## Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

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Mathematics. - "General considerations on the curves of contact of surfaces with conts, with application to the lines of saturation and binodal lines in ternary systems." (Communicated by Prof. D. J. Korteweg and Prof. F. A. H. Schreinemakers).

## Introduction.

It is a known fact that in the study of the ternary solutions which for given temperature and pressure can be in equilibrium with a solid substance a great part is played by the curve of contact of the tangential cone of the $\zeta$-surface with a given point as vertex.
If namely we project the vertex of the cone and its curve of contact on the horizontal plane, then the projection of the curve of contact represents a ternary line of saturation, namely the serics of the solutions, which for assumed temperature and pressure are saturated with the solid substance indicated by the projection of the vertex of the cone.

The form of the line of saturation of a solid substance being thus determined by the form of the curve of contact of a cone, it was our aim to investigate which peculiarities this curve of contact could display in some points of a given surface and in particular of the $\zeta$-surface.

We choose as origin of the system of coordinates a point 0 of the surface. We assume the $X$ - and $Y$-axis in the tangential plane of the surface in point $O$.
For the equation of the surface in the vicinity of point $O_{\text {we can }}$ then write:
$z=c_{1} x^{2}+c_{2} x y+c_{3} y^{2}+d_{1} x^{3}+d_{9} x^{2} y+d_{3} x y^{2}+d_{4} y^{3}+e_{1} x^{4}+e_{2} x^{3} y+\ldots$ (1)
The equation of a langential plane in a point $x, y, z$ of this surface becomes:

$$
Z-z=(X-a) \frac{\partial z}{\partial x}+(Y-y) \frac{\partial z}{\partial y} .
$$

If we wish to let this tangential plane pass through a point $P(p . q)$ of the $X . Y$-plane, then we must have

$$
(p-x) \frac{\partial z}{\partial x}+(q-y) \frac{\partial z}{\partial y}+z=0
$$

If in this equation we substitnte the values of $z, \frac{\partial z}{\partial x}$ and $\frac{\partial z}{\partial y}$ out of '1) we get:

$$
\begin{align*}
& \left(2 e_{1} p+c_{2} q\right) x+\left(c_{2} p+2 c_{3} q\right) y+\left(3 d_{1} p+d_{2} q-c_{1}\right) x^{2}+ \\
+ & \left(2 d_{2} p+2 d_{3} q-c_{2}\right) x y+\left(d_{3} p+3 d_{4} q-c_{8}\right) y^{2}+ \\
+ & \left(4 e_{2} p+e_{2} q-2 d_{1}\right) x^{3}+\left(3 e_{2} p+2 e_{2} q-2 d_{2}\right) x^{2} y+ \\
+ & \left(2 e_{2} p+3 e_{4} q-2 d_{3}\right) x y^{3}+\left(e_{4} p+4 e_{5} q-2 d_{4}\right) y^{3}+\ldots=0=0 \tag{2}
\end{align*}
$$

The above form (2) is therefore the equation of the curve of contact of a cone touching the surface and having point $P(p \cdot q)$ as vertex.
We shall now distinguish three cases :
I. $O$ is not a parabolic point.
II. $O$ is a parabolic point.
III. $O$ is a point of osculation.

## 1. Point $O$ is not a parabolic point.

As $O$ is an elliptic or a hyperbolic point, it follows that $c_{1} c_{3}-\frac{1}{4} c_{2}^{2} \geq 0$. We now assume the line $O P$ as $X$-axis, so that $q=0$. We can now distinguish two cases according to $O P$ being an asymptote of the indicatrix or not.
$I_{A}$. The line $O P$ is not an asymptote of the indicatrix.
We assume $O P$ as $X$-axis and the conjugate diameter of the indicatrix as $Y$-axis; so $q=0$ and $c_{2}=0$. From (2) follows then:

$$
\begin{equation*}
2 c_{1} p x+\left(3 d_{1} p-c_{2}\right) x^{2}+2 d_{2} p x y+\left(d_{3} p-c_{3}\right) y^{2}+\cdots=0 . \tag{3}
\end{equation*}
$$

The curve of contact tonches therefore the $Y$-axis in. point 0 . As the $\lambda$-axis (the line $O P$ ) and the $Y$-axis are conjugate diameters of the indicatrix, it follows that the line $O P$, connecting the vertex $P$ of a cone with a point $O$ of its curve of contact, and the tangent in point $O$ to this curve of contact are conjugate diameters of the indicatrix of point 0 .
In general the curve of contact in the vicinity of point $O$ is of finite curvature and determined by:

$$
\begin{equation*}
2 c_{1} p x+\left(d_{3} p-c_{s}\right) y^{2}=0 . . . . . . . \tag{4}
\end{equation*}
$$

If $p$ is chosen in such a way that $d_{3} p-c_{3}=0$ then the equation is

$$
\begin{equation*}
2 c_{1} p w+\left(e_{4} p-2 d_{4}\right) y^{3}=0 \tag{5}
\end{equation*}
$$

so that the curve of contact has a point of inflection in point $O$.
Several ternary lines of saturation with one or more points of inflection are known. We find e.g. on the line of saturation of the
(512)
nituil of ambric acid in the system: water -alcohol - nitril of ambric acid ${ }^{2}$ ) at $4^{\circ} .5$ two points of inflection.
$\Lambda_{B_{-}}$. The line $O P$ is an asymptote of the indicatrix.
1-1

- We assume ' $O P$ as $X$-axis, the other asymptote as $Y$-axis so that $q=0, \cdot c_{1}^{\prime}=0$ and $c_{s}=0$.

