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Chemistry. - In the absence of Dr. J. M. van Bemmelen, Prof. II. Kaneridingii Onnes presents a paper from Dr. F. A. II. Schreinemarers entitled: "Notes on equilibria in termury Systems."
(Read March 30, 1101).
The exporimental difficulties encountered in the determination of the composition of conjugate liquid phases are sometimes so great that, however desirable a knowledge of these compositions may be, the investigation of them has to be abandoned. Such cases occur for instarice:

1. When the two liquids, which are in equilibrium, form an emulsion which does not separate into two phases, or does so only after an extremely long time.
2. When analytical chemistry does not provide us with the means of quantitatively determining the components.
Nothwithstanding this we may in such cases gain our object, if only approximately, and by indirect means, as I will demonstrate in what follows.

Let us take as an example the system : Water, Phenol and Acetone. A short communication on this system is to be found in the proceedings of the Academy 1899-1900 and a more full account in Zeitschr. f. Phys. Chem. 33.78. The results communicated in those papers concern the forms and positions of the connodal curves at different temperatures. To obtain these, the following course was adopted. Varying quantities of phenol were introduced into a mixture of water and acetonc of known composition, obtained by direct weighing of the components, and the temperature was determined at which the two liquid phases furmed passed into a single one. In this mamer mixtures of water and acetone contaiuing
$1,83,4,24,7,94,12,2,15,6,24,6,31,840,3,50,2,59,9$ and 64,9 porcent of acetone were tested.
From theso doterminalions wo may easily obtain the connodal curves for different temporatures by interpolation and this method should always be applied when it is only possible to weigh the components. The difficulties mentionced in 1 and 2 are thas without influence. Table I contains the compositions of the solutions of the commodal curve at $56^{\circ} .5$ obtaincd in this way.

TABLEI.
Compositions of the solutions of the connodal line at 5605 .
pCt W. $85,589.089 .186 .582 .579 .1 \quad 67.9 \quad 59.348 .1 \quad 36.9 \quad 26 \quad 22.7$
$\begin{array}{llllllllllllllllll}\text { pCt Ac. } & 0 & 1.7 & 3.9 & 7.5 & 11.5 & 14.6 & 22.2 & 27.7 & 32.5 & 37.1 & 34 & 22.8\end{array}$
$\begin{array}{llllllllllllll}\mathrm{pCt} & \mathrm{Ph} . & 14.5 & 9.3 & 7.0 & 6.0 & 6.0 & 6.3 & 9.9 & 13.0 & 19.4 & 26.0 & 40 & 54.5\end{array}$
pCt W. $23.9 \begin{array}{lllllllll} & 25.9 & 27.9 & 30.8 & 32.0 & 34.5 & 36.9 & 38.8 & 40\end{array}$
$\begin{array}{llllllllll}\text { pCt Ac. } & 16.1 & 12.1 & 9.1 & 5.7 & 4.5 & 3.0 & 1.6 & 0.7^{-} & 0\end{array}$
$\begin{array}{llllllllll}\mathrm{pCt} & \mathrm{Ph} . & 60.0 & 62.0 & 63.0 & 63.5 & 63.5 & 625 & 61.5 & 60.5 \\ 60\end{array}$


By means of table I the connodal curve for $56^{\circ} 5$ may now be drawn; in Fig. 1 it is indicated by the curve $a_{1} a a_{2}$. It is, of course, known that the liquid phase $a_{1}$ may be in equilibrium with $a_{2}$ because both are only binary liquids, but how matters are situa-
ted as regards the ternary phases is quite unknown, as is also the position of the foldpoint $\alpha$. It is known, for instance, that at the given temperature a liquid phase $b_{2}$ may be in equilibrium with another, but with which other is not known; it is also known for instance that a liquid exists which may be in equilibrium with another one; with which other, however, is as yet unknown.

