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pinacone: hydrole, which are dependent on the group introduced.
It is to be expected that these differences will continue to exist also in another medium provided this remains neutral, for instance when we reduce with aluminiunt amalgam in another saturated alrohol. This indeed proved to be the case :

| Ketone | Solvent | Formed hydrole |
| :---: | :---: | :---: |
| Benzophenone | $\left\{\begin{array}{l}\text { C }{ }_{2} \mathrm{H}_{5} \mathrm{OH} \\ \mathrm{CH}_{3} \mathrm{OH} \\ \left\{\begin{array}{c}\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH} \\ \mathrm{CH}_{3} \mathrm{OH}\end{array}\right.\end{array}\right.$ | 68\% |
|  |  | 68 " |
|  |  | 94" |
| o-Chlorobenzophenone |  | 93 " |

On the other hand it was ascertained that a ketone which in a neutral solution gave almost exclusively hydrole, yet yielded in a feebly acid solution nothing else but pinacone.

2 grams of $p p^{\prime}$ di-chlorobenzophenone yielding in a neutral solution with $\mathrm{AlHg} 96^{\circ}{ }_{1}$, of hydrole gave with zinc dust and the acetic acid-alcohol mixture 1.99 grams of pure pinacone m. p. $180^{\circ}$.
0.1820 and 0.1926 gram gave $0.2060^{\prime}$ and 0.2207 gram AgCl

Calculated for $\mathrm{C}_{80} \mathrm{H}_{18} \mathrm{O}_{2} \mathrm{Cl}_{4} 28.1 \% \mathrm{Cl}$ (Frund 28.0-27.7).
This also agrees with the assumption that the formation of pinacone, in the absence of OH -ions and in this method of reduction, takes place very much more rapidly than that of other possible reduction products and that the hydrole formation in a neutral medium must be attributed to the presence of OH -ions at the boundary layer.

The measurement of the velocity with which some pinacones are converted into the mixture of ketone and hydrole will be the subject of a following com̀munication.

## Lab. Organic Chemistry

 Technical University.Delft, May 1913.
Chemistry. - "Equilibria in ternary systems". VIII. By Prof. Schreinemarers.
Let us now consider the case when a liquid $L$ is saturated with the solid compounds $F$ and $F^{\prime \prime}$ and at the same time in equilibrium with a vapour $G$. As the system ${ }^{\cdot} F+F^{\prime}+L+G$ contans the three components in four phases it is monovariant; hence we can consider the vapour pressure of the systern and the composition of $L$ and $G$ as functions of the lemperature.

$$
7^{+}
$$

On a change in $T$ the liquid therefore traverses a curve in a concentration diagram; this is also the case with the currelated vapour. We will call these curves the saturation and vapour saturation curves of $F+F^{\prime \prime}$ under their own vapour pressure, or also the liquidum and the vapour curve of the four-phase equilibrium $F^{\prime}+F^{\prime}+L+G$. The relation between pressure and temperature will also be represented by a curve in a $P, T$-diagram.
In fig. 4 this $P, T$-curve is represented by $L S D R$; in fig, 1, 2 and $3 a c$ is the liquidrum and $a_{1} c_{1}$ the vapour curve of the system $F+F^{\prime \prime}+L+G$. Point $a$ of the curve $a c$ therefore represents a liquid saturated at a definite $P$ and $T$ with $F+F^{\prime}$; point $a^{\prime}$ indicites the correlated vapour.

Let us represent the composition, the entropy, the volume and the $\zeta$ of $F$ by : $a, \beta, 1-a-\beta ; \eta, v$ and $\zeta$ that of $F^{\prime}$ by: $\alpha^{\prime} \beta^{\prime}, 1-\alpha^{\prime}-\beta^{\prime}, \eta^{\prime} v^{\prime}$ and $\zeta^{\prime}$ that of the liquid by: $x, y, 1-x-y, H, V$ and $Z$ that of the vapour by: $x_{1}, y_{1}, 1-x_{1}-y_{1}, H_{1}, V_{1}$ and $Z_{1}$,

The conditions of equilibrium then are:

$$
\left.\begin{array}{c}
Z-\left(\begin{array}{ll}
x & \alpha
\end{array}\right) \frac{\partial Z}{\partial x}-(y-\beta) \frac{\partial Z}{\partial y}=\zeta  \tag{1}\\
Z-\left(x-\alpha^{\prime}\right) \frac{\partial Z}{\partial x}-\left(y-\beta^{\prime}\right) \frac{\partial Z}{\partial y} \doteq \zeta^{\prime} \\
Z_{1}-\left(x_{1}-\alpha\right) \frac{\partial Z_{1}}{\partial x_{1}}-\left(y_{1}-\beta\right) \frac{\partial Z_{1}}{\partial y_{1}}=\zeta \\
\frac{\partial Z}{\partial x}=\frac{\partial Z_{1}}{\partial x_{1}}-\frac{\partial Z}{\partial y}=\frac{\partial Z_{1}}{\partial y_{1}}
\end{array}\right\} .
$$