Then the curve of contact is determined by:

$$
c_{2} p y+3 d_{1} p a^{3}+\left(2 d_{2} p-c_{3}\right) w y+d_{8} p y^{2}+\ldots=0 \quad . \quad \therefore(6)
$$

So the generatrix $O P$ of the cone touches the curve of contact in $\left.0^{\circ}\right)$.

We have here thus the case that through point $P$ we can draw a tangent to the line of saturation of the solid substance represented by $P$. This point of contact, however, being a byperbolic point, this case can appear only on the unstable part of the line of saturation.

## 1I. Point $O$ is a parabolic point.

As $O$ is a parabolic point, it follows that $c_{1} c_{3}-\frac{1}{4} c_{2}{ }^{2}=0$. Point $O$ lies thus on the parabolic or spinodal line of the surface.
$\int \dot{I}_{A}$. The line OP does not coincide with the direction of the awis of the parabola.


Fig. 1.

- In fig. 1 let $a O b$ be the spinodal line, $c O d$ the section of the tangential plane in $O$ with the surface; $O Y^{\prime}$ is the tangent in the cusp 0 of this section and at the same time the direction of the axes.

We now assume $O P$ as $X$ - and $O Y$ as $Y$-axis, so that $q=0, c_{2}=0$ and $c_{3}=0$.
Then we find for the equation of the curve of contact:

$$
2 c_{1} p x+\left(3 d_{1} p-c_{1}\right) x^{2}+2 d_{2} p x y+d_{3} p y^{2}+\ldots+0
$$

$0 r^{\prime}$ :

$$
\begin{equation*}
2 c_{1} x+d_{3} y^{2}=0 \tag{7}
\end{equation*}
$$

- So the curve of contact touches in $O$ the line $O Y$. The direction of the curve of contact in the vicinity of its point of intersection with the . spinodal. line-is therefore independent of the position of the vertex $P$ of the cone.

[^0](513)

We can express this property also as follows: all the'lines of saturation passing- through a point $O^{\prime \prime}$ of the spinodal line touch each other in this point $O$.

We have drawn the curve $c O d$ in fig. 1 in such a way that the tangent $O Y$ intersects the spinodal line in $\cdot O$. That this is true in general is evident from the following.
The equation of the spinodal line is:

$$
\begin{equation*}
\frac{\partial^{2} z}{\partial \cdot x^{2}} \cdot \frac{\partial^{2} z}{\partial y^{2}}-\left(\frac{\partial^{2} z}{\partial x \partial y}\right)^{2}=0 \tag{8}
\end{equation*}
$$

If now we calculate out of (1) the values of $\frac{\partial^{2} z}{\partial x^{2}}, \frac{\partial^{2} z}{\partial y^{2}}$ and $\frac{\partial^{2} z}{\partial x \partial y}$, after having put there $c_{2}=0$ and $c_{3}=0$, we' find for (8):

$$
\left(2 c_{1}+6 d_{1} x+2 d_{2} y+\ldots\right)\left(2 d_{3} x+6 d_{4} y+. .\right)-\left(2 d_{2} x+2 d_{3} y+\ldots\right)^{2}=0 .
$$

As $c_{1}$ is not'zero, we find by first approximation for the equation of the spinodal line:

$$
\begin{equation*}
2 d_{3} x+6 d_{4} y=0 . \tag{9}
\end{equation*}
$$

From this ensues therefore that the tangent in 0 to the spinodal line $a O b$ forms an angle with the line $, O Y, \cdot$ unless $d_{4}=0$.
If however $d_{4}=0$, then it follows from (9) that the tangent in $O$ to the spinodal line coincides with the line $O Y$. As then at the same time

$$
c_{2}=0, c_{3}=0 \text { and } d_{4}=0
$$

point 0 under consideration is a plaitpoint ${ }^{1}$ ?. Hence: only in a plaitpoint the spinodal line and the curve of contact of a cone can touch each other.

## $1 l_{A . x}$. Point $O$ is a plaitpoint.

As $c_{2}=0, c_{3}=0$ and $d_{4}=0^{\circ}$ ), the equation of the curve of contact becomes

$$
2 c_{1} v+d_{3} y^{2}+\ldots=0 \text {. . . . . . , }(10)
$$

So all the curves of coniact passing through the plaitpoint touch each other there and their curvature is independent of the distance from the vertex $P$ of the cone to the plaitpoint.
That this curvature is also independent of the direction of the line $O P$ and therefore quite independent of the situation of $P$ will soon be evident.
From (8) follows for the equation of the spinodal line:

[^1]\[

$$
\begin{gathered}
\left(2 c_{1}+6 d_{1} x+2 d_{2} y+. .\right)\left(2 d_{8} x+2 e_{3} x^{2}+6 e_{4} x y+12 e_{5} y^{2}+. .\right)- \\
-\left(2 d_{9} x+2 d_{8} y+3 e_{2} x^{2}+4 e_{3} x y+3 e_{4} y^{2}+. .\right)^{2}=0
\end{gathered}
$$
\]

or at first approximation for the equation of that line in the vicinity of the plaitpoint:

$$
\begin{equation*}
4 c_{1} d_{3} x+\left(24 c_{1} e_{5}-4 d_{8}^{2}\right) y^{2}=0 \tag{11}
\end{equation*}
$$

The equation of the binodal line in the vicinity of point $O$ is ${ }^{1}$ :

$$
\begin{equation*}
d_{3} a+2 e_{5} y^{2}=0 \tag{12}
\end{equation*}
$$

We now write (10), (11) and (12) in such a way that the coefficient of $x$ is the same for these three; so we find:

$$
\begin{align*}
& \text { for the curve of contact: } 2 c_{1} d_{d} x+d_{8}^{2} y^{3}=0 .  \tag{13}\\
& ", \quad \text { spinodal line: }{ }^{\circ} 2 c_{2} d_{3} x+2\left(6 c_{2} e_{5}-d_{3}^{2}\right) y^{2}=0 .  \tag{14}\\
& " \# \text { binodal line: } \quad 2 c_{1} d_{3} x+4 c_{1} e_{5} y^{2}=0 . \tag{15}
\end{align*}
$$

We shall now restrict ourselves, as only this is liable to realisation, to a plaitpoint of the first kind ${ }^{1}$ ), so that

$$
\begin{equation*}
4 c_{1} e_{5}-d_{3}{ }^{2}>0 \tag{16}
\end{equation*}
$$

thus also $c_{1} e_{5}>0$ and $6 c_{1} e_{5}-d_{3}{ }^{3}>0$.
From this ensues immediately that in the vicinity of the plaitpoint the curve of contact, the spinodal line, and the binodal line are curved in the same direction.

Out of (16) we can deduce:

$$
\begin{equation*}
2\left(6 c_{1} e_{5}-d_{\mathrm{s}}{ }^{2}\right)>4 \hat{c}_{1} e_{\mathrm{s}}>d_{\mathrm{s}}{ }^{2} . \tag{17}
\end{equation*}
$$

If we call the radii of curvature of the spinodal line, the binodal line, and the curve of contact $R_{s}, R_{b}$, and $R_{r}$, it follows from (13), (14) and (15):

$$
\begin{equation*}
\left.R_{s}=\frac{c_{1} d_{\mathrm{s}}}{\left(12 c_{2} e_{\mathrm{s}}-2 d_{3}{ }^{2}\right) \sin \theta}, R_{b}=\frac{c_{1} d_{3}}{4 c_{1} e_{3} \sin \theta}, R_{r}=\frac{c_{1} d_{3}}{d_{3}^{2} \sin \theta}\right\} \tag{18}
\end{equation*}
$$

where $\theta$ represents the angle between the line $O P$ and the tangent in the plaitpoint to the binodal line.

In connection with (17) follows from this that the spinodal line has the smallest radius of curvature and the curve of contact the largest.

From (18) we can furthermore deduce:

$$
\begin{equation*}
\frac{2}{R_{f}}=\frac{3}{R_{b}}-\frac{1}{R_{s}} \tag{18a}
\end{equation*}
$$

Out of this relation it is evident that $R_{r}$ is also independent of the direction of the line $O P$; for $R_{b}$ and $R_{s}$ are quantities, which depend exclusively on the shape of the surface at point $O$.

[^2]If we introduce instead of the radii of curvature $R$ the curvatures $K$ we find

$$
2 K_{1}=3 K_{b}-K_{s} \text {. . . . . . . }\left(18^{b}\right)
$$

For the rest the curve of contact has nothing remarkable in the vicinity of the plaitpoint except that its course there is in a high degree independent of the situation of the vertex $P$ of the cone, if but this vertex is not too close to the plaitpoint or not too close to the tangent to the spinodal line in the plaitpoint.


Fig. 2.

In fig. $2 s O s^{\prime}$ represents the spinodal line, $b O b^{\prime}$ the binodal line, and $r O r^{\prime}$ the curve of contact of the cone $P$, or in other words the line of saturation of the solid substance $P$. As ensues out of the curvatures ( $18^{a}$ and $18^{\prime}$ ) of these three lines, these must have a position with respect to each other as in fig. 2.
If we draw in this figure a line mnp parallel to and in the vicinity of $O P$, then $n p$ must be equal to $2 m \mathrm{~m}$. If namely we calculate $x_{r}, x_{s}$, and $x_{b}$ out of (13), (14) and (15) we find for a same value of $y$ :

$$
2\left(x_{b}-x_{r}\right)=x_{s}-x_{b} .
$$

In so far as the binodal line has been drawn in fig. 2 the conjugated pairs of fluids represented by it are metastable; they all break up into the solid substance $P$ and a solution of the line of saturation $r O^{\prime}$.
In fig. 3 the point $P$ lies on the other side of the tangent in $O$ as in fig. 2. Line $r O r^{\prime}$ is the line of saturation, $b O b^{\prime}$ the binodal line; the spinodal line has not been drawn.
In the vicinity of the plaitpoint the line of saturation must be curved, as has been represented in fig. 3, in the same direction as the binodal line. In its furiher course two or more


Fig. 3. points of inflection can of course appear. If e.g. $P$ is a ternary solid substance, so that the line of saturation is a curve enclosing point $P$, then at least two points of inflection must appear, as has been assumed in fig. 3.