If we now wish to analyse the conjugated liquid phases which occur in this system we meet with the difficulties stated in I; with certain concentrations of phenol aud acetone the two layers only formed emulsions which did not separate even after waiting for hours; as we shall see, however, the top layer was present chiefly on the surface and the other at the bottom of the emulsion. In order to learn the composition of the two layers which were in equilibrium with each other, I proceeded in the following manner.
Into a small bottle, I weighed known quantities of water, acetone and phenol so that the composition of the total liquid was accurately known. Let $l$ in fig. 1 be the point showing the composition of this mixture and $c_{1}$ and $c_{2}$ the two liquid phases into which the mixture separates at $56^{\circ} 5$. In order to obtain equilibrium, the two layers were thoroughly shaken which caused an emulsion to form. After this lad been at rest for some time a portion was removed by means of a pipette from both the top and the bottom and submitted to anal ysis.

The composition of the one part is indicated in the figure by $l_{1}$, that of the other by $l_{2}$ and it is natural that the three points $l, l_{1}$ and $l_{2}$ must be situated on a straight line which is to be used as a check on the analysis. If the straight line $l_{1} l_{2}$ is now drawn and its points of intersection with the connodal curve $c_{1}$ and $c_{2}$ determined, these will then indicate the composition of the two liquid phases which are in equilibrium with each other and which constitute the emulsion. In this manner, I have determined the position of different chords of the connodal curve and therefore, also the compositions of the liquid phases which are in equilibrium at $56^{\circ} 5$. From the determinations communicated in table 2, to which have also been added the determinations of some clear solutions, it appears that the chords have the positions approximately indicated in fig. 1. For instance $b_{2}$ lies further from the side $W .-P h$ than $b_{1}$, $c_{2}$ further than $c_{1}$ or in other words, if we call the solution of branch $\alpha_{1} \alpha$ the aqueous and that of $a_{2} a$ the phenolic layer, acetone dissolves more readily in the phenolic thau in the aqueous layer.

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## 'T A BLE II.

Composition of the conjugated solutions at $56^{\circ} 5$.

Brauch $a_{1} \alpha$.

| pCl. W. | pCl. Ac. | pCl. Ph. | pCl. W. | pCt. Ac. | pCl. Pl . |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 88.5 | 0 | 14.5 | 40 | 0 | 60 |
| 88.8 | 1.2 | 10.0 | 29.3 | 7.3 | 63.4 |
| 89.1 | 3.9 | 7.0 | 230 | 17.1 | 59.4 |
| 88.62 | 5.28 | 6.1 | 22.5 | 22.8 | 54.7 |
| 86.7 | 7.3 | 0.0 | 22.5 | 28.0 | 49.5 |
| 85.5 | 8.5 | 6.0 | 22.9 | 28.8 | 48.3 |
| 76.0 | 169 | 7.1 | 28.6 | 36.1 | 35.3 |
| 75.1 | 17.5 | 7.4 | 28.8 | 36.3 | 34.9 |
| 69.5 | 21.5 | 9.0 | 34.0 | 37.5 | 28.5 |

From the foregoing it is plain how the difficulties mentioned in 1 may be got over if we can only determine quantitatively the three components or two of them. If this is also impossible, there is still at our disposal another method for determining the situation of the chords, namely determinations of vapour tensions.

Let us take, for instance, a mixture represented in figure 1 by $q_{1}$; at $56^{\circ} 5$ this mixture will separate into the two liquid phases $b_{1}$ and $b_{2}$ possessing a certain vapour pressure. If we take a mixture $q_{2}$ this will also separate into two layers $l_{1}$ and $b_{2}$ although the relative quantities of these phases will, of course, be different. The vapour tonsion however, will be the same. This js, of comrse, also the case if we take mixtures like $q_{3}$ and $q_{4}$ and generally for all mixtures represented by points on the chord $b_{1} b_{2}$.

