formed were so bent that, when the other third of the foil was rolled into cylindrical shape and slipped over the lower part of the bulb of the pipette, where it was held by its own elasticity, they formed a number of small paddles, those on one side directed upwards, those on the other directed downwards. Such a stirrer permits of a rapid and complete mixing of liquids.

To make a determination, a certain amount of one liquid is introduced into the pipette and weighed therein. The other liquid is weighed in the tube which is provided provisionally with a cork. The aluminum stirring contrivance is then slipped over the bulb of the pipette, and the latter passed into the tube, being held in place by a tightly fitting cork; the pipette is not pushed deep enough into the tube to have its orifice dip in the mixture of liquids, and the paddles reach to the bottom of the tube. A weighed dish of mercury is allowed to catch the expelled mercury of the empty calorimeter for exactly half an hour before the liquids are introduced; by this means the calorimeter correction just before the determination is obtained. After the introduction of the tube and pipette, the calorimeter is allowed for a half hour or so to get again into its normal state. After this has come to pass, a fresh dish of mercury is put under the mercury tube, the cork holding the pipette is lifted, the glass rod is raised a little, and the liquid in the pipette allowed to run out. The pipette is then tightly closed, and twisted around for a half minute or so to thoroughly mix the two liquids. The cork is again inserted in the tube, and the whole left for exactly half an hour. At the expiration of that time, the mercury vessels are changed, and the calorimeter left to itself for another half hour, when the mercury vessels are again changed, and the tube and pipette removed. The pipette is again weighed, and the difference between the two weights gives the amount of liquid. The amount of mercury expelled from the apparatus during the last half hour should, if the thermal equilibrium, disturbed by the heat evolved or absorbed by the mixture of the liquids, has reestablished itself, and if no change in the velocity of the freezing of the water itself has supervened, be equal to the amount expelled in the first half hour; in other words, the corrections in each case should be equal. This I found to be invariably the case. The heat effect of the mixing of the liquids is accordingly to be obtained from the excess or deficit of the amount of mercury expelled or absorbed in the next to the last half hour compared with that expelled during the first and the last half hours. This difference divided by 0.01544 gives the number of lesser calories measuring the heat effect of the mixing of the liquids.

By a most scrupulous attention to details in manipulation and to observance of time, as well as to care in weighing, I think that the determinations are exact to one-tenth calorie, and even to less than that.

I give in the following experiments the data obtained in the determination of the thermal effect of mixing such liquids as have been found in the foregoing pages to show the simplest behavior, and have hence been grouped into the first class. The negative sign before a datum is indicative of an absorption of heat, and consequent formation of ice and expulsion of mercury, while the positive sign indicates an evolution of heat etc.

Experiment 1.—Heat effect of mixing chlorbenzene and toluene:

Chlorbenzene	3.0028	grams.
Toluene	4.3032	"
Calorimeter correction in weight of mercury	—0.0013	"
Weight of mercury moved	—0.0018	"
" " " " due to mixing of liquids	—0.0005	"
Thermal effect measured in lesser calories	—0.032	"

Experiment 2.—Heat effect of mixing chlorbenzene and toluene:

Chlorbenzene	3.7715	grams.
Toluene	4.2190	"
Calorimeter correction in weight of mercury	—0.0014	"
Weight of mercury moved	—0.0020	"
" " " " due to mixing of liquids	—0.0006	"
Thermal effect measured in lesser calories	—0.033	"

Experiment 3.—Heat effect of mixing brombenzene and toluene:

Brombenzene	4.9530	grams.
Toluene	4.3680	"
Calorimeter correction in weight of mercury	—0.0009	"
Weight of mercury moved	—0.0020	"
" " " " due to mixing of liquids	—0.0011	"
Thermal effect measured in lesser calories	—0.072	"

Experiment 4.—Heat effect of mixing brombenzene and toluene:

Brombenzene	1.1611	grams.
Toluene	7.3887	"
Calorimeter correction in weight of mercury	—0.0010	"
Weight of mercury moved	—0.0005	"
" " " " due to mixing of liquids	+0.0005	"
Thermal effect measured in lesser calories	+0.032	"

Inasmuch as benzene solidifies at a temperature somewhat above that of melting ice, was not possible to carry out determinations in the ice-calorimeter with it in the pure state; accordingly I prepared a mixture containing 97.37 per cent. benzene and 2.63 per cent. chlorbenzene, which was used in experiment five.