If now we change the temperature or the pressure, then the $\zeta$ surface changes according to position and form; point $P$ rises and falls. Now the binodal line and the line of saturation of course also change their form.


Fig. 4.

We now imagine temperature or pressure changed a little in such a direction that the two curves of fig. 3 move away from each other. We then obtain fig. 4, in which the line of saturation has been represented but partly. " It is clear that it now likewise has to show two points of inflection. If both curves move still farther from each other, thên of course both points of inflection can vanish.
If we change temperature or pressure in opposite direction, then we cause both curves of fig. 3 to overlap somewhat. We..thèn find fig. 5 , in which $b a a^{\prime} b^{i}$ represents the binodal line and raa'r $r^{\prime}$ the line of saturation of $P$.

On the part $\alpha \alpha \alpha^{\prime}$ not represented of the binodal line lies the plaitpoint; the part $\alpha a^{\prime}$ of the line of saturation lies between the part $a a^{\prime}$ of the binodal line and the straight line $\alpha a^{\prime}$. The line of saturation of $P$ is only partly drawn.

As long as $a$ and $a^{\prime}$ lie but close enough to each other, $a r$ and $a^{\prime} r^{\prime}$ must lie as in 'fig. ' 5 , they must run namely from $a$ and $a^{\prime}$ to that side of line $a a^{\prime}$, where the stable part of the


Fig. 5.
binodal line lies. In their further course the linest $a r$ and ${ }^{\prime} a^{\prime} r$ can of course intersect the line $a a^{\prime}$.

We now have besides a series of solutions saturated witfi' $P$ ( $a r^{3}$ and $a^{\prime} b^{\prime}$ ) and a series of conjugate solutions ( $a b$ and $a^{\prime} b^{\prime}$ ) also a' conjugate pair of fluids $L_{a}+L_{a^{\prime}}$ saturated with solid $P$.

As the pieces $a a^{\prime}$ left out of the binodal line and of the line of saturation lie inside the three-phase-triangle $P a a^{\prime}$, the fluids represented by, them separate into $P+L_{a}+L_{a^{\prime}}$ :

Examples of lines of saturation with two points of inflection, between which 'a curvature in the same direction as the 'binodal' line, we find e.g. in the system ${ }^{1}$ ): water-Agi $\mathrm{O}_{3}$ ethylene cyanide.

At $\pm 11^{\circ}$ the line of saturation of $2 \mathrm{C}_{2} \mathrm{H}_{4}(\mathrm{CN})_{2} \cdot \mathrm{AgNO}_{3} \cdot \mathrm{H}_{2}^{\prime} \mathrm{O}^{\prime}$ touches the binodal line in its plaitpoint and two points of inflection' appear as in fig. 3.

With a rise of temperature both lines move away 'from eách' other ; the lines of saturation determined experimentally at $12^{\circ}, 20^{\circ}$, and $25^{\circ}$ show distinctly the type of fig. 4.

[^3]

Fig. 6

If we lower the temperature below $11^{\circ}$, then the isotherins in the vicimty of the three-phase-triangle show a form as in fig. 5. Lines of saturation are also known which turn in their whole course their concave side to the platpoint of the binodal line; they have a form as $r r^{\prime}$ in fig. 6.

In the system ${ }^{1}$ ) water $(C)$--ether $(A)$-malonic acid $(P)$ such a line of saturation and binodal line are determined at $15^{\circ}$.
In the system ${ }^{2}$ ): water ( $C^{\prime}$ ) - ethylene cyanide ( $A$ ) -- benzore acid $(P)$ we find above $51^{\circ}$ likewise ssotherms as in fig. 6 . When lowerng the temperature the two curves of fig. 6 approach each other; at $51^{\circ}$ the line of saturation $r r^{\prime}$ of the benzoic acid touches the binodal line in its plattpoint $O$. At still lower temperatures a three-phase-triangle appears and the isotherms in the vicinity of that triangle show a form as in fig. 5.

Also in the systems ${ }^{1}$ ): water-phenol-alkal lines of saturation appear of the type as m fig. 4.
$11_{\Delta}$. The line OP has the direction of the axis of the parabola.
We assume $O P$ as $Y$-axis, then $p=0, c_{2}=0$ and $c_{3}=0$. So the equation of the curve of contact becomes:

$$
\begin{equation*}
\left(d_{2} q-c_{1}\right) \cdot v^{2}+2 d_{3} q x y+3 d_{4} q y^{2}+\ldots=0 \tag{19}
\end{equation*}
$$

So the curve of contart has in point $O$ a node, therefore it consists, as is drawn in fig. 8 , of two intersecting branches rad and $r^{\prime} a b$.

By a variation of parameter (on the $\zeta$-surface temperature and pressure come into consideration for this) out of fig. 8 are formed fig. 7 and fig. 9 . So fig. 8 is the transition form between fig. 7 and fig. 9.


Fig. 7.


Fig. 8.