Hence, we have five relations between the six variables $x, y, x_{1}, y_{1}, P$, and $T$, so that we can consider the vapoiur pressure of the system and the composition of $L$ and $G$ as functions of the temperature as stated above. If we differentiate the equations (1) and eliminate $d x_{1}$ and $d y_{1}$ we obtain:
$[(x--\alpha) r+(y-\beta) s] d x+[(x-\alpha) s+(y-\beta) t] d u=A d P-B d T$
$\left[\left(x-\alpha^{\prime}\right) r+\left(y-\beta^{\prime}\right) s\right] d x+\left[\left(x-\alpha^{\prime}\right) s+\left(y-\beta^{\prime}\right) t\right] d y=A^{\prime} d P-B^{\prime} d T^{\prime}$
$\left[\left(x_{1}-x\right) r+\left(y_{1}-y\right) s \mid d x+\left[\left(x_{1}-x\right) s+\left(y_{1}-y\right) t\right] d y=C d P-D d^{2} \Gamma\right.$
$A, B, C$ and $D$ have herein the values indicated in communication II; $A^{\prime}$ and $B^{\prime}$ are found from $A$ and $B$ by substituting in the latter $a, \beta, v$ and $\eta$, by $a^{\prime}, \beta^{\prime}, v^{\prime}$ and $\eta^{\prime}$. If we eliminate $d x$ and $d y$ from (2), (3) and (4) we get:

$$
\begin{equation*}
\frac{d P}{d T}=\frac{n \eta+n^{\prime} \eta^{\prime}+m H+m_{1} I_{1}}{n v+n^{\prime} v^{\prime}+m V+m_{1} V_{1}} \tag{5}
\end{equation*}
$$

In this:

$$
\left.\begin{array}{l}
n=\left[\beta^{\prime}\left(x-x_{1}\right)+\alpha^{\prime}\left(y_{1}-y\right)+x_{3} y-x y_{1}\right] \lambda \\
n^{\prime}=\left[\beta\left(x_{1}-x\right)+\alpha\left(y-y_{1}\right)+x y_{1}-x_{1} y\right] \lambda  \tag{6}\\
m=\left[x_{1}\left(\beta^{\prime}-\beta\right)+y_{1}\left(\alpha-a^{\prime}\right)+\alpha^{\prime} \beta-\alpha \beta^{\prime}\right] \lambda \\
m_{1}=\left[x\left(\beta-\beta^{\prime}\right)+y\left(\alpha^{\prime}-\alpha\right)+\alpha \beta^{\prime}-\alpha^{\prime} \beta\right] \lambda
\end{array}\right\}
$$

in which $\lambda$ is an arbitrary factor. The significance thereof is as follows: In each fourphase equilibrium $F+F^{\prime}+L+G$ a reaction can always take place, which we represent by :

$$
\begin{equation*}
n \text { quant. } \bar{F}+n^{\prime} \text { quant. } F^{\prime}+m \text { quant. } L+m_{1} \text { quant. } G=0 \tag{7}
\end{equation*}
$$

It is evident that the four reaction coefficients in (7) cannot have the same sign. With the aid of the known compositions of the four phases we find from (7) that $n, n^{\prime}, m$ and $m_{1}$ have the values given in (6). The numerator of (5) therefore represents the change in entropy, the denominator the change in volume occurring in reaction (7). If we call the heat to be supplied or withdrawn in this reaction $\Delta W$ and the change occurring in volume $\Delta V$, then (5) changes into the well-known relation:

$$
\begin{equation*}
T \frac{d P}{d T}=\frac{\Delta W}{\Delta V} \tag{8}
\end{equation*}
$$

which, of course, we might have deduced in a different manner.
Before applying this formula we will first investigate more closely the hquidum and the vapour curve and the reactions which can appear in the system $F+p^{\prime \prime}+L+G$.

Let us first consider the point of mtersection $S$ of the liquidum curve $a c$ (fig. 1, 2 and 3) with the line $F F^{\prime \prime}$; the vapour appertaining to this liquid $S$ is indicated by $S_{1}$. As the three points $F$, $F^{\prime \prime}$, and $S$ of this four-phase equilibrium $F+F^{\prime}+$ liquid $S+$ vapour $S_{\mathrm{i}}$ are situated on a straight line, a reaction occurs in which the vapour does not take part. Accordng to the situation of the three points $F, F^{\prime \prime}$, and $S$ in regard to each other this reaction will be $F+F^{\prime} \rightleftarrows L$ or $F^{\prime} \rightleftarrows F+L$ or $F \rightleftarrows F^{\prime}+L$.

If the three points are situated as in fig. 1 or 2 , the reaction is $F+F^{\prime} \rightleftarrows L$; the liquid $S$ is then formed by the joint fusion of the compounds $F$ and $\overrightarrow{F^{\prime \prime}}$, so that the point $S$ is a point of the melting point line of the complex $F+F^{\prime}$. As this liquid, however, can be also in equilibrium with a vapour $S_{1}$, the point $S$ is the minimum melting point of the complex $F+F^{\prime \prime}$.
If the three points are situated as in fig. 3 the reaction $B^{\prime \prime} \rightleftarrows F+L$ occurs ; the point $S$ is then the incongruent minimum melting point of the complex $F+F^{\prime \prime}$.