All mixtures represented by points on the chord $b_{1} b_{2}$ have therefore, the same vapour tension. Inversely the position of the chord may be determined when the compositions of different mixtures having the same vapour tensions at the same temperature are known.
In the system: watcr-acetone-phenol I have made many determinations of vapour tension which I hope to communicate more fully, later on; I will now mention only a few of the determinations and
show how the position of the chords may be determined from them. The vapour tension of each of the mixtures investigated has been determined at 10 to 15 different temperatures; in what follows I only mention the vapour tensions at $56^{\circ} 5$ which have been obtained from these determinatious by interpolation.

Let us first consider the side $W-P / 2$ of fig. 1 , that is mixtures which contain only water and phenol.

## TABLE 3.

Vapour tensions at $56^{\circ}$ 5.
$0 \%$ Ac.

| 10 Ph . | 0 | 20 | ธ. 58 | 7.42 | 10.88 | 145 | 60.0 | 69.2 | 76.7 | 80.34 | 88.06 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $P$ in m.M. | 125 | 125 | 127 | 127 | 127 | 126 | 126 | 121 | 122 | 118 | 102 |
| 7.94\% Ac. |  |  |  |  |  |  |  |  |  |  |  |
| Pl. 0 | 01.222 .41 | 5.931 | 0215 | 1919 | 81 | 9340. | 849.2 | 862.6 | 7 | 712 | 80.7 |


| \% Plı. | 0 | 1.39 | 3.03 | 6.14 | 0.63 | 14.30 | J9.81 | 29.74 | 38.81 |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| P in m.M. | 387 | 360 | 350 | 318 | 202 | 262 | 232 | 193 | 171 |
| $\%$ | Pl. | 49.60 | 60.13 | 66.98 | 74.88 | 53.00 |  |  |  |
| P in m.M. | 155 | 144 | 137 | 130 | 115 |  |  |  |  |

$22.52 \%$ Ac.
$\begin{array}{lllllllll}\% & \text { Ph. } & 0 & 3.08 & 8.38 & 13.95 & 20.01 & 24.38 & 24.72\end{array} 35.95$
$\begin{array}{lllllllll}\mathrm{P} \text { iu } \mathrm{m} \text { M. } & 446 & 408 & 350 & 318 & 277 & 253 & 226 & 205\end{array}$

| $\%$ | $\%$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |

$\begin{array}{llllll}\mathrm{P} \text { in m.M. } & 180 & 167 & 155 & 140 & 122 .\end{array}$
$31.82 \%$ A $c$.
$\begin{array}{llllllllll}\% & \text { Pl. } & 0 & 4.10 & 7.68 & 13.36 & 20.13 & 24.77 & 20.99 & 34.13 \\ 30.29\end{array}$
$\begin{array}{llllllllll}\mathrm{P} \text { in } \mathrm{mN} . & 524 & 468 & 428 & 379 & 335 & 302 & 274 & 251,5 & 224\end{array}$
$\begin{array}{llllllll}\% & \text { Ph. } & 40.93 & 45.57 & 51.48 & 57.61 & 62.06 & 71.00 \\ 79.77\end{array}$
$\begin{array}{llllllll}\mathrm{P} \text { in m.M. } & 218 & 202 & 186 & 170 & 160 & 141 & 123 .\end{array}$
The vapour tensions are given in table 3 under 0 pCt . of acetone. It will be seen that as the quantity of phenol increases, the pressure first risos from $125-127$ in.m., falling again to $126 \mathrm{~m} . \mathrm{m}$. when the liquid contains 14.5 per cent of phenol. If more phenol is added, two liquid phases appear and the pressure remains $126 \mathrm{~m} . \mathrm{m}$. until the mixture contains 60 per cent of phenol; if still more phenol is added, thore only remains one liquid phase and the vipour tension 47*


Fig. 2
decreases continuously. This is represented in the usual way in fig. 2. The amount of phenol is given on the horizontal and the pressure on the rertical-axis. A line is thus obtained which is indicated diagrammatically by the one marked 0 pCt . of acetone. At the left hand side A consist of a part with a maximum, in the centre, where both liquid phases occur, of a horizontal part and for the remainder of a slanting line. Passing now, in fig. 1, along the side $W-V^{\circ} h$ from $W$ to $P h$, the pressure at first increases, reaches a maximum and then decreases until $a_{1}$ in reached; from $a_{1}$ to $a_{2}$ the pressure remains constant and fiom $a_{2}$ to $F h$ it again decreases; the prossure therefore remains constant in the region in which two liquid phases are present.