Experiment 5.—Heat effect of mixing benzene and chlorbenzene:

Mixture of benzene and chlorbenzene	3.0208	grams.
Chlorbenzene	6.3470	"
Calorimeter correction in weight of mercury	—0.0013	"
Weight of mercury moved	—0.0030	"
" " " " due to mixing of liquids	—0.0017	"
Thermal effect measured in lesser calories	—0.101	"

An inspection of the above data shows that none of the heat effects is much above the limit of accuracy of which the method was judged capable. It was deemed worth while, however, to make some determinations of the heat effects brought about by mixing liquids by means of thermometric measurements, especially for mixtures of benzene and other liquids, as benzene in the pure state could not be used in the ice-calorimeter. The apparatus used, although simple, is capable of telling with considerable accuracy whether there occurs a change in temperature when two liquids are mixed. It consisted of a large U tube, in one branch of which was fitted a thermometer graduated in hundredths of a degree, such as described by Beckmann,[1] and recommended for cryoscopic and ebullioscopic work, and in the other a pipette similar to the one described above in connection with the ice-calorimeter. The U tube had a very narrow side tube towards the top of one branch, which when stopped with cotton wool permitted the egress of air without any evaporation of the liquids in the large tube to speak of. The stirrer employed was similar to the one used with the pipette in the ice-calorimeter.

A weighed quantity of one liquid was put into the U tube, and a quantity of the other liquid was weighed in the pipette. The thermometer and pipette were put in the tube tightly by means of good corks, the whole apparatus supported on a retort stand, and wrapped snugly with a thick layer of cotton wool. The apparatus was then set in a room the temperature of which could be easily kept within twenty-five to thirty degrees C. for several hours. By working at this rather high temperature, the disturbing effect due to the proximity of the person of the operator was considerably lessened. When the apparatus had remained in the room for a couple of hours, the thermometer was read off at intervals of a minute for ten minutes, the contents of the pipette made to flow into the U tube, the two liquids were mixed as rapidly as possible by a twirling and up and down motion of the pipette, around which was clasped the aluminum stirrer, and then the temperature was read off at each minute for ten minutes longer. The pipette was then again weighed so as to get the actual amount of the liquid discharged by it, since it never occurred that it emptied itself completely.

The experiments carried out by means of this thermochemical apparatus limit themselves to mixtures of benzene with monochlorbenzene and with chloroform. They, together with those

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[1] *Ztschr. phys. Chem.*, **2**, 644. *1888.*

carried out with the ice-calorimeter, are perhaps sufficient to serve as experimental corroboration of the theoretical relations between heat of solution and vapor-tension.

It is perhaps best to append the whole series of determinations in order that the reader may judge for himself of the accuracy of the results.

Change of Temperature on Mixing Four Grams Monochlorbenzene and 26.524 Grams Benzene.

Before mixing.		After mixing.	
Minutes.	Thermometer readings.	Minutes.	Thermometer readings.
1	2.242°	11	2.339°
2	2.258°	12	2.348°
3	2.272°	13	2.369°
4	2.291°	14	2.381°
5	2.307°	15	2.388°
6	2.318°	16	2.390°
7	2.330°	17	2.396°
8	2.344°	18	2.394°
9	2.352°	19	2.388°
10	2.365°	20	2.380°

Change of Temperature on Mixing 6.55 Grams Monochlorbenzene and 17.54 Grams Benzene.

Before mixing.		After mixing.	
Minutes.	Thermometer readings.	Minutes.	Thermometer readings.
1	2.591°	11	2.709°
2	2.603°	12	2.751°
3	2.618°	13	2.803°
4	2.622°	14	2.820°
5	2.630°	15	2.829°
6	2.638°	16	2.838°
7	2.641°	17	2.847°
8	2.649°	18	2.853°
9	2.651°	19	2.861°
10	2.655°	20	2.872°

Change of Temperature on Mixing 10.86 Grams Monochlorbenzene and 7.31 Grams Benzene.