In the point of intersection $D_{1}$ of the vapour line $a_{1} c_{1}$ with the line $F F^{\prime \prime}$ the correlated liquid has the composition $D$. As of this four-phase equilibrium $F+F^{\prime}+\operatorname{liquad} D+$ vapour $D_{1}$ the three phases $F, F^{\prime}$ and $D_{1}$ are situated on a straight line, a reaction occurs in which the liquid takes no part. According to the situation of the three points $F, F^{\prime \prime}$ and $D_{1}$, in regard to each other this reaction is : $F+\vec{F}^{\prime \prime} \nleftarrow G$ (fig. 1) or $F^{\prime} \rightleftarrows F+G$ (fig. 2) or $F \vec{\not} F^{\prime}+G$. (fig. 3).

The point $D_{1}$ is, therefore a point of the congruent or incongruent sublimation curve of the complex $E+F^{\prime}$. As, however, this vapour $D_{1}$ may also be in equilibrium with a liquid $D$, the point $D_{1}$ is the maximam sublimation point of the complex $F+F^{\prime}$.

Hence, we find: the point of intersection $S$ of the line $E F^{\prime}$ with the liquidum curve of the four-phase equilibrium $F+F^{\prime}+L+G$ represents the minimum meltung point (congruent or incongruent); the point of intersection $D_{1}$ of this line with the rapour curve of this four-phase equilibrum represents the maximum sublimation point (congruent or incongruent) of the complex $F+F^{\prime}$.

Let us now ascertain which reaction can occur in the four-phase equilibrium $F+F^{\prime}+L+G$ if the liquid is represented by a point in the proximity of $S$. We will call that side of the line $F B^{\prime \prime}$, where the vapour $S_{1}$ conjugated with the liquid $S$ is found, the vapour side, the other side of $F F^{\prime \prime}$ the liquidum side. We distinguish three cases.

1. In the point $S$ the reaction $F+F^{\prime} \rightleftarrows 2$ takes place. We imagine in fig. 1 or 2 , on the part of the liquidum curve situated at the vapour side of $F F^{\prime \prime}$, a liquid $L$ in the vicinity of the point $S$, the correlated vapour $G$ will then be represented by a point of the vapour curve situated in the vicinity of $S_{1}$. As the point $L$ now lies within the triangle $E F^{\prime} G$ the reaction $F+F^{\prime}+G \vec{\leftarrow} L$ will occur. If we take a liquid $L$ situated in the vicinity of $S$ at the liquidum side of $F F^{\prime}$, the lines $F F^{\prime}$ and $L G$ then intersect each other in a point between $F$ and $F^{\prime}$ and also situated between ${ }^{-} L$ and $G$ so that the reaction $F+F^{\prime} \rightleftarrows L+G$ talses piace.

It is evident that this goes on independently of the situation of the point $D_{1}$.
2. In the point $S$ the reaction $F^{\prime} \rightleftarrows F+L$ occurs. If we take in fig. 3 a liquid $L$ in the vicinity of $S$ and at the vapour side of the line $F F F^{\prime}$, and a vapour $G$ in the vicinity of $S_{1}$, the lines $F L$ and $F^{\prime} G$ will intersect each other so that the reaction $F^{\prime}+G \rightleftarrows F+L$ occurs. If we take a liquid $L$ in the vicinity of $S$ at the liquidum side of the line $F F F^{v}, F^{\prime}$ then lies within the triangle $f L G$ and so the jeaction $F^{\prime} \rightleftarrows F+L+G$ takes place.
3. In the point $S$ the reaction $F \rightleftarrows F^{\prime \prime}+L$ occurs. In the previoüs reactions $F$ and $F^{\prime \prime}$ should then, however, be exchanged.

We can allow the liquid of the four-phase equilibrium $F+F^{\prime \prime}+L+G$ to traverse the liquidum curve from $a$ to $c$; the vaponr then traverses the vapour curve from $a_{1}$ to $c_{1}$.-We will call this direction, where the equilibrium arrives first in the minimum melting point and then .in the maximum sublimation point of the complex $F+F^{\prime}$, the positive direction:

We now allow the equilibrium to move over a short distance from the one side of the minimum melting point towards the other. At the one side, as noticed above, a four-phase reaction takes place different to that at the other side; in the minimum melting point itself both reactions coincide and the vapour does not participate in the reaction. Hence, in this moring we obtain a succession of three reaction types which we will call a reaction series.


Fig. 1.


Fig. 2.


Fig. 3.
We now may summarise the previous results in the foliowing manner; if a four-phase complex $F+F^{\prime}+L+G$ moves in a positive direction through the minimum melting point of the complex $F+F^{\prime \prime}$ there occurs the reaction series:

$$
F+F^{\prime}+G \rightleftarrows L \quad F+F^{\prime} \rightleftarrows L \quad F+F^{\prime} \rightleftarrows L+G
$$

$\begin{array}{lll}\text { or } F^{\prime}+G \rightleftarrows F+L & F^{\prime} \rightleftarrows F+L & F^{\prime} \rightleftarrows F+L+G\end{array}$
or $F+G \rightleftarrows F^{\prime \prime}+L \quad F \longleftrightarrow F^{\prime}+L \quad F \longleftrightarrow F^{\prime \prime}+L+G$
which we will call $A, B$, and $C$, respectively. It is evident that this only applies so long as the four-phase equilibrium is found in the vicinity of the minimun melting point.