It is different, however, if we move along a line through the triangle, for instance from $r_{3}$ to $P h$, along the line $r_{3} P l /$ from $r_{3}$ to $d_{1}$ we then move in the homogenous ficld; from $d_{1}$ to $e_{2}$ we traverse the hetcrogenous and from $e_{2}$ to $P h$ we find ourselves again in the homogenous ficld. It is, of course, plain that if we move over the parts $r_{3} d_{1}$ and $e_{2} P h$ the pressure will be continually altering, as was the case with the parts $W a_{1}$ and $a_{2} P / 4$; on the part $d_{1} e_{2}$, the behaviour is, however, different from that on $a_{1} a_{2}$. On the part $a_{1} a_{2}$ the vapour tension remains unchanged; on $d_{1} e_{2}$ it changes continuously. This will be easily unterstood if we reflect that the pressure at $d_{1}$ is the same as the pressure of the two conjugated phases $d_{1}+d_{2}$; at $l$ the vapour pressure is that of the system $c_{1}+c_{2}$; in $q_{3}$ the vapour pressure corresponds to that of the system $l_{1}+l_{2}$; in $e_{2}$ the vapour pressure is the same as that of the system $e_{1}+e_{2}$. We thercfore see that if wo move from $d_{1}$ to $e_{2}$ the vapour pressure must be changing continually just as it alters along the connodal line from $d_{1}$ to $e_{1}$ or from $d_{2}$ to $e_{2}$. From the determinations it follows that the vapour prossure increases along the comnodal line from $a_{1}$ and $a_{2}$ in the direction of the fuldpoint $\alpha$.

If, therefore, we move from $d_{1}$ to $e_{2}$ we must notice a continual decrease of the vapour pressure.

All the solutions situated on the line $r_{3} P h$ have the peculiarity that the relation between water and acetone is the same in all of them. The vapour tensions of the solutions on this line may therefore be represented as though we had a binary mixture of the components of which one is phenol and the other a mixture of water and acetone in constant proportion. We, therefore, put down in figure 2 the amount of phenol on the horizontal and the pressure on the vertical axis. Let us take as oxample the solutions in which the relation between water and acetone is $84.4: 15.6$ or in other words those which contain 15.6 percent of acetone if we disregard the presence of the phenol. These determinations are given in table 3 marked 15.6 percent acetone. Under $P$ the vapour pressure in m.m. is given and under pCt. $P h$ the total amount of phenol in the liquids. The first determination, therefore, gives the vapour tension of a mixture which contains no phenol, that is of a mixture of water and acetone containing 15.6 percent of acetone. As may be plainly seen from this series, the vapour pressure decreasss continually with increasing quantities of phenol.
In fig. 2 this series is indicated by the curve marked 15,6; the curve is not continued to its endpoint, 100 percent of phenol, but only to 83 percent. It must, of course, end at the same point as the line indicating the vapour tension of water and phenol culy.

In table 3 some other determinations are given under 7.94, 22.52 and 31.82 percent acetone, the significance of which will be sufficiently apparent after the foregoing explanation. The corresponding rapour pressure curves in fig. 2 are marked by the same figurcs. Each of these curves consists of three parts, namely the two portions at the sides which relate to the homogenous liquids and the portion in the middle (between the two crosses) which relates to the mixturcs which separate into two liquid phases on the connodal curve. In the two points where these three meet, they exhibit a discontinuity.
From fig. 2 the situation of the chords of the connodal curve at $56^{\circ} .5$ may be obtained.
Let us draw an horizontal line $s s_{1}$ which intersects some of the vapour tension curves; each point of intersection indieates a solution or a complex; all the solutions and complexes situated on this line have the same vapour tension. Lei us confine ourselves to the complexes only or to those parts of the vapour tension curves, which are indieated in figure 1 by points within the connodal curve and therefore belong to the heterogenous field. Let us draw the line
$s s_{1}$ in such a way that it indicates for instance a vapour tension of 180 mm . We then have 4 complexes, indicated on the curves by $7.94,15.6,22.52$ and 31.82 percent acetone, which at $56^{\circ} .5$ have a vapour pressule of $180 \mathrm{~m} . \mathrm{m}$. and must therefore in fig. 1 be situated on the same chord as for instance the points $q_{1}, q_{2}, q_{3}$ and $q_{4}$.