Fig. 9.
${ }^{1}$ ) E. A. Klobbie. Z. f. Phys. Chem. 24. 625.
${ }^{2}$ ) F. A. H. Schreincmakcrs. Z f. Phys. Chem. 26. 249 (1898).
1roceedings Royal Acad. Amsterdam. Vol. XIV.

In fig. $7 \mathrm{ss} s^{\prime}$ represents the spinodal line; rab and $r^{\prime} e d$ are two branches of the curve of contact having in $a$ and $e$ a, tangent passing through point $P$. In these points $a$ and $e$ we have the case considered sub $l_{B} ; a$ and $e$ lie therefore both on the hyperbolically curved part of the surface.

If we pursue the branches $a b$ and ecl, these can of course pass into each other ${ }^{1}$ ); in fig. 7 this continuation is represented by the dotted curve bcd.

In fig. 9 the curve of contact consists of the two branches $r r^{\prime}$ and abcd, separated from each other by the spinodal line $s s^{\prime 2}$ ).

The equation (19) can, however, also represent an isolated point; the curve of contact then consisis of a single isolated point, lying on the spinodal line. For a small change in parameter this point then vanishes or a closed curve of contact is generated.

Inversely the closed curve of contact abcd of fig. 9 can thus contract so as to disappear in a point of the spinodal line.

To investigate whether the curve can possess other nodes or isolated points (in ordinary not conical points), we cause the $Y$-axis to coincide with $O P$. This is of course always possible and then we have $p=0$.

From (2) follows now as condition for a node $c_{2} q=0$ and $2 c_{3} q=0$. So we find:

$$
c_{2}=0 \quad c_{2}=0 \text { and therefore also } c_{1} c_{3}-\frac{1}{4} c^{2}{ }_{2}=0 .
$$

This is just the condition for the generation of case $I I_{B}$. So we find the nodes and isolated points only in case $I_{B}$, except of course in the points of osculation which can be regarded as a special case of it, where $c_{1}=0$.

So we can say:
"Nodes and isolated points of the curve of contact always lie on the spinodal line."

There would be an exception only if point $P$ were on the surface itself; then of course there would always be in that place an isolated point or node; this however we do not discuss.

$$
1 I_{B x} . \quad \text { Point } O \text { is a plaitpoint. }
$$

We assume (fig. 10) $O P$ as $Y$-axis so that besides $\downarrow \approx=0, c_{2}=0$ and $c_{3}=0$, we find also $d_{4}=0^{3}$ ).

[^4](519)


Fig. 10.

$$
\begin{equation*}
A x^{2}+B x y+C x^{3}+D x^{2} y+E x y^{3}+F y^{3}+\ldots=0 \tag{20}
\end{equation*}
$$

To satisfy this by

$$
x=k y^{2}
$$

we must have $B l+F=0$. From this ensues now, as $B=2 d_{\mathbf{a}} \mathcal{I}$ and $F=4 q e_{\mathrm{a}}$ :

$$
\begin{equation*}
x=--\frac{2 e_{5}}{d_{3}} y^{2} \tag{21}
\end{equation*}
$$

thus reproducing the equation (12) of the binodal lire in the yicinity of the platpoint.

Therefore the curve of conlact coincides in the vicinity of the plaitpoint with the binodal line.

This coincidence does not hold for the higher terms, as is natural and as is shown still more clearly by the following.

We put namely:

$$
x=k y^{2}+m y^{3}
$$

and we substitute this value in (20). As will immediately become evident, we must include in (20) still the term $y^{4}$. We write for it $G y^{4}$.

So we find:

$$
(B k+F) y^{3}+\left(A k^{2}+B m+E k+G\right) y^{4}+\cdots=0 .
$$

From this ensues:

$$
\begin{equation*}
m=-\frac{A / k^{2}+E k+G}{B}: \ldots . \tag{22}
\end{equation*}
$$

Now follows out of (2): $A=d_{2} q-c_{1}, B=2 d_{3} q, E=3 e_{4} q-2 d_{3}$. If we calculate the coefficient $G$ of $y^{4}$ in (2) we find:

$$
G=\left(f_{b} p+5 f_{\mathrm{f}} q-3 e_{6}\right),
$$

so here, as $p=0$ :

$$
G=5 f_{0} q-3 e_{6}
$$

So we find, if we put for the curve of contact $m=m_{1}$ :

$$
\begin{equation*}
m=\frac{\left(c_{1}-d_{2} q\right) \frac{4 e_{5}{ }^{2}}{d_{3}{ }^{2}}+\left(-2 d_{3}+3 e_{4} q\right) \frac{2 e_{5}}{d_{3}}+3 e_{5}-5 f_{0} q}{2 d_{3} q} \tag{23}
\end{equation*}
$$

For the second term $m_{0} y^{3}$ of the binodal line we have: ${ }^{1}$ )

$$
\begin{equation*}
m_{b}=\frac{2\left(e_{\mathrm{e}} e_{\mathrm{s}}-d_{\mathrm{s}} f_{\mathrm{b}}\right)}{d_{\mathrm{s}}^{2}} \tag{24}
\end{equation*}
$$

so that the curve of contact and the binodal line differ in the term $y^{3}$. We now write:

$$
\begin{aligned}
& x_{1}=k y^{2}+m_{2} y^{3}-\ldots \\
& x_{b}=k y^{2}+m_{b} y^{3}+\ldots
\end{aligned}
$$

from which ensues:

$$
\begin{equation*}
x_{r}-v_{b}=\left(m_{r}-m_{b}\right) y^{3}+. \tag{25}
\end{equation*}
$$