If we ascertain what reactions can occur in the four-phase equilibrium $F+F^{\prime \prime}+L+G$ when the vapour is represented by a point in the vicinity of $D_{1}$ we find in an analogous manner as above: if a fourphase equilibrium $F+F^{\prime}+L+G$ moves in a positive direction through the maximun sublimation point of the complex $F+F^{\prime}$ the following reaction series appears:

$$
\begin{aligned}
& F+F^{\prime} \rightleftarrows L+G \quad F+F^{\prime \prime} \rightleftarrows G \quad F+F^{\prime}+L \rightleftarrows G \\
& \text { or } F^{\prime} \rightleftarrows F+L+G \quad F^{\prime} \rightleftarrows F+G \quad F^{\prime}+L \rightleftarrows F+G \\
& \text { or } F \rightleftarrows F^{\prime \prime}+L+G \quad F \rightleftarrows F^{\prime}+G \quad F+L \rightleftarrows F^{\prime \prime}+G \quad
\end{aligned}
$$

which we will call $A_{1}, B_{1}$, and $C_{1}$ respectively. We notice that the last reaction of series $A, B$ and $C$ agrees with the first reaction of series $A_{1}, B_{1}$ and $C_{1}$.

The above reaction series, as has been already stated, are only valid so long as the four-phase equilibrium is present in the vicinity of the minimum melting point or the maximum sublimation point; at a greater distance other reactions may occur besides the above mentioned ones. We will explain this with a single example and choose therefore fig. 1. If the system is found in the maximum sublimation point, bence the liquid in $D$ and the vapour in $D_{1}$, the reaction $F+F^{\prime \prime} \rightleftarrows G$ takes place. If now the system moves in a positive direction, hence the liquid from $D$ towards $c$ and the vapour from $D_{1}$ towards $c_{1}, G$ gets within the triangle $F F^{\prime} L$ causing the reaction $F+F^{\prime}+L \rightleftarrows G$ to take place. (Also see reaction series $A_{1}$ ).

If now the system moves farther in a positive direction, the point $G$ can arrive outside the triangle $F F^{\prime} L$, this, for instance, is the case with the system $F+F^{\prime}+L_{c}+G_{c_{1}}$.
The reaction $F+F^{\prime}+L \rightleftarrows G$ then becomes $F^{\prime}+L \rightleftarrows F^{\prime}+G$; by way of transition the three-phase reaction: $F^{\prime}+L \rightleftarrows G$ occurs. This is the case at the moment that the conjugation line liquidvapour passes through the point $F^{\prime \prime}$.
If the four-phase equilibrium moves still further in a positive drection, the point $L$ can arrive within the triangle $F F^{\prime} G$; the reaction $L \rightleftarrows \vec{F}+F^{\prime \prime}+G$ then takes place. By way of transition, at the moment that the conjugation line liquid-vapour passes through the point $F$, the three-phase reaction $L \rightleftarrows F+G$ appears.
On moving the four-phase equilibrium in a positive direction we thus get first the reaction series $A$ and $A_{1}$ followed by the reactions: $F^{\prime \prime}+L \rightleftarrows G ; F^{\prime \prime}+L \rightleftarrows \vec{\rightleftarrows}+G ; L \rightleftarrows F^{\prime}+G$ and $L \rightleftarrows F+F^{\prime}+G$. This latier reaction is the same as the first reaction in series $A$.

From all this it follows that in the system $F+F^{\prime \prime}+L+G$ many reactions are possible as a rule; in the vicmity of the minimum melting point, however, always one of the reaction series $A, B$ or $C$ occurs and in the vicinity of the maximum sublimation point one of the series $A_{1}, B_{1}$ or $C_{1}$.-

- Let us now consider the four points $F, F^{\prime}, S$ and $D_{1}$ situated on a straight line. In fig. 1 these lis in the order $F S D_{1} F^{\prime}$ or in the reverse order $F^{\prime} D_{1} S F$; in fig. 2 the order is $F S F^{\prime} D_{1}$ or $D_{1} F^{\prime} S F$; in fig. 3 it is $D_{1} F F^{\prime} S$ or $S F^{\prime \prime} F D_{1}$.

In all, we can distinguish 24 cases; as, however, each succession from the right to the left corresponds with a succession from the left to the right, there are only twelve types. If we replace the point $S$ of the liquidum curve by $L$ and the point $D_{1}$ of the vapour curve by $G$ we find:

- $\quad F F^{\prime} L G, \quad F F^{\prime} G L, \quad F^{\prime} F L G, \quad F^{\prime} F G L, \quad F L G F^{\prime}$, $F G L F^{\prime}, \quad F L F^{\prime} G, \quad F G F F^{\prime} L, \quad F^{\prime} L F G, \quad F^{\prime} G F L$, $L F F F^{\prime \prime} G$ and $X F^{\prime \prime} F G$.
We now allow the four-phase equilibrium to move in a positive durection starting from a point juṣt before the minimum melting point, to a point just behind the maximum sublimation point. To this movement belongs a definite reaction series which however, is dependent on the situation of the points $F, F^{\prime \prime}, S$ and $D_{1}$, in regard to each other, so that to each type belongs a definite reaction series. Each of these sermes commences of course, with one of the. series $A, B$ or $C$ and terminates with one of the series $A_{1}, B_{1}$ or $C_{1}$,

From a consideration of the different cases we can deduce the following table in which the different types and then correlated reaction series are united.