Before mixing.		After mixing.	
Minutes.	Thermometer readings.	Minutes.	Thermometer readings.
1	1.830°	11	1.421°
2	1.803°	12	1.400°
3	1.790°	13	1.395°
4	1.775°	14	1.372°
5	1.762°	15	1.370°
6	1.760°	16	1.420°
7	1.761°	17	1.435°
8	1.733°	18	1.450°
9	1.710°	19	1.445°
10	1.691°	20	1.438°

CHANGE OF TEMPERATURE ON MIXING 12.81 GRAMS CHLOROFORM AND 11.87 GRAMS BENZENE.

Before mixing.		After mixing.	
Minutes.	Thermometer readings.	Minutes.	Thermometer readings.
1	1.489°	11	3.316°
2	1.520°	12	3.348°
3	1.531°	13	3.321°
4	1.540°	14	3.280°
5	1.561°	15	3.262°
6	1.573°	16	3.236°
7	1.582°	17	3.186°
8	1.608°	18	3.160°
9	1.621°	19	3.138°
10	1.632°	20	3.132°

It is apparent from these results that the change of temperature when benzene and monochlorbenzene are mixed does not exceed but a few hundreths of a degree, and even when the relative amounts of the liquids are about the same the change is in one case positive, in another negative, so that it is perhaps legitimate to judge that the change of temperature is largely due to the probability that the two liquids are at slightly different temperatures to begin with, and that in reality no or but an exceedingly slight heat effect occurs when these two liquids are mixed.

In the mixing of benzene and chloroform, however, there is a considerable rise of temperature, as indeed might be expected, since mixtures of chloroform and benzene do not in their vapor-tensions present the simplest phenomena. I have experimented with several other mixtures of liquids not belonging to the first class, especially with the ice-calorimetric method, and have found that they present certain abnormalities, some absorbing heat, and some evolving heat; these determinations, together with certain theoretical considerations, will form the substance of a subsequent paper.

Considering the above experiments as a whole, we may conclude that they are in entire corroboration of the formulas (A), (B), (C), and (D).

Nernst[1] found by the comparison of the theoretical conclusions with certain experimental data that the maximum of work, ob-

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[1] Ueber die mit der Vermischung Konzentrirter Lösungen verbundene Aenderung der freien Energie: Sonderabdruck aus Nr. 12 der Nachrichten von de Königlichen gesellschaft der Wissenschaften zu Göttingen. v. J.. 1892.

tainable by mixing two concentrated solutions with the same solvent, is "often" equal to the concurrent thermal change.

He then proposes to call "a homogeneous mixture of two substances, of which the maximum of work which can be obtained by a change of its composition, is measured by the concomitant thermal phenomena," an "ideal concentrated solution."

The contrast between "ideal dilute solutions" and "ideal concentrated solutions" is best shown by a consideration of the equation which rules over all Nature's happenings: this, according to Helmholtz,[1] is

$$F - Q = T \frac{\delta F}{\delta T}$$

wherein F represents the decrease in the "free energy" (freie Energie); Q that of the "total energy" (Gesamtenergie), and T the initial and final temperature, assumed to be the same in the operation under consideration. The characteristic of the "ideal dilute solutions" is that $Q = 0$ and that of the "ideal concentrated solutions" is that $F = Q$.

My object in mentioning these acute distinctions by Nernst is to call attention to the fact that there are certain combinations of substances (liquids) which, when mixed, develop no or very little heat, no matter what the relative proportions may be; that is, there exist "ideal dilute solutions" which may have any composition whatsoever, or, in other words, concentrated solutions may often follow the laws supposed to belong exclusively to dilute solutions. It is questionable, then, whether the notion of "ideal concentrated solutions" is necessary in science.