Out of (25) it is evident, that the linodal line $b O b^{\prime}$ and the curve of contact $r\left(r^{\prime}\right.$ must have with respect to cach other a position as in fig. 10. In this figure the part $r O$ of the curve of contact has been drawn outside, the part $r^{\prime} O$ inside the binodal line.
If we calculate with the help of (23) and (24) $m_{2}-m_{b}$ we then see that the sign of this difference depends on $q$, thus on the position of $P$. It is therefore also possible that for the same surface $r O$ lies inside and $r^{\prime} O$ outside the binodal line.

The curve of contact:

$$
n=-\frac{2 e^{5}}{d_{3}} y^{2}+\cdots
$$

and the spinodal line (11):

$$
x=-\frac{6 c_{1} e_{5}-d_{3}{ }^{2}}{c_{1} d_{3}} y^{2}+\ldots
$$

differ already in the coefficient of $y^{2}$. Hence for a plaitpoint of the first kind the curve of contact will always fall as in fig. 10, just like the binodal line, on the outer side of the spinodal line.

As we have seen above the curve of contact consists of two branches intersecting in the plaitpoint; one is the branch rOr ${ }^{\prime}$, considered above, the other the branch $r_{1} O r_{1}{ }^{\prime}$.

lig. 11.


Fig. 12.

If in fig. 10 we restrict ourselves to that part of the lines representing stable conditions, we find fig. 11. Also the case represented

[^5]in fig. 12 can of course appear, so that the binodal line vanishes because it falls inside the sector $P O r^{\prime}$.

Remarkable in both cases is that the stable part of the line of saturation of $P$, although it represents an unbroken series of solutions, yet shows a discontinuity. This makes its appearance in the critical solution saturated with solid $P$.

## III. Point $O$ is a point of osculation.

As in a point of osculation we have $c_{1}=0, c_{2}=0$ and $c_{3}=0$, we get from (2) for the equation of the curve of contact:

$$
\left(3 d_{1} p+d_{2} q 1 x^{2}+\left(2 d_{2} p+2 d_{3} q\right) x y+\left(d_{2} p+3 d_{4} q\right) y^{2}+\ldots=0\right.
$$

or if we make the $X$-axis to coincide with $O P$ :

$$
\begin{equation*}
3 d_{1} x^{2}+2 d_{2} x y+d_{3} y^{2}+\ldots=0 . \tag{26}
\end{equation*}
$$

So the curve of contact consists either of an isolated point or it shows in $O$ a node. From (26) it is evident that the directions of the two tangents are independent of the distance from point $P$ to point $O$; they depend only on the direction of the line $O P$.

The above-mentioned property that the curve of contact and the binodal line are curved in the same direction in the vicinity of the plaitpoint ( $\left[I_{\Delta v}\right.$ ) caused us to surmise that this also would be the case with a second branch of the binodal line, should such a one pass through the plaitpoint ${ }^{1}$ ).

This surmise can be affirmed in the following way and it can also be shown that the curvation of such a branch corresponds entirely to that of the curves of contact passing through the plaitpoint.

To that end we assume again as $Y$-axis the
 tangent to the spinodal and the binodal line of the plaitpoint $O_{1}$ (fig. 13); for the $X$-axis we choose the line of conjugation $O_{1} O_{2}$ and we put $O_{1} O_{2}=p$.

The tangential plane in a point $x_{1}, y_{1}, z_{1}$ in the vicinity of $O_{1}$ is:

$$
Z-z_{1}=\left(X-u_{1}\right) \frac{\partial \tilde{z}_{1}}{\partial x_{1}}+\left(Y-y_{1}\right) \frac{\partial z_{1}}{\partial y_{1}},
$$

the one in a point $x_{2}, y_{2}, z_{2}$ in the vicinity of $O_{2}$ is:

$$
Z-z_{2}=\left(X-v_{2}\right) \frac{\partial z_{2}}{\partial u_{2}}+\left(Y-y_{2}\right) \frac{\partial \grave{z}_{2}}{\partial y_{2}}
$$

[^6]The condilions that $x_{1}, y_{1}, z_{1}$ and $x_{2}, y_{3}, z_{2}$ are conjugated points thus become:

$$
\begin{array}{r}
\frac{\partial z_{1}}{\partial x_{1}}=\frac{\partial z_{2}}{\partial x_{2}} \cdot \cdots \cdot \cdot \cdot . \cdot . \cdot \\
\frac{\partial z_{1}}{\partial y_{1}}=\frac{\partial z_{2}}{\partial y_{2}} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \\
v_{\cdot} \cdot \frac{\partial z_{1}}{\partial x_{1}}+y_{1} \frac{\partial z_{1}}{\partial y_{1}}-z_{1}=v_{2} \frac{\partial z_{2}}{\partial x_{2}}+y_{2} \frac{\partial z_{3}}{\partial y_{2}}-\tilde{z}_{2} \cdot \cdot \tag{29}
\end{array}
$$

