It is very peculiar that finely divided non-volatile acids, e. g. stearic acid, render the lipase already inactive in a culture liquid. If thus we add finely divided stearic acid to a boiled fluorescens liquefaciëns culture it splits no more fat. When we now filtrate the fatty acid, the filtrate contains very little or no lipase, but it is bound to the fatty acid on the filter and can again become active by neutralisation of the acid.

Lipase can thus be almost quantitatively removed from a liquid by means of finely divided fatty acid.

The lipase is not, however, bound to the fatty acid if the liquid which contains it reacts feebly acid. If then the fatty acid is filtrated off, the filtrate contains the lipase, which after neutralisation of the former again becomes active.

From this investigation follows that the group of the melting fluorescents secrete a fat-splitting enzyme which tolerates heating from 99°—100° C. for 5 minutes, or a minute's boiling without being perceptibly decomposed. This enzyme is called *thermo-tolerant* lipase.

It is by this property distinguished from the enzymes known till now and likewise from the lipase formed by the group of *B. lipo-lyticum*, *B. stutzeri*, *B. fluorescens non liquefaciëns*, and from that of the moulds: *Oïdium lactis*, *Penicillium glaucum*, *Aspergillus niger* and *Cladosporium butyri*.

The properties of the lipase of the latter micro-organisms and those of the thermo-tolerant lipase exhibit for the rest a great similarity as is shown by the way of diffusion through agar and gelatin media, and by the behaviour of both enzymes towards soluble acids and non-volatile fatty acids.

Chemistry. — *"On retrogressive melting-point lines."* (Second Com-
munication) By Prof. A. SMITS. (Communicated by Prof. J. D.
VAN DER WAALS.)

(Communicated in the meeting of May 27, 1911).

Introduction.

In my first paper on this subject[1] 1 started the discussion of retrogressive melting-point lines in the system H_2O—Na_2SO_4, which discussion will now be completed, and improved in a single point.

To reach a stricter accuracy in my reasoning I will now derive

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[1] These Proc. Sept. (1909) p. 227.

the equation of the melting-point line at varying vapour pressure from the differential equations drawn up by VAN DER WAALS for two-phase equilibria in a binary system.

If we combine the following two equations:

$$v_{SL}dp = (x_S - x_L)\left(\frac{\partial^2 \zeta}{\partial x^2_L}\right)_{PT} dx_L + \eta_{SL}dT \quad . \quad . \quad . \quad (1)$$

and

$$v_{GL}dp = (x_q - x_L)\left(\frac{\partial^2 \zeta}{\partial x^2_L}\right) dx_L + \eta_{GL}dT \quad . \quad . \quad (2)$$

i.e. if we seek the intersection of the two liquid surfaces, we get an equation for the three phase equilibrium $S + L + G$. If as here, we want to find the equation of $\frac{dx_l}{dt}$, we eliminate $\frac{dp}{dt}$, which quantity for the equilibrium between liquid and vapour in the case under consideration is equal to that for the equilibrium between solid and liquid.

So from the equations (1) and (2) follows:

$$\frac{x_S - x_L}{v_{SL}}\left(\frac{\partial^2 \zeta}{\partial x^2_L}\right)_{PT}\frac{dx_L}{dT} + \frac{\eta_{SL}}{v_{SL}} = \frac{x_g - x_L}{v_{qL}}\left(\frac{\partial^2 \zeta}{\partial x^2_L}\right)_{PT}\frac{dx_L}{dT} + \frac{\eta_{qL}}{v_{qL}}$$

or

$$\frac{dx_L}{dT} = \frac{1}{\left(\frac{\partial^2 \zeta}{\partial x^2_L}\right)_{PT}} \frac{\eta_{qL}v_{SL} - \eta_{SL}v_{qL}}{(x_S - x_L)v_{qL} - (x_q - x_L)v_{SL}}$$

If finally instead of the decrease of entropy we write the development of heat divided by the absolute temperature, we get the equation which will be applied in the further discussion.