15. VAPOR-TENSIONS OF MIXTURES OF ACETIC ACID WITH BENZENE AND WITH TOLUENE.

Two series of determinations were carried out on the mixtures of benzene and acetic acid, one at 35° and one at 20°, but one, however, for the mixtures of toluene and acetic acid, at 35°. In order to apply to the experimental results of the work, our mode of calculation of the vapor-tensions, it is necessary to know the molecular mass of gaseous acetic acid at the above two temperatures. Now acetic acid even in the vaporous condition is

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[1] Zur Thermodynamik chemischer Vorgange. Sitzungs-Berichte der Berliner Akedemie, 22, *1882*.

made up in part of polymerized molecules, so that it is not legitimate to set its molecular mass equal to that corresponding to the formula $C_2H_4O_2$. What the actual molecular mass of the gaseous acid at 35° and 20° is, can be easily calculated by the aid of the vapor-density determinations of Bineau[1] which are the more applicable to the case in hand as his vapor-density measurements were made under the same conditions as my vapor-tension determinations ; that is to say, Bineau measured the amount of acetic acid that diffused into a definite volume of air at a fixed temperature. The molecular mass of acetic acid as deduced from Bineau's observations, is 104 for 35° and 110 for 20°. It may be worth while to remark that an error of five in the molecular mass will not entail an error of one millimeter in the vapor-tension : we may with all confidence then adopt the above molecular masses of acetic acid in state of vapor as quite accurate.

The necessary data of the experiments are given in tables XI to XIII, the superscription to each vertical column renders any explanation of them here superfluous.

TABLE XI.

Vapor-Tensions of Mixtures of Benzene and Acetic Acid at 35°.
Vapor-Tension of Benzene at 35° is 146 mm. of Mercury.
Vapor-Tension of Acetic Acid at 35° is 26.5 mm. of Mercury.

Per cent. of $C_2H_4O_2$ in liquid mixture.	Per cent of $C_2H_4O_2$ in gaseous mixture.	Grams $C_2H_4O_2$ in vapor.	Grams C_6H_6 in vapor.	Tension of $C_2H_4O_2$ in mm.	Tension of C_6H_6 in mm.	Volume of air in mm.	Barometer in mm.	Internal pressure in mm.
6.44	2.45	0.0461	1.3759	3.5	140.0	1955	758	14
15.17	4.74	0.0834	1.3580	6.4	129.2	1958	758	15
37.10	8.25	0.0700	1.5840	10.5	117.0	1020	767	16
43.99	11.02	0.0867	0.5243	13.2	106.5	1019	766	16
49.86	12.26	0.0931	0.4849	14.0	103.1	1020	766	17
53.24	13.33	0.0969	0.4731	14.9	97.6	1020	766	17
54.65	13.82	0.0990	0.4630	15.3	97.3	1020	766	17
56.60	14.62	0.1063	0.4677	16.4	96.0	1020	766	17
73.87	20.18	0.1156	0.4585	18.4	72.7	1019	766	16
80.00	26.91	0.1351	0.2751	22.3	59.3	1020	766	17

TABLE XII.

Vapor-Tensions of Mixtures of Benzene and Acetic Acid at 20°.
Vapor-Tension of Benzene at 20° is 75.6 mm. of Mercury.
Vapor-Tension of Acetic Acid at 20° is 11.7 mm. of Mercury.

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[1] Recherches sur les Relations des Densités des Vapeur avec les Équivalent Chimiques : *Ann. chim. phys.*, 18, 226, *1846*.

Per cent. of $C_2H_4O_2$ in liquid mixture.	Per cent. of $C_2H_4O_2$ in gaseous mixture.	Grams $C_2H_4O_2$ in vapor.	Grams C_6H_6 in vapor.	Tension of $C_2H_4O_2$ in mm.	Tension of C_6H_6 in mm.	Volume of air in cc.	Barometer in mm.	Internal pressure in mm.
53.24	11.99	0.0440	0.2291	6.6	48.7	1018	760	16
80.00	21.97	0.0576	0.2100	9.1	33.0	1018	760	16
97.28	64.66	0.0674	0.0276	11.4	6.2	1018	760	16

TABLE XIII.

Vapor-Tensions of Mixtures of Toluene and Acetic Acid at 35°.

Vapor-Tension of Toluene at 35° is 47.2 mm. of Mercury.

Vapor-Tension of Acetic Acid at 35° is 26.5 mm. of Mercury.