The composition of these complexes may be ascertained from fig. 2; from the figure we may obtain the amount of phenol in the complex, whilst the relation between the other two components, that is between water and acetone, is known. Thus it is found, for instance, that the point of intersection of the line $s s_{1}$ with the vapour tension curve of 15.6 percent acetone indicates an amount of phenol of 34.6 percent. The complex, therefore, contains $100-34.6=65.4$ percent of water and acetone of which $\frac{15.6}{100} \times 65.4$ percent is acetone and $\frac{84.4}{100} \times 65.4$ percent is water. We, therefore, find that this complex consists of 55.2 percent of water, 10.2 percent of acetone and 34.6 percent of phenol. In the same manner, the composition of the complexes, indicated by the othor parts of intersection may be calculated.

In the foregoing, we have drawn the line $s s_{1}$ in such a manner that it indicated a vapour tension of $180 \mathrm{~m} . \mathrm{m}$. ; this vapour tension may, of course, be taken differently; we then obtain other points of intersection and consequently other complexes and also other chords. In table 4 a few results of these calculations are given for $180,220,260$ and $300 \mathrm{~m} . \mathrm{m}$.

## TABLE 4.

Temperature $56^{\circ} 5$.
Composition of the complexes with a vapour pressure of $180 \mathrm{~m} . \mathrm{m}$.

| pCt. W. | pCt. Ac. | pCt. Ph. |
| :---: | :---: | :---: |
| 73.8 | 6.4 | 19.8 |
| 55.2 | 10.2 | 34.6 |
| 43.4 | 12.6 | 44.0 |
| 31.6 | 14.8 | 53.6 |

Composition of the complexes with a vapour pressure of 220 m.m.

| pCt. W. | pCt. Ac. | pCt. Ph. |
| :---: | :---: | :---: |
| 83.7 | 7.3 | 9.0 |
| 65.3 | 12.1 | 22.6 |
| 53.0 | 15.4 | 31.6 |
| 40.7 | 18.9 | 40.4 |

Composition of the complexes with a vapour pressure of $260 \mathrm{~m} . \mathrm{m}$.

| pCt. W. | pCt. Ac. | pCt. Ph. |
| :---: | :---: | :---: |
| 72.2 | 13.3 | $\mathbf{1 4 . 5}$ |
| 59.7 | 17.3 | 23.0 |
| 46.1 | 21.5 | 32.4 |

Composition of the complexes with a vapour pressure of $300 \mathrm{~m} . \mathrm{M}$.

| $\mathrm{pCt} . \mathrm{W}$. | $\mathrm{pCt} . \mathrm{Ac}$. | $\mathrm{pCt} . \mathrm{Ph}$. |
| :---: | :---: | :---: |
| 77.3 | 14.3 | 8.4 |
| 64.7 | 18.8 | 16.5 |
| 51.2 | 23.8 | 25.0 |

Let us first take the 4 complexes which at $56^{\circ} .5$ have a vapour tension of $180 \mathrm{~m} . \mathrm{m}$.; if these are placed in the triangle it will be seen, that they are situated on a straight line; the same is the case with the 4 complexes with a vapour pressure of $260 \mathrm{~m} . \mathrm{m}$. and also with the three complexes whose vapour pressure amounts to $300 \mathrm{~m} . \mathrm{m}$.