As we wish to apply this equation up to temperatures at which critical phenomena appear, it deserves recommendation to write v_{sf} and w_{sf} instead of v_{sL} and w_{sL}, so that the equation takes the following form:

$$T\frac{dx_L}{dT} = \frac{1}{\left(\frac{\partial^2 \zeta}{\partial x_L^2}\right)_{PT}} \frac{w_{qL}\cdot v_{sf} - w_{sf}\cdot v_{qL}}{(x_s - w_L)v_{qL} - (x_q - x_L)v_{sf}} \quad . \quad . \quad . \quad (3)$$

Now with regard to the sign of the quantities v_{sf} and w_{sf}, we must refer to the relation indicated by the equation:

$$w_{sf} = \left[p + \left(\frac{\partial \varepsilon_f}{\partial v}\right)_{T\lambda}\right]v_{sf} + (\varepsilon_{sf})_v \quad . \quad . \quad . \quad . \quad (4)$$

in which $(\varepsilon_{sf})_v$ denotes the loss of energy that takes place when 1 gr. mol. of the solid phase is dissolved in an infinitely large

quantity of the coexisting fluid phase, the volume remaining constant.

It may be said of this quantity that it is negative as a rule, and so, that during the process mentioned no loss of energy, but increase of energy takes place, and that this negative value is generally so great, that it far exceeds the first term of the second member of equation (4), which is generally negative, but which can also be positive, so that w_{sf} is negative.

Yet this is not *always* the case. In the first place an exothermal chemical reaction may take place during the solution of the solid phase in consequence of which the energy at constant volume does not *increase*, but *decrease*, so that $(\varepsilon_{sf})_r$ becomes positive, and when this term exceeds the negative value of the first term, w_{sf} is positive.

As the reaction is here an exothermal one, the chemical equilibrium will be shifted in the endothermal direction with rise of temperature, in consequence of which $(\varepsilon_{sf})_r$ will become less strongly positive, and can finally become negative again. A consequence of this it will be that w_{sf} passes through *zero* at rise of temperature, after which it becomes negative again.

In the second place, as VAN DER WAALS Sr. [1] showed, it may be derived from the course of the isobars $\left(\dfrac{\partial v}{\partial x}\right)_p$ that the line $v_{sf} = 0$ gets outside the connodal line in the neighbourhood of the plaitpoint $(L = G + S)$. As now this quantity is negative outside the locus $v_{sf} = 0$, whereas it has a positive value inside it till the line $\dfrac{\partial^2 \psi}{\partial v^2} = 0$ is reached, where it increases up to ∞ and becomes again negative inside this latter locus, we can predict that in the neighbourhood of the mentioned plaitpoint the quantity v_{sf} can assume rather high positive values *in the stable* region.

In this case the term $\left[p + \left(\dfrac{\partial \varepsilon_{sf}}{\partial v}\right)_{Tx}\right] v_{sf}$ will begin to preponderate, and this too may bring about that the quantity w_{sf} becomes zero, and then negative, *but this reversal of sign is confined to the critical neighbourhood, whereas the reversal discussed in the first place is only possible, when the phenomenon of solution is accompanied by an exothermal chemical reaction.*

Let us once more consider after this introduction how to explain the phenomena observed for the system $H_2O - Na_2SO_4$.

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[1] These Proc. Oct. 1903, p. 230, Nov. 1903, p. 357.