In consequence of the choice of the $Y$-axis we find:

$$
z_{1}=c_{1} x_{1}{ }^{2}+d_{1} x_{1}{ }^{3}+d_{2} x_{1}{ }^{2} y_{1}+d_{3} v_{1} y_{1}{ }^{2}+e_{1} v_{1}{ }^{4}+\ldots
$$

If we put $x_{2}=p+\xi_{2}$, so that $\boldsymbol{\xi}_{2}$ is a small quantity we have:

$$
z_{2}=c_{1}^{\prime} \xi_{2}{ }^{2}+c_{2}^{\prime} \xi_{2} y_{\mathrm{s}}+c_{3}^{\prime} y_{2}{ }^{2}+\ldots \ldots
$$

We now write the equations (27) (28) and (29) in full; we then directly leave out the terms which are certainly small with respect to those written, down, setting aside of what order $x_{1} y_{1} \xi_{2}$ and $y_{2}$ will prove to be with respect to each other. We then find:

$$
\begin{align*}
2 c_{1} v_{1}+d_{3} y_{:}^{3}+\ldots=2 c_{1}^{\prime} \xi_{2}+c_{2}^{\prime} y_{2}+\ldots . & .  \tag{27}\\
d_{2} v_{1}{ }^{2}+2 d_{3} v_{1} y_{1}+4 e_{5} y_{1}^{3}+\ldots=c_{2}^{\prime} \xi_{2}+2 c_{2}^{\prime} y_{2}+\ldots & \text { (27) }  \tag{}\\
c_{1} x_{1}^{2}+2 d d_{3} v_{1} y_{1}{ }^{2}+3 e_{5} y_{1}^{4}+\ldots=2 p c_{1}^{\prime} \xi_{2}+2 c_{2}^{\prime} y_{2}+\ldots & \text { (29) } \tag{29}
\end{align*}
$$

If we solve out of (27)' and (28)' $\xi_{2}$ and $y_{2}$ at first approximation we find:

$$
\xi_{2}=\alpha v_{1}+\beta y_{1}{ }^{2} \text { and } y_{2}=a^{\prime} x_{1}+\beta^{\prime} y_{1}{ }^{2}
$$

where $\alpha, \dot{\beta}, a^{\prime}$ and $\beta^{\prime}$ have definite values.
From this ensues that $\xi_{2}$ and $y_{2}$ will be of the same order of magnitude as $x_{1}$ and $y_{1}{ }^{2}$, when namely those two correspond in order. If on the contrary $x_{1}$ and $y_{1}{ }^{2}$ are of different order, then $\xi_{2}$ and $y_{3}$ must be of the lowest order as one of them (namely $x_{1}$ or $y_{1}{ }^{2}$ ).

From (29)' however ensues that $2 p c_{1}^{\prime} \xi_{2}+p c_{2} y_{2}$ and so also $2 c_{1}^{\prime} \xi_{2}+c_{2}^{\prime} y_{2}$ are of higher order than $x_{1}$ or $y_{1}{ }^{2}$ or both; hence out of (27)' may be concluded at first approximation:

$$
\begin{equation*}
2 c_{1} x_{1}+d_{3} y_{1}{ }^{2}=0 \tag{30}
\end{equation*}
$$

The equation of the branch $b O_{1} b^{\prime}$ of the binodal line (fig. 13) is therefore represented at first approximation by (30). This equation (30), however, corresponds entirely to (10) representing a curve of contact which touches the binodal line $a O_{1} a^{\prime}$ (fig. 13) in the plaitpoint.

In an entirely similar way as in $\left[I_{A . y}\right.$ we can now deduce:
"an accidental branch of a binodal line passing through a plaitpoint is in this point always curved in the same direction as the binodal line to which the plaitpoint belongs."

Between the radii of curvature $\mathcal{R}_{b}, l_{R_{b}}$ and $R_{s}$ exists of course also the relation

$$
\frac{2}{R_{\iota}^{\prime}}=\frac{3}{R_{b}}-\frac{1}{R_{s}}
$$

in which $R_{b}$ represents the radius of curvature of the binodial line to which the plaitpoint belongs and $R_{b}^{\prime}$ the radius of curvature of the accidental branch of the binodal line passing through the plaitpoint.

We now substitute in (28)' and (29) :

$$
v_{1}=-\frac{d_{3}}{2 c_{1}} y_{1}^{2}
$$

and we find:

$$
\begin{align*}
& c_{2}^{\prime} \xi_{2}+2 c_{3}^{\prime} y_{2}=\frac{4 c_{1} e_{5}-d_{3}{ }^{2}}{c_{1}} y_{1}^{3}+\ldots . .  \tag{31}\\
& 2 c_{1}^{\prime} \xi_{2}+c_{2}^{\prime} y_{2}=\frac{3\left(4 e_{1} e_{5}-d_{3}^{2}\right)}{4 p c_{2}} y_{2}{ }^{4}+\ldots . \tag{32}
\end{align*}
$$

From this now follows:

$$
\begin{equation*}
\left(c_{3}^{\prime} \xi_{3}+2 c_{3}^{\prime} y_{3}\right)^{4}=a\left(2 c_{1}^{\prime} \xi_{2}+c_{2}^{\prime} y_{2}\right)^{3} \cdot . \quad . \tag{33}
\end{equation*}
$$

in which:

$$
\alpha=\frac{64}{27} \cdot \frac{4 c_{1} e_{5}-d_{3}{ }^{3}}{c_{1}} \cdot p^{3} .
$$