We have, therefore, again found four chords; for the determination of each of these, of course, only two points were needed; the others only serve as a check to control the accuracy obtained.

It is worthy of attention that the chords derived from table 4 are, theoretically, not altogether comparable with those from table 2; the latter belong to a connodal line at $56^{\circ} .5$ at a constant pressure, the former, to a connodal line at $56^{\circ} .5$ at its own vapour pressure. As however, a small change in the pressure has generally a very small influence on the composition of the two liquid phases in equilibrium, the chords determined in the two ways are practically
comparable. That this is the case is seen when the chords obtained from the figures given in the two tables are set out in the triangular diagram.

An examination of figure 2 reveals some further peculiarities which may be explained. From the vapour tension curve, marked 0 percent acctone, it is seen that the vapour tension of water is increased by the addition of small quantities of phenol. I have already shown in a former article that this is in accordance with the formula of van der Wanls which applies in this case. But it we add phenol to a water-acetone mixture it is different, for, if we take mixtures of water and acetone containing $7.93,15.6,22.52$ or 31.82 percent of acetone, we notice from the corresponding vapour tension curves in fig 2 that the vapour pressure falls. The question is now whether the addition of a new substance to a binary mixture has the same influence as the addition of the same to a simple liquid. As I will show this is by no means the case.

We take for example a liquid of the composition

$$
1 \text { Mol A } \quad x_{1} \operatorname{Mol.B} \quad y_{1} \operatorname{Mol} C .
$$

which is in cquilibrium with a vapour of the composition

$$
1 \text { Mol A } \quad x \operatorname{Mol} B \quad \text { y Mol C. }
$$

Let us call the thermodynamic potential, the entropy and the volume of this liquid $\zeta_{1}, \eta_{1}$ and $V_{1}$ and that of the vapour phase $\zeta, \eta$ and $V$.

In equilibrium we have:

$$
\left.\begin{array}{c}
\zeta_{1}-x_{1} \frac{\partial \zeta_{1}}{\partial x_{1}}-y_{1} \frac{\partial \zeta_{1}}{\partial y_{1}}=\zeta-x \frac{\partial \zeta}{\partial x}-y \frac{\partial \zeta}{\partial y}  \tag{I}\\
\frac{\partial \zeta_{1}}{\partial x_{1}}=\frac{\partial \zeta}{\partial x} \quad \frac{\partial \zeta_{1}}{\partial y_{1}}=\frac{\partial \zeta}{\partial y}
\end{array}\right\}
$$

Assuming that the relative quantities of the components $A$ and 3 is kept constant in the liquid, $x_{1}$ is also constant. If we also keep the temperature constant the only variable quantitics remaining are $y_{1} x y$ and $P$. From the equations (I) we obtain:

$$
\begin{gather*}
-\left(s_{1} x_{1}+t_{1} y_{1}\right) d y_{1}+\left(V_{1}-r_{1} \frac{\partial V_{1}}{\partial x_{1}}-y_{1} \frac{\partial V_{1}}{\partial y_{1}}\right) d p= \\
=-(r x+s y) d x-(s x+t y) d y+\left(V-x \frac{\partial V}{\partial x}-y \frac{\partial V}{\partial y}\right) d p \\
s_{1} d y_{1}+\frac{\partial V_{1}}{\partial x_{1}} d p=r d x+s d y+\frac{\partial V}{\partial x} d p  \tag{II}\\
t_{1} d y_{1}+\frac{\partial V_{1}}{\partial y_{1}} d p=s d x+t d y+\frac{\partial V}{\partial y} d p
\end{gather*}
$$

in which

$$
s_{1}=\frac{\partial^{2} \zeta_{1}}{\partial x_{1} \partial y_{1}} \quad t_{1}=\frac{\partial^{2} \zeta_{1}}{\partial y_{1}^{2}} \quad r=\frac{\partial^{2} \zeta}{\partial x^{2}} \quad s=\frac{\partial^{2} \zeta}{\partial x \partial y} \quad t=\frac{\partial^{2} \zeta}{\partial y^{2}}
$$