If we begin with the melting-point line of $Na_2SO_4 . 10 H_2O$, we observe that the quantity v_{sf}, which stands here instead of v_{sl}, is
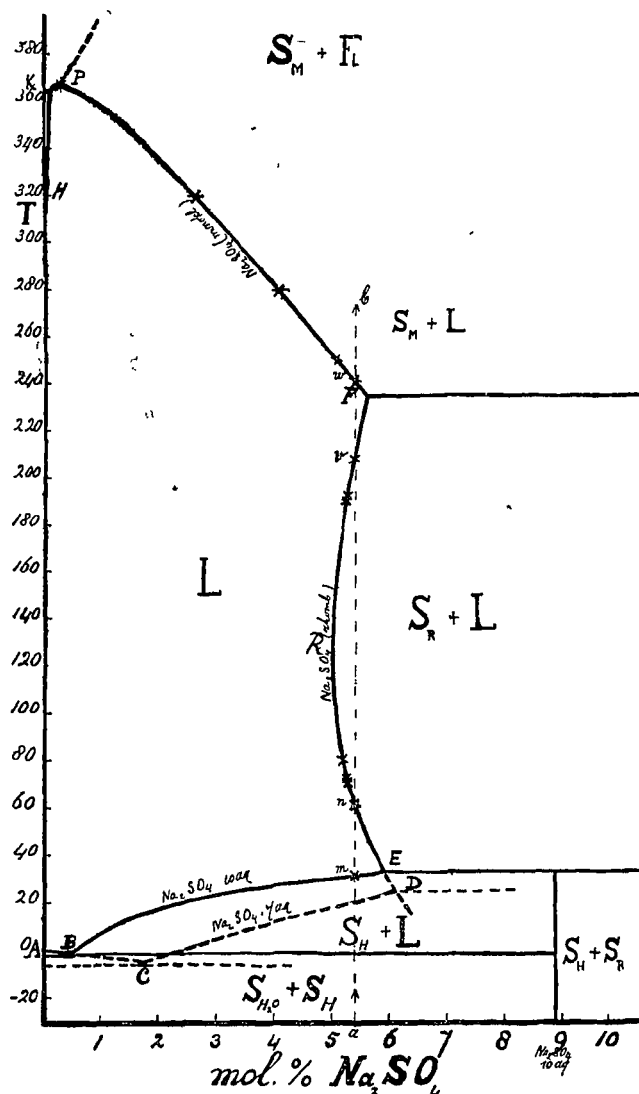

Fig. 1.

negative, whereas w_{gl} and v_{gl} are positive, and as $w_{sf} v_{gl} > w_{gl} v_{sf}$, the numerator of equation (3) is positive.

In the denominator $x_g - x_l$ is negative, but in spite of this the denominator is positive because of the great value of v_{gl}.

Numerator and denominator are positive, and $\left(\dfrac{\partial^2 \zeta}{\partial x^2 \, l}\right)_{pT}$ is positive in the stable region, so that $T\dfrac{dx_l}{dt}$ is *positive*.

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At the transition temperature of the hydrate $Na_2SO_4 . 10H_2O$ intersection takes place of the melting-point line of this hydrate and that of the anhydrous salt and now the remarkable fact occurs, that the melting point line of the anhydrous salt is a retrogressive one.

If we now for the present fix our attention on the temperature of the transition point, the hydrate and the anhydrous salt are in equilibrium with the same solution and with the same vapour; so w_{sf} refers to the same fluid phase for these two solid substances, and now it is the question whether this quantity w_{sf} can have another sign for the anhydrous salt than for the hydrate.

It is natural to assume that the solution in equilibrium with the solid hydrate, contains hydrated molecules, and when this is so, the quantity w_{sf} may greatly deviate for the anhydride from that for the hydrate, for then as was said before, $(\varepsilon_{sf})_v$ can become positive in consequence of the chemical reaction, on account of which w_{sf} too can assume a positive value.

In this case the numerator is negative, whereas the denominator has remained positive, in consequence of which $T\dfrac{dx_l}{dT}$ has become negative.

So the fact that the melting point line of the anhydrous salt is at first really retrogressive is an indirect proof for the presence of hydrated molecules in the solution discussed here.

Now we see further that the melting-point line of the anhydride bends again to the right at higher temperature, and so it takes a course to the right.