The equation (33) represents at approximation the curve $c O_{2} c^{\prime}$ (fig. 13); its tangent in point $O$ is determined by

$$
\begin{equation*}
2 c_{1}^{\prime} \xi_{2}+c_{2}^{\prime} y_{2}=0 \tag{34}
\end{equation*}
$$

The line determined by (34) is the diameter conjugated to the $X$ axis of the indicatrix in $O_{2}$; so we find that the tangent in $O_{2}$ and the conjugated line in $\mathrm{O}_{1} \mathrm{O}_{2}$ are conjugated diameters of the indicatrix in $O_{2}$. This property however has been known already for a long time ${ }^{1}$ ).

- We now take that tangent in $O_{2}$ as new $Y$-axis, whilst we keep the line $O_{1} O_{2}$ as the $X$-axis.

Equation (33) now changes into:

$$
(\lambda X+\mu Y)^{4}=v X^{3}
$$

where $\lambda, \mu$ and $v$ have definite values. From this ensues as a first approximation of the binodal line in the vicinity of point $\mathrm{O}_{2}$ :

$$
\mu^{4} Y^{4}=\boldsymbol{v} X^{3}
$$

01

$$
Y^{4}=K X^{3} \text {. . . . . . . . (35) }
$$

If we calculate the radius of curvature in point $\mathrm{O}_{2}$ we then find

[^7]that it is zero The branch $\mathrm{cO}_{2} \mathrm{c}^{\prime}$ of the binodal line has thus in point $O_{2}$ a somewhat angular shape, without however an angular point being really formed.

This shape is, indeed, the preparation to the wellknown form shown in fig. 14, generated in $\mathrm{O}_{3}$ when the conjugated branch $b 0_{1} b^{\prime}$ in fig. 13 begins to intersect the plait $a O_{1} a^{\prime}$.

Moreover it is evident from the fact that $\xi_{2}$ and $y_{2}$ in the vicinity of the points $O_{1}$ and $O_{2}$ are of the same order of magnitude as $\dot{y}_{1}{ }^{3}$ and therefore much smaller
Fig. 14. than $y_{1}$, that the connode $O_{1}$ will displace itself there much quicker than the connode $\mathrm{O}_{2}$.

Astronomy. - "The Milhy way and the star-streams." By Prof. J. C. Kapteyn.

In a lecture, delivered before the Congress of Physicists and Physicians in the month of April, I arrived at the conclusion that "in passing from the stars of the spectral type $B^{1}$ ) (Helium-stars) to those of the type $A$ (Sirius-stars) and from these to those of the type $G$ (solar-stars) there is a gradual change in the direction of the streams.

The stream-velocity was also found to be different. Owing to want of materials, however, the latter result was still even more uncertain than the former. Partly by the publication of Campbede's radial velocities of $B$ stars ${ }^{2}$ ), partly by (not yet published) observations made on Mount Wilson, I have been able this summer materially to diminish this uncertainty.

It is true, that the increase of our data represents but a small fraction of what is urgently wanted. Still however, so much seems to have been gained already, that there is a pretty strong probability in favour of the conclasion that: not only the direction but also the velocity of the two great star-streams gradually changes in passing from type $B$ to type $A$ and thence to type $G$.

In these circumstances I feel justified in no longer suppressing a conclusion which was not yet communicated in my April lecture.

In what follows, stream-direction and stream-velocity will mean direction and relocity relative to the solar system, unless the contrary

[^8]
[^0]:    c ${ }^{1}$ F. A. H. Schreinemakers. Z. f. Phys. Chem.' 2 ' 114 (1898).
    : '2) See also: H. A. Lorentz. Z. f. Phys. Chem. 22 523.,

[^1]:    ${ }^{1}$ ) D. J. Korteweg Arch. Néerl. (I) 2460 (1891).
    ${ }^{\text {a }}$ ) D. J. Kortewge. l.c. 63 (1891).

[^2]:    ${ }^{1}$ ) D. J. Korteweg. l.c. 61 (1891).

[^3]:    1) W. Middelberg. Z. f. Phys. Chem. 43. 305 (1903). .. "- -!' = "...门
[^4]:    1) Comp. F. A. H. Scircincmakers. Z. f. Phys. Chem. 22. 532 (1897).
    ${ }^{2}$ ) Comp. F. A. H. Scirdinemakers. Z. f. Phys. Cilem. 22531 (1897).
    ${ }^{3}$ ) D. J. Kortrwig. Arch. Néerl. (I). 24 61. (1891).
[^5]:    ${ }^{1}$ ) D. J. Kortdweg, l.c. 69, 70.

[^6]:    ${ }^{1}$ ) Comp. the paper of Mr. Kuencn (Proceedings of Oct. 1911, p. 420).

[^7]:    ${ }^{\text {l }}$ ) D. J. Kortrwde. 1. c. p. 299.

[^8]:    a) In what follows the notations of Harvard college observatory have been adopled.
    $\left.{ }^{2}\right)$ Lica Bulletin No. 195.