If we multiply the second equation by $x$ and the third by $y$ and add the results to the first we find:

$$
\begin{gather*}
{\left[s_{1}\left(x-x_{1}\right)+t_{1}\left(y-y_{1}\right)\right] d y_{1}+\left[V_{1}+\left(x-x_{1}\right) \frac{\partial V_{1}}{\partial x_{1}}+\left(y-y_{1}\right) \frac{\partial V_{1}}{\partial y_{1}}\right] d p=V d p} \\
\frac{d p}{d y_{1}}=\frac{s_{1}\left(x-x_{1}\right)+t_{1}\left(y-y_{1}\right)}{V-V_{1}+\left(x_{1}-x\right) \frac{\partial V}{\partial x_{1}}+\left(y_{1}-y\right) \frac{\partial V_{1}}{\partial y_{1}}} \cdot . \text { (III) } \tag{III}
\end{gather*}
$$

This equation shows the change in pressure which occurs when we add new substance to a liquid made up of the components $A$ and $B$. Let us assume that the quantity $y_{1}$ of the new substance is exceedingly small so that $y$ is also very small. We then find for the limit value ${ }^{1}$ ):

$$
t_{1}=\frac{R T}{y_{1}}
$$

Formula III now becomes:

$$
\frac{d p}{d y_{1}}=\frac{s_{1}\left(x-r_{1}\right)+R T\left(\frac{y}{y_{1}}-1\right)}{V-V_{1}+\left(r_{1}-r\right) \frac{\partial V_{1}}{\partial x_{1}}} \cdot \cdot \cdot \cdot \cdot \cdot(I V)
$$

[^0]which may, therefore, be applied when only small quantities of the new substance are added. As will be readily understood, the sign of the denominator is always positive; as to the sign of the numerator, this cannot be judged without further information. The quantity $\frac{y}{y_{1}}$ is the partition coefficient of the new substance between vapour and liquid. This coefficient decides whether, on adding a new substance to a simple liquid, an increase or decrease of $P$ will take place; this, however, is by no means the case here, as there is, in addition, another term $s_{1}\left(x-r_{1}\right)$ which may be either positive or negative.

The value of $\frac{d p}{d y_{1}}$ from IV may also be considered as a function of $x_{1}$, that is of the composition of the binary mixture to which the new substance is added. It may, therefore, happen that if $x_{1}$ is allowed to vary within wide limits, $\frac{d p}{d y_{1}}$ may change sign.

We, therefore, come to the following conclusion:
${ }_{n}$ if we ald a new sultstance to a binary mixture, either an „incrase or a decrease of the vapour tension may take place accor${ }_{n}$ ding to the composition of the binary mixture."
This is in accordance with observations made on the system water, acetone and phenol. If we take water and add phenol to it the vapour pressure increases (sce fig. 2). This is also the case when, instead of pure water, we use water containing but little acetone. If, however, we use mixtures containing 7.94 or more of acetone a decrease of vapour tension will be noticed as shown in fig. 2.
The difference between the behaviour of a single substance and of a binary mixture is cven more cvident when the andition af a now substance, which does not appear in the vapour phase, is considered.

In formule IV we must then put $y=0$ and we obtain:

$$
\begin{equation*}
\frac{d p}{d l_{1}}=\frac{s_{1}\left(x-x_{1}\right)-n T^{\prime}}{V-V_{1}+\left(x_{1}-x\right) \frac{d V_{1}}{d x_{1}}} . \tag{V}
\end{equation*}
$$

The numerator of this fraction may now be either positive or negative so that we come to the following conclusion:
nif we add to a binary mixture new substance not passing
,into the vapour, the vapour tension may be either increased or "decreased."
We, therefore find an important deviation from the law of decrease of vapour tension in the case of simple substances. Let us assume that the binary mixture has a maximum or minimum vapour pressure. We then must put $x=x_{1}$, causing the term $s_{1}\left(x-x_{1}\right)$, to disappear from the formula; $\frac{d p}{d y}$ will consequentiy bo negative so that we find that:
„if we add to a binary mixture with a maximum or minimum „vapour pressure a new substance, which does not pass into the "vapour, pressure is decreased."