Per cent. of $C_2H_4O_2$ in liquid mixture.	Per cent. of $C_2H_4O_2$ in gaseous mixture.	Grams $C_2H_4O_2$ in vapor.	Grams C_7H_8 in vapor.	Tension of $C_2H_4O_2$ in mm.	Tension of C_7H_8 in mm.	Volume of air in cc.	Barometer in mm.	Internal pressure in mm.
49.00	32.66	0.0911	0.1661	15.0	31.8	1020	760	18
60.88	37.91	0.1025	0.1485	17.4	28.5	1020	760	18
83.37	56.36	0.1252	0.0858	22.2	16.7	1020	760	18

From the above data curves were constructed on a large scale with percentages of composition as abscissas and vapor-tensions as ordinates (one inch on the axis of abscissas corresponded to five per cent.: one inch on axis of ordinates to ten mm. of pressure); these proved to be perfectly regular, and passed directly through most of the points.

The points for acetic acid either fell upon or very close to the straight line connecting the left hand origin of the coordinate system with the point on the right hand axis of ordinates corresponding to the value of the vapor-tension of pure acetic acid at the temperature in question, *viz.*: 26.5 for 35°, and 11.7 for 20°, the acetic acid vapor-tension curve is simply a straight line, then, when the composition is expressed in percentages. An interesting conclusion to be drawn from this fact is that the partial tension of acetic acid is the same, be it mixed with benzene or with toluene: the specific influence of the diluting liquid seems to be extremely slight; if, indeed, there is any at all. This circumstance also indicates that the molecular condition of the acid is the same when it is dissolved in either of the hydrocarbons so as to form solutions of the same strength; this insight into the molecular structure of acetic acid enables us to determine by a little calculation its molecular mass not only in the dissolved but also in the pure state. In the following section will be set forth the *modus operandi.*

From the curves drawn as just described above, the partial pressures of the various constituents of the mixtures were taken for concentrations corresponding to ten, twenty, thirty, …… ninety per cent. of acetic acid; the data thus obtained are given in Table XIV.

TABLE XIV.

Partial Pressures of Benzene, Acetic Acid, and Toluene.

Per cent. of $C_2H_4O_2$ in liquid mixture.	Partial pressure of C_6H_6 at 35° in mm.	Partial pressure of $C_2H_4O_2$ at 35° in mm.	Partial pressure of C_7H_8 at 35° in mm.	Partial pressure of C_6H_6 at 20° in mm.	Partial pressure of $C_2H_4O_2$ at 20° in mm.
10	138.4	2.8	44.5	71.4	1.2
20	130.9	5.6	41.6	67.5	2.3
30	122.2	8.2	38.6	63.1	3.5
40	112.6	11.1	35.0	58.2	4.8
50	102.4	13.6	31.9	53.2	6.0
60	90.7	16.2	27.8	47.1	7.2
70	76.7	19.1	23.1	40.1	8.4
80	59.1	21.7	18.4	31.1	9.6
90	35.1	24.2	11.1	18.5	10.7

16. THE MOLECULAR MASS OF LIQUID ACETIC ACID AND A GENERAL METHOD OF DETERMINING MOLECULAR MASSES OF LIQUIDS.

The data given in the preceding section on the vapor-tensions of mixtures of acetic acid and benzene, taken in connection with the fact that the partial tension of benzene in its solutions is directly proportional to its concentration, permit of determining the molecular mass of the acid when diluted to any degree whatsoever with the hydrocarbon; and this special case may be generalized so as to permit of universal application. Furthermore, if the molecular mass of a substance be known in solutions of every degree of concentration, it is possible by a little extrapolation to pass over to the molecular mass of the pure liquid. It is, of course, assumed in making such an extrapolation that no break occurs in the continuity of the phenomenon, that is, the addition of very small quantities of a normal liquid to an associated one occasions correspondingly small changes in the degree of complexity of the molecules of the latter.

The way in which I have gone about to get at the molecular mass of acetic acid in benzene and toluene solution is as follows:

In a system of coordinates, molecular masses of acetic acid from 0 to 100 were laid off on the axis of abscissas (twenty inches long), and on the axis of ordinates, the vapor-tensions were taken from 0 to 150 mm. of mercury (fifteen inches long). A straight line was drawn from the point 100 on the axis of abscissas and 0 on the right-hand axis of ordinates to the point 0 on the axis of abscissas and 146 (benzene at 35°), 75.6 (benzene at 20°), and 47.2 (toluene at 35°). Upon this straight line must lie all the points corresponding to the partial tensions of benzene or toluene dissolved in acetic acid. So points were marked along it giving the value of the partial tensions of benzene and toluene in solutions containing ten, twenty, thirty, etc., per cent. of acetic acid, the data being taken from table XIV.