Type:

1) $F L G F^{\prime}$
2) $F G L F^{\prime}$
3) $F F^{\prime} L G$
4) $F F^{\prime} G L$
5) $F^{\prime} F L G$
6) $F^{\prime} F G L$
7) $F L F^{\prime \prime} G$
8) $F^{\prime \prime} L F G$
9) $\overrightarrow{F G} G^{\prime} F L$
10) $F^{\prime} G F L$
11) $L F^{\prime \prime} F G B ; F^{\prime} \rightleftarrows L+G ; F+F^{\prime} \rightleftarrows L+G ; F \rightleftarrows L+G ; C_{1}$
12) $L F F^{\prime} G C ; F \rightleftarrows L+G ; F+F^{\prime} \rightleftarrows L+G ; \quad F^{\prime} \rightleftarrows L+G ; B+$

The last reaction of $A$ beng the same as the first of $A_{1}$, the reaction series $A A_{1}$ consists of live reactons, two of which are three-phased. The same applies to the series $B B_{1}$ and $C C_{1}$. In the cases marked 7-10 each series consists of seven reactions of which three are three-phased; in the cases marked 10-12 each series consists of nune reactions, four of which are three-phased.

From the above table we also notice that if the liquidum point $I$ and the vapour point $G$ appear in direct succession (type 1-6) the reaction series consists of 5 reactions; if the points $L$ and $G$ are separated from each other by a solid phase the reaction series consists of 7 reactions (type 7-10) and if $L$ and $G$ are separated from each other by both solid phases (type 11-12) it consists of 9 reactions.
The reaction series appertaining to a definite type may be readuly dedaced from a chagram in which the points $F, F^{\prime}, S$ and $D_{1}$ are situated according to that assumed type. In fig. 1 they lie according to type 1 or $F L G F^{\prime}$, in fig. 2 according to type 7 or $F L F^{\prime} G$, in fig. 3 according to type 11 or $G F F F^{\prime \prime} L$. We now allow the fourphase equilibrium in these figures to move in a positive direction, starting from a point just before the minimum melting point, to a point just behind the maximum sublımation point. The liquid then traverses curve $a c$ from a point close to $S$ and situated between $S$ and $a$ to a point close to $D$ and situated between $D$ and $c$. The rapour then traverses curve $a_{1} c_{1}$ from a point situated close to $S_{1}$ and situated between $S_{1}$ and $a_{1}$ to a point close to $D_{1}$ and situated between $D_{1}$ and $c_{1}$,
If now we consider the situation of the four points $F, F^{n}, L$ and $G$ in regard to each other and the changes occurring in this system owing to the moving of the system, we notice that in fig. 1 occurs the reaction series 1 or $A A_{1}$ in fig. 2 the reaction series 7 and in fig. 3 the reaction series 11 .

The three-phase reactions $F \rightleftarrows L+G$ or $\vec{F}^{\prime} \rightleftarrows L+G$, which we find in the series 7-12 can only appear in exceptional circumastances; we shall see later that in this case the four-phase curve of the complex $F+F^{\prime}$ comes into contact with the three-phase curve of the compound $F$ or $F^{\prime \prime}$.

We will now consider more closely the $P, T$-curve of the fourphase equalibrium $F+F^{\prime}+L+G$ and for this take the relation $T \frac{d P}{d T}=\frac{\Delta W}{\Delta V}$.

As noticed previously this curve meets in the minimum melting
point $S$ the melting point curve $S d{ }^{\prime}$ ", and "in the maximum sublimation point $D$ the sublimation curve $\alpha^{\prime \prime} D$ of the complex $F+F^{\prime}$. These curves are indicated in fig $\frac{1}{}$ by the same letters.

If the system $F+F^{\prime \prime}+L+G$ is found in the minimum meltung point $S$ the reaction:

$$
F+F^{\prime} \rightleftarrows L \quad \text { or } \quad F^{\prime} \rightleftarrows F+L \quad \text { or } \quad F \rightleftarrows F^{\prime}+L
$$

takes place (Series $A, B$ or $C$ ). We always take these and the following reactions in the direction from the left to the right. As we always assume that in these reactions heat must be supplied for the formation of liquad from the solid substance, $\Delta W$ for each of these reactions is positive.

During the fusion or transformation the volume may, however, increase as well as decrease; $\Delta V$ can, therefore, be positive as well as negative. Here, we will call $\Delta V$ positive so that in agreement with fig. ${ }^{`} \pm, \frac{d P}{d T}$ is positive in the point. $S$ in case of the four-phase curve as well as of the meltng point line $S\left(l^{\prime \prime}\right.$.


Fig. 4.
We now consuder the equilibrium $F+F^{\prime}+L+G$ in a point $X$ (not drawn in the figure) on branch $L S$ in the immediate vicmity of the point $S$. The equilibrium has thus been shifted in the negative durection. From the reaction series $A, B$, and $C$, it follows that the reaction
$F+F^{\prime}+G \rightleftarrows L$ or $\quad F^{\prime}+G \rightleftarrows F+L$ or $\quad F+G \rightleftarrows B^{\prime \prime}+L$ now occurs. These differ from the previous three-phase reactions only in so far that in the first term only the vapour phase has been introduced. So long as the point $Y$ lies very close to $S$, only a very little quantity of vapour will take part in the reaction: $\Delta W$ and $\Delta V$ are, therefore, both still positive.
If, however $X$ gets removed from $S$ still further in the negative
direction, the quantity of vapour taking part in the reartion becomes greater. Now, at the same $P$ and $T$, a substance has in the gaseous condition a much larger volume than in the liquid or solid state; at a definite position of $X$ the small increase in volume that occurs at the formation of liquid will be just compensated by the condensation of the vapour taking part in the reaction. Let this be the case in the point $N$ of fig. 4. In this point $N$, therefore, $\Delta V=0$ so that the tangent stands vertically. The point $X$, thus traverses a curve as $S N$ in fig. 4 on which the pressure increases with a rising temperature.