We, therefore, come to the conclusion that the law of the decrease of rapour pressure for a simple liquid is still applicable to a binary mixture with a maximum or minimum vapour pressure, but that in general either an increase or a decrease of vapour pressure may occur with binary mixtures.

When calculating the formula II from I we have taken the pressure as variable and the temperature as constant. If we now take the pressure as constant and the temperature as variable we find in a similar manner that:
„if we add to a binary mixture a new substance which does not pass into the vapour, the boiling point may be either increased or decreased. Only binary mixtures with a maximum or minimum boiling point obey the ordinary law of increase of boiling point for simple substances."

In the equilibria of the system water, ethylalcohol and sodium carbonate investigated in our laboratory by Mr. Ketner, we also meet with an example of the deviations which binary mixtures show on adding a third substance, in contrast to simple substances.

The boiling point of water rises when sodium carbonate is added to it; if however, we take mixtures of water and alkohol, the boiling point is depressed by the addition of this salt, provided that the amount of alcohol in the mixture exceeds a certain limit. The determinations are given in table V . As will be seen these determinations have been made for alcoholic mixtures containing:
$0,1.2,2.2,5.0,9.8,21.3,35.6,45.4$ and 55.0 percent of alkohol.

Under percentage of salt are given the quantity of added $\mathrm{Na}_{2} \mathrm{CO}_{3}$ to 100 parts of the water-alcohol mixture; under $\Delta T$ the change in

## (714)

the boiling point, the sign + indicating the increase and - the decrease of the boiling point.

## TABLE V.

Change in the boiling point of water-alcoholmixtures on addition of $\mathrm{Na}_{2} \mathrm{CO}_{3}$.

| 0 \% Alcohol. |  | 1.2 \% Alcohol. |  | 2.2 \% Alcohol. |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| \% salt | $\triangle T$ | $\%$ salt | $\Delta \mathrm{T}$ | \% salt | $\triangle T$ |
| 0.65 | $+0^{\circ} .10$ | 0.80 | $+0.05$ | 0.44 | $+0.01$ |
| 1.62 | $+0^{\circ} .21$ | 1.79 | + 0.13 | 0.91 | + 0.01 |
|  |  | 2.57 | +0.16 | 1.75 | + 0.03 |
|  |  | 3.38 | +0.20 | 2.52 | 0.00 |

$5.0 \%$ Alcohol. $9.8 \%$ Alcohol $21.3 \%$ Alcohol.

| $\%$ salt $\Delta T$ | $\%$ salt $\Delta T$ |  | $\%$ salt $\Delta T$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 0.48 | -0.04 | 0.67 | -0.03 | 0.61 | -0.14 |
| 1.31 | -0.07 | 1.33 | -0.12 | 1.04 | -0.27 |
| 2.15 | -0.14 | 2.02 | -0.22 | 1.72 | -0.46 |
|  |  | 2.67 | -0.30 | 2.37 | -0.60 |
|  |  |  |  | 3.23 | -0.91 |

$35.6 \%$ Alcohol $45.4 \%$ Alcohol $55.0 \%$ Alcohol
$\%$ salt $\triangle T \quad \%$ salt $\Delta T \quad \%$ salt $\triangle T$
$\begin{array}{llllll}0.52 & -0.14 & 0.43 & -0.08 & 0.16 & -0.03\end{array}$
$\begin{array}{lllllll}1.06 & -0.29 & 0.84 & -0.16 & 0.60 & -0.15\end{array}$
$1.62-0.45$
$\begin{array}{llll}1.45 & -0.31 & 1.19 & -0.25\end{array}$
$\begin{array}{llll}2.09 & -0.42 & 1.80 & -0.35\end{array}$
$2.63-0.52$


[^0]:    1) Zettschr. fur Plys. Chem, 95, 927.