The value of the abscissas which these points determine give the number of molecules of acetic acid contained in 100 molecules of the mixture. All that has to be done now is to solve for every case this problem: Given a mixture containing m parts of a liquid A, having a molecular mass z, and n parts of a liquid B, having a molecular mass y; the mixture is made up of r molecules of A, and s molecules of B. What is the value of x in the terms of y, m, n, r, and s?

In the case before us, we will take acetic acid for the liquid A, and benzene, or toluene as the case may be, for B; then n is equal to $(100-m)$, and s to $(100-r)$.

It is easily found that the solution of our problem is

$$x = \frac{m\,s\,y}{r\,n} \text{ or } x = \frac{m\,(100-r)\,y}{(100-m)\,r}.$$

In the accompanying tables, XV, XVI, and XVII, the values of m, r, and x, are given.

TABLE XV.

Molecular Mass of Acetic Acid dissolved in Benzene at 35°.

Percent. $C_2H_4O_2$ in liquid mixture.	Molecules $C_2H_4O_2$ in 100 molecules of liquid mixture.	Molecular mass of acetic acid.
10	5.2	158
20	10.6	164
30	16.6	167
40	23.1	173
50	30.0	182
60	37.7	193
70	47.2	203
80	59.3	213
90	75.6	227
100	100.0	240

TABLE XVI.

Molecular Mass of Acetic Acid dissolved in Benzene at 20°

10	5.1	161
20	10.5	166
30	16.2	172
40	22.6	177
50	29.6	186
60	37.2	198
70	46.7	208
80	58.7	218
90	75.2	231
100	100.0	244

TABLE XVII.

Molecular Mass of Acetic Acid dissolved in Toluene at 35°.

Per cent. of $C_2H_4O_2$ in liquid mixture.	Molecules $C_2H_4O_2$ in 100 molecules of liquid mixture.	Molecular mass of acetic acid.
10	6.1	159
20	12.4	163
30	19.0	168
40	26.5	170
50	32.8	188
60	41.3	196
70	51.2	204
80	61.1	213
90	78.4	228
100	100.0	240

Considering tables XV and XVII first, we see that the values of x are approximately the same, the molecular mass of the acid becoming less and less as it is more and more diluted with benzene or toluene. It is remarkable that these two series of values for x fall out so nearly the same, for in the mixture of toluene and acetic acid, the differences of their vapor-tensions is so slight that the line of partial pressures of toluene is nearly horizontal, and an error of one millimeter in the determination of the partial pressure may occasion an error of four units in the molecular concentration; in the mixture of benzene and acid, however, the error arising from this source is not more than three-tenths of a unit, the angle made by the line of partial pressures being considerably greater than in the case of the other mixture.

For the determinations carried out at 20° on the mixture of benzene and acetic acid, it is seen that the number of molecules of acid is less, and hence their molecular mass is greater, than when the determinations were carried out at 35°. This is just what is to be expected for the lowering of temperature has been found to be invariably accompanied by an increase in the condensation of the molecule.

I have sketched the curves corresponding to the values of m and x given in the foregoing tables. in a system of coordinates with percentage composition as axis of abscissas and molecular masses as axis of ordinates.

The curves for the mixture of acetic acid and benzene at 35° practically coincides with that of the mixture of acetic acid and toluene at 35°, while the curve for the mixture of benzene and acetic acid at 20° is parallel and slightly above the other two. The curves are perfectly regular in form, and if prolonged to cut the right-hand axis of ordinates cannot give values varying by more than one unit; accordingly it may be claimed that the point where the axis of ordinates is cut by the extrapolated curve gives to about one unit the molecular mass of acetic acid in the liquid state at the temperature taken for the determinations. The results of my extrapolations gives as the molecular mass of liquid acetic acid at 35°, 240, and, at 20°, 244.