If the point $X$ moves further in the negative direction $\Delta V$ becomes negative; $\Delta W$, however, is still positive. Hence, the point $X$ traverses a curve like $N M$ in fig. 4 on which the pressure increases with a falling temperature.

When, however, the point $X$ moves away further from $N$, the quantity of vapour taking part in the reaction accordingly increases. The quantity of heat generated at the condensation of this vapour will, therefore, also increase. This, in a definite point $M$ will now just compensate the heat required for the formation of liquid so that $\Delta W$ becomes $=0$. In the point $M$ the tangent is therefore horizontal.

On further moving the point $X$ in the negative direction $\triangle W$ becomes negative; $\Delta W$ and $\Delta V$ now being both negative the point $X$ will tiaverse a curve like $M L$ in fig. 4 on which with a falling temperature the pressure decreases likewise.

We now allow the ${ }^{-}$point $X$ to move away fiom $S$ as far as just past the point $D$ (fig. 4). The three-phase reaction :

$$
F+F^{\prime} \rightleftarrows L \text { or } F^{\prime} \rightleftarrows F^{\prime}+L \text { or } F \rightleftarrows F^{\prime}+L
$$

occuring in the point $S$ then appears in one of the reactions:

$$
F^{\prime}+F^{\prime}+L \rightleftarrows G \text { or } F^{\prime}+L \rightleftarrows F+G \text { or } F+L \rightleftarrows F^{\prime}+G .
$$

This transition takes place according to one of the reaction series 1-12 and depends on the situation of the points $F, F^{\prime \prime}, L$ and $G$ in regard to each other. As in each of these reactions $\Delta W$ and $\Delta V$ are positive the point $X$ will traverse a curve $S D R$ on which the pressure diminishes with a falling temperature.

If the point $X$ moves away further in a positive direction, other reactions may again take place as we have already demonstrated by a single example; hence exists the possibility that the curve $D R$ in its further progress changes its direction. We will refer to this later. From the above considerations follows: on moving in a positive direction the fourphase equilibrium $h^{\prime}+F^{\prime \prime}+L+G$ attains
successively a pressure and a temperature maximum, the minimum melting- and the maximum sublimation point.

We have assumed in the above considerations that, in the threephase reaction appearing in the point $S$, the rolume increases. If the volume decreases, the point $S$ arrives on the branch $M N$ of the four-phase curve and the melting point line $S\left(l^{\prime \prime}\right.$ proceeds from $S$ towards lower temperatures.

We have noticed above that the four-phase equilibrium $F+F^{\prime \prime}+L+G$ is represented in fig. 4 by points of the curve $L S D R$. On supply or withdrawal of heat or on change in volume one of the four three-phase equilibria:

$$
F+F^{\prime}+L, F+R^{\prime \prime}+G, F+L+G \text { or } F^{\prime}+L+G
$$

is formed from this equilibrium.
The question now arises: by which points of the $P, T$-diagram are these equilibria represented.

Let us take at the temperature $T_{x}$ and the pressure $P_{x}$ a correlated point $x$. of the curve $L S D R$. As we have already stated, to such a point applies the rule that we find:
to the right of $x$ the three-phase systems formed from the four-phase system ${ }^{`} F+F^{\prime}+L+G$ on suppls of heat ( $\Delta W>0$ ), to the left of $x$ those formed on withdrawal of heat ( $\Delta W<0$ ), above $x$ those formed with decrease in volume $(\Delta V<0)$ and below $x$ those formed with increase in volume ( $\Delta V>0$ ).

Here, the supply or withdrawal of leat musi take place at the consiani pressure $P_{a}$ and the change in volume at the constant temperature $T_{x}$.

In order to apply the above rule we must, of course, know the reaction to take place in the point $a$. Let us take as an example a four-phase complex belonging to type 1 so that the reaction series $A$ and $A_{1}$ appear.
Let us first take the point $x$ on the branch $L M$ (fig. 4). From series $A$ it follows that in this point the reaction $E+F^{\prime}+G \rightleftarrows L$ takes place; further we have noticed that in this reaction $\Delta V$ and $\triangle W$ are negative in the point $x$ (in the direction from the left to the right). We now easily find which three-phase equilibria are situated to the right or to the left of $x$ and which above or below that point. As this applies to all points of the branch $L M$ we find: at the right of and below branch $L M$ exists the system $F+F^{\prime \prime}+G$; at the left of and above this branch exist the three other systems: $F+F^{\prime \prime}+L, F+L+G$ and $F^{\prime \prime}+L+G$.
If we take the point $a$ on branch $M N$ (fig. 4 ) the reaction will still be $F+F^{\prime}+G \leftrightarrows L$, but $\Delta T$ is positive and $\Delta V$ negative. We now find: at the left of and below branch $M N$ exists the syso
tem $\dot{F}+F^{\prime \prime}+G$, at the right of and above this branch exist the three other systems.