This too, might be anticipated, as was set forth in the introduction, for at rise of temperature the hydration will decrease, and with it $(\varepsilon_{sf})_v$ will become smaller and smaller positive, pass through zero, and finally assume again a negative value. So w_{sf} too will pass through zero, and become negative again, and a consequence of this will be that for a certain *negative* value of w_{sf} the numerator becomes *zero*, and so also $T\dfrac{dx_l}{dt}$, so that the melting-point line gets a vertical tangent.

Above this temperature $T\dfrac{dx_l}{dt}$ is again positive, and it would have been possible that as far as the sign of $T\dfrac{dx_l}{dt}$ was concerned, no more change had occurred up to the melting point of Na_2SO_4. If however, like here, we are dealing with a system of the type of *ether—anthraquinone*, we must get the case already mentioned in

the introduction, and the melting point line must approach the plait $(G = L)$ with rise of temperature. But we know that v_{sf} passes through zero at this approach and becomes greater and greater positive, which has the consequence that also w_{sf} can pass through zero, after which it continually increases in positive value.

Now it follows from equation (4) that w_{sf} becomes zero for a positive value of v_{sf}. So if $v_{sf} = 0$, w_{sf} has still a negative value; so at that moment numerator and denominator are still positive. This is also still the case when v_{sf} is positive and w_{sf} still negative, but on approach to the plaitpoint v_{sf} continually increases in positive value, in consequence of which w_{sf} also becomes positive, and then for a certain positive value of v_{sf} and corresponding positive value of w_{sf}, the numerator will become $=$ zero, in consequence of which the melting point line gets a vertical tangent for the second time.

Above this point $w_{sf} \cdot v_{gL}$ begins to exceed more and more the first term $w_{qL} \cdot v_{sf}$, the denominator becoming smaller, so that $T \dfrac{\partial x_l}{dT}$ becomes larger and larger negative, and the melting point line becomes more retrograde, till the plaitpoint has been reached, at which numerator and denominator become $= 0$. But as then also

$$\left(\frac{\partial^2 \zeta}{\partial x_2^{\,2}} \right)_{PT} = 0,$$

$$T \frac{dx_l}{dT} \text{ will be } = -\infty .$$

It is of importance to point out here, that the positive sign of w_{sf} at the critical end-point p also follows from the circumstance that for a critical end-point, for which:

$$\frac{w_{qL}}{x_j - x_L} \text{ and } \frac{v_{qL}}{x_g - x_L} = 0$$

follows from equations (1) and (2),

$$T \frac{dp}{dT_{slg}} = T \left(\frac{dp}{dT_{sf}} \right)_x = \frac{w_{sf}}{v_{sf}}$$

or in words, that the line for the equilibrium between solid-fluid at constant x touches the three-phase line just in the plaitpoint p.

As now $T \dfrac{dT_{slg}}{dp}$ is positive in this point, while v_{sf} is also positive, it follows from this that also w_{sf} must have a positive value in the
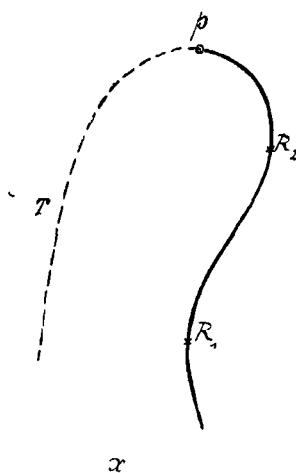
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point p. I mentioned this here because for the same reason w_{sf} is generally negative at the second critical end-point q.

So when no other complications had made their appearance, the melting-point line of Na_2SO_4 would have had a shape as has been given schematically in fig. 2.