It is interesting to compare these results with those obtained by Ramsay and Shields.[1] These investigators found by the determination of the superficial tension of acetic acid that its molecular mass between the temperature limits, 16° and 46°, was equal to 217.2 (60×3.62); although this result leaves room for considerable uncertainty as to what the molecular mass of the acid is at any given temperature between these limits, it is in corroboration of my results; for, as has been well established, the degree of association in the molecules of a complex liquid is greater the lower the temperature, and my results pertain to temperatures which are lower or about the same as the mean of the two extreme temperatures given by the two English chemists.

The method of determining the molecular masses of liquids described in this section is the only one as yet devised, which permits of the determination at any given temperature of the mass of the molecule.

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[1] Ueber die Molekulargewichte der Flüssigkeiten. *Ztschr. phys. Chem.*, 12, 470, *1893*.

It is founded on empirical results and depends upon no hypothesis other than the universally recognized one of Avogadro. It is applicable to all cases where the substances under examination can be accurately analyzed. It calls for no special apparatus, even a modest laboratory being provided with the necessary pieces. It requires no great amount of manipulative skill, and the results are obtained in relatively short time. I hope that it will be rigidly tested by chemists, and any omissions of this mere sketch be supplied.

RESUMÉ.

The main results of this article may be summed up as follows:

1. A method of determining the partial pressures of mixtures of liquids has been elaborated, and its sources of error discussed.

2. Although the method can be said to give the vapor-tensions of pure liquids with an accuracy equal to that obtainable by the best of other methods only when the liquids are not very volatile, the results obtained by it for mixtures of liquids of not too different volatilities are accurate enough to serve as the experimental basis for theoretical deductions and generalizations.

3. A number of mixtures of representative liquids have been investigated as regards their vapor-tensions.

4. In some cases, extremely simple relations were found; in others, certain complexities presented themselves.

5. A recalculation of Regnault's determinations of the vapor-tensions of some mixtures of normal liquids as well as a consideration of Raoult's conclusions and Brown's work on the boiling-points of solution showed that it was permissible to apply what was found true for any one temperature to any other.

6. The relations between the concentrations in the gaseous and liquid phases were found to be quite simple and entirely in accordance with the provisions of the theoretical relations established by Planck and Nernst.

7. The changes of temperature occurring when certain liquids were mixed were found to be very small, and the resulting mixtures were those which exhibited the simplest relations in their vapor-tensions.

8. The vapor-tensions of mixtures of acetic acid with benzene and with toluene were determined, and the results were such as

to permit of the determination of the molecular mass of the dissolved and liquid acid.

9. A general method for the determination of the molecular masses of associated liquids at any given temperature was developed and illustrated with acetic acid.

The experimental part of this investigation was done in a laboratory in the School of Mines at Paris, placed at my disposition by the authorities of that noble institution; and I here take the pleasant privilege of thanking them for the courtesy thus extended to me. My cordial thanks are also due to M. Emilio Damour, *Ingénieur civil des Mines*, for his foreseeing kindness in furnishing me with apparatus and material; especially are my thanks due, however, to M. H. LeChatelier, *Ingénieur en chef des Mines*, whose wise direction and good counsel have been of great value to me throughout the work.

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WARNING AGAINST THE USE OF FLUORIFEROUS HYDROGEN PEROXIDE IN ESTIMATING TITANIUM.

BY W. F. HILLEBRAND.

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DUNNINGTON[1] has pointed out a source of error to be guarded against in estimating titanium in rocks and minerals by Weller's method, due, as he believes, to the partial reversion, in certain cases, of ordinary titanic to meta-titanic acid, which does not afford a yellow color with hydrogen peroxide. It remains for me to indicate another source of error in the possible presence of fluorine in the hydrogen peroxide.

For two years the colorimetric method has given reasonable satisfaction in this laboratory, but recently a new lot of hydrogen peroxide was purchased of a different brand from that hitherto used, and, after a time, it was noticed that the results obtained were in some instances far too high, and that no two determinations agreed.

It is known that hydrogen peroxide does not produce a yellow color in titanium solutions carrying hydrofluoric acid or fluorides, and moreover the addition of even a drop of the dilute acid to

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[1] This Journal, 13, 210.