If the point $x$ is situated on the branch $N S$ the reaction will stillbe the same, but $\Delta W$ and $\Delta V$ are both positive. Hence, we find the system $F+F^{\prime \prime}+G$ at the left of and above branch $N S$, the three other systems at the right of and below this branch.

If the point $x$ gets on the branch $S D$ a quite different reaction, namely $F^{\prime}+F^{\prime \prime} \rightleftarrows L+G$ takes place; in this reacton $\Delta V$ and $\Delta W$ are both positive. From this we deduce: at the lefl of and above branch $D S$ we find the systems $F+F^{\prime}+L$ and $F+F^{\prime}+G^{\prime}$; at the right of and below this branch we find the two other systems.

If the point $x$ gets on the branch $D R$ the reaction again changes and becomes $F^{\prime}+F^{\prime}+L \leftrightarrows G$ (see the last reaction of series $A_{1}$ ); $\Delta V$ and $\Delta W$ are both positive. From this we deduce: at the left of and above branch $D R$ we find the system $F+F^{\prime}+L$, at the right of and below this branch the three other systems.

- Above we have deduced the situation of the four three-phase systems in regard to the curve $L S D R$ in the assumption that the four-phase equilibrium belongs to type 1: if, however, the system appertains to one of the other types $2-12$ the situation may be found in the same manner.

When the four-phase equilibrium traverses the curve LSDR (fig. 4) one of the following three-phase reactions will occur in definite points.
a) $F+F^{\prime} \rightleftarrows L ; \quad F^{\prime} \rightleftarrows F+L ; F \rightleftarrows F^{\prime}+L$
b) $F+G^{\prime} \rightleftarrows G ; \quad F^{\prime} \rightleftarrows F+G ; F \rightleftarrows F^{\prime}+G$
c) $F \rightleftarrows L+G ; \quad F+L \rightleftarrows G ; \quad F+G \leftrightarrows L$
d) $F^{\prime \prime} \rightleftarrows L+G ; \quad F^{\prime}+L \vec{\rightleftarrows} G ; \quad P^{\prime \prime}+G \rightleftarrows L$.

In each of the reaction series 1-6 are found two of these threephase reactions; in each of the series 7-10 three, and in each of the series $11-12$ four of the same. The last two of the group $c$ and $d$ can only take place when the forr-phase equilibrinm moves away further from the point $S$ or from $D$.
Previonsly we already found:
If in the four-phase equilibrium a reaction of group $a$ takes place it finds itself in the minimum melting or conversion melting point of the complex $F+F^{\prime}$; in a $P, I$-diagram the four-phase curve then meets the melting point curve or the conversion curve of the complex $F+F^{\prime \prime}$ (Point $S$ in fig. 4).

If in the four-phase equilibrium appears a reaction of group $b$ it finds itself in the maximum sublimation or conversion sublimation'
point of the complex $F+F^{\prime \prime}$; in a $P, T$-diagram the four-phase curve then meets the sublimation curve of the complex $F+F^{\prime \prime}$ (Point $D$ in fig. 4).

Further we have:
If in the four-phase equilibrium occurs a reaction of group $c$ (or $d$ ) the four-phase curve meets in a P,T-diagram the three-phase or boundary curve of $F$ (or $F^{\prime \prime}$ ).
We may readily deduce this last property in the following manner. Suppose in a point $x$ appertaining to the temperature $T_{x}$ and the pressure $P_{x}$ of the four-phase curve there occurs a three-phase reaction of group $c$. If now we remove from the equilibrium $F+F^{\prime \prime}+L+G$ the compound $F^{\prime}$ we retain in the point $x$ the three-phase equilibrium $F+L+G$. As according to our assumption a reaction of group $c$ occurs between these three phases, they have such a composition that between them a phase reaction is possible. Now, as we have noticed previously, such an equilibrium $F+L+G$ is represented in a $P, T$-diagram by a curve that we have called the three-phase or boundary curve of $F$ ( $K F$ in fig. 3 (III); $m K F M$ in fig. 4 (IV). From this it follows that the boundary curve of the compound $F$ passes through the point $a$ of the four-phase curve.
$\dot{A s}$ the direction of both curves is determined by $T \frac{d P}{d T}=\frac{\Delta T}{\Delta V}$ and as in the point $x \Delta W$. and $\Delta V$ are the same for both curves, these curves must meet in the point $x$.

We may summarise the previous considerations as follows: if in a point $x$ of a four-phase curve occurs a three-phase reaction the four-phase curve in the $P, T$-diagram comes into contact with a three-phase curve appertaining to that reaction. To a reaction of group a appertains the melting point curve, to one of group $b$ the sublimation-curve of the complex $F+F^{\prime}$; to one of $c$ the boundary curve of $F$ and to one of $d$ the boundary curve of $F^{\prime \prime}$.