The found melting-point line, however, deviates from this, for before the point R_2 has been reached the rhombic modification of Na_2SO_4 has changed into the monoclinic one, in consequence of which a very interesting part of the melting-point line disappears and already below the point R_2 a new melting point line joins the first; the new line immediately runs back, which proves that $w_{sf}v_{gL}$ is already stronger positive than $w_{gL}v_{sf}$ for the new modification.

If we now proceed to discuss the second critical end-point q, where also:

$$T\left(\frac{dp}{dT}\right)_{SLG} = T\left(\frac{dp}{dT}\right)_{SG} = \frac{w_{sf}}{v_{sf}}$$

we see at once that if — as is the case for ether-anthraquinone — the expression $T\left(\frac{dp}{dT}\right)_{SLG}$ in q is negative, w_{sf} will have to be negative, because v_{sf} is undoubtedly positive in that point. So it follows from this circumstance, which is the normal one in my opinion, that the positive value of v_{sf} in the point q does not suffice to make also w_{sf} positive; so the locus $w_{sf} = 0$ seems already to have retreated inside the liquid branch of the connodal line at q.

So somewhat above the point q the numerator of the second member of equation (3) is positive, the denominator also being positive, so:

$$T\frac{dx_l}{dT} = \text{positive}$$

Rise of temperature does not bring about any change in this; when the temperature falls to the second critical end-point q

$$T\frac{dx_l}{dT} \text{ becomes } = +\infty.$$

So if also the point q had lain on the ascending branch of the three-phase line, so that in this case $T\frac{dp}{dT}$ would have been positive

Fig. 2.

x

in q, w_{sf} and w_{sf} would still have had the same sign as for p, but it will never occur that w_{sf} has such a large positive value there that in consequence of this the numerator will become negative.
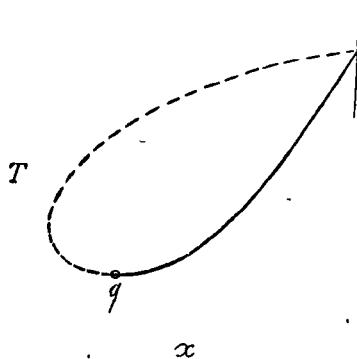

Fig. 3.

_So the second part of the melting-point line must always have a shape as is schematically represented in fig. 3.

This second branch of the melting-point line, which has been determined for the system *ether-anthraquinone*, could not be investigated for the system H_2O— Na_2SO discussed here for want of suitable material.

I hope to discuss the course of the melting-point lines under constant pressure in a following communication.

Amsterdam, May, 1911.

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Anorg. Chem. Laboratory
of the University.

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Chemistry. — "*On retrogressive vapour-lines*". (First communication). By Prof A. SMITS. (Communicated by Prof. J. D. VAN DER WAALS).

In connection with the discussion of the Tx-projection of the liquid line of the three-phase region of a system that belongs to the type ether-anthraquinone we shall now proceed to the discussion of the vapour line corresponding to it.

We may arrive at the equation of this vapour line by combination of the following two differential equations:

$$v_{sg}\ dp = (v_s - x_g)\left(\frac{\partial^2 \zeta}{dx^2{}_g}\right)_{PT} dx_q + \eta_{sg}\ dT \quad \ldots \quad (1)$$

and

$$v_{lg}\ dp = (x_l - x_q)\left(\frac{\partial^2 \zeta}{\partial x^2{}_g}\right)_{PT} dx_g + \eta_{lq}\ dT \quad \ldots \quad (2)$$

in which we come to the following expression for the said vapour-line:

$$T\frac{dx_g}{dT} = \frac{1}{\left(\frac{\partial^2 \zeta}{\partial x^2{}_g}\right)_{PT}}\ \frac{w_{lq}\cdot v_{sf} - w_{sf}\cdot v_{lq}}{(v_s - x_g)v_{lq} - (x_l - x_g)v_{sf}} \quad \cdot \quad (3)$$

if we, namely, write v_{sf} and w_{sf} instead of v_{sg} and w_{sg}.