From the reaction series $1-12$ it appears that in each four-phase equilibrium occurs one reaction of group $a$ and one of group $b$. In harmony with our previous considerations it follows that each four-phase curve meets the melting-point curve and the sublimation curve of $F+F^{\prime}$. If now in a four-phase system occurs one of the series $7-10$ the four-phase curve meets the boundary curve of $F$ (series 8 and 10) or of $F^{v}$ (series 7 and 9); if one of the series 11 or 12 appears, it meets the two bomdary curves. These points of contact lie between the minimum melting and the maximum sublimation point of the carves coming into contact with each other,

If one of the reaction series $1-6$ occurs the curves $K F, K^{\prime} F^{\prime \prime}$
and $S D$ will be situated in regard to each other as in fig. 1 (VII); if series 7 or 9 appears $K^{\prime} F^{\prime}$ meets the curve $D S$; if 8 or 10 occurs $K F^{\prime}$ meets $D S$ and if 11 or 12 appears $K^{\prime} F^{\prime}$ as well as $K F$ meets. that curve.

As a rule the case drawn in fig. 1 (VII) and corresponding with 'series 1-6 is the one likely to occur. If, however, the minimum melting or the maximum sublimation point of the complex $F+F^{\prime}$ is situated but a very little lower, or somewhat higher, than the same points of one or of both compounds separately, $K F$ or $K^{\prime} F^{\prime}$ or both will then lie in the vicinity of $D S$ and contact may take place.

We now imagine drawn in the figs. 1,2 , or 3 the straight lines $a F$ and $a F^{\prime \prime}$; the first may be considered as being part of a rectilinear solution path of $F$, the second as a part of such a paih of $F^{\prime}$ under its own vapour pressure. We have noticed previously (communication IV) that the $P, T$-curves of these paths meet the melting point line of the compound in the minimum melting point. -We now imagine drawn, as'in fig. 1 (VII), the melting point lines $F d$ and $F d^{\prime}$ in fig. 4 also.

We now take on the four-phase curve $L S D R$ of fig. 4 a point corresponding with point $a$ of fig. 1-3 which we will also call $a$. From this point a the two $P, T$-curves of the solution paths of $\vec{P}$ and $F^{\prime}$ then proceed; the one meets the melting point line of $F$, the other that of $F^{\prime \prime}$ in the minimum melting point.

It is now evident that from each arbitrass point $X$ of the curve $L S D R$ in lig. 4 proceed two solution paths of which the one meets the melting point line of $F$ and the other the melting point line of $F^{\prime}$; in fig. 1 (VII) are drawn only the two paths proceeding from the point $S$.

The paths proceeding from an arbitrary point $X$ of the four-phase curve generally intersect this curve in $X$. Contact takes place if in the point $X$ occurs a reaction of group $c$ or $d$; in the first case the solution path of $F$, in the second case that of $F^{\prime}$ meets the four-phase curve in the point $X$.

We have seen previously (communication IV): if in a point $X$ of a solution pailh of $F$ a reaction is possible between the three plases it comes into contact in the point $X$ with the boundary curve of $F$. Previonsly we have deduced also: if in the point $X$ of a four-phase carve occurs a reaction of group $c$ it meets in the point $X$ the boundary curve of $F$. From this now follows: if in a point $X$ of a four-phase curve occurs a reaction of group $c$, the fourphase curve, the boundary curve of $F$ and the solution path of $F$ come into conlact with each other in the point $X$.

This may be also shown in the following mannor. The direction of the solution path of $F$ is determined by 5 (IV), that of the boundary curve by 16 (IV) and that of the four-phase curve by 8 .
If now between the phases occurs a reaction of group $c$ we get:

$$
\frac{y-\beta}{x-\alpha}=\frac{y_{1}-y}{x_{1}-a}=\frac{y_{1}-\beta}{x_{1}-\alpha} .
$$

. From this relation follows:

$$
\frac{M}{N}=\frac{x-\alpha}{x_{1}-x}
$$

so that 5 (IV) passes into 16 (IV).
With the aid of the above relation we readily find from (2) and (3) the formula 16 (VI), with which the above mentioned property is indicated.
(To be continued).

Physics. - "Further experiments with liquid helizm. H. On the galvanic resistance of pure metals etc. VII. The potential difference necessary for an electrical current through mercury below $4^{\circ} .19 \mathrm{~K}$." By Prof. H. Kameringen Onnes. (Continued.)
§ 11. Local nature of the loss of heat by a mercury thread enclosed in a glass capillary carrying a current, when the temperature sinks below $4^{\circ} .19 \mathrm{~K}$. While the supposition that the thread should accidentally consist of some other substance than mercury for a small part of its length, is in contradiction to the regularity of the potential phenomena, yet on the other hand the supposition that the mercury thread has a microresidual resistance similar to the ordinary resistance in OHm's law (therefore independent of the strength of current, see $\S 4$ ), gives rise to no less difficulties ${ }^{1}$ ). Such a microresistance proper to the mercury will be evenly distributed over the whole thread. If we calculate from the potential differences observed during the warming up at low temperatures and the strength of current to which they belong, the resistance of the thread under the conditions of the experiment, then we find that the thread, when the threshold value of the strength of current is only very slightly exceeded, must for a part of its length be partly heated distinctly above the vanishing point. Let us take for example the experiments

[^0]
[^0]:    ${ }^{1}$ ) Besides those mentioned in $\S 9$, the difficulties here treated also present themselves if we try to explain the polential phenomena by an even distribution of additive mixtureresistance.

