Chemistry. — "*On retrogressive melting-point lines.*" By Prof.
A. Smits and J. P. Treub. (Third communication). (Commu-
nicated by Prof. J. D. van der Waals).

It has appeared from the preceding communication on the $(PT)_x$-
lines for the equilibrium solid-fluid that in the system ether-anthra-
quinone not only the locus for $v_{sf} = 0$, but also that for $w_{sf} = 0$
enters the stable region in the neighbourhood of the plait, which
involves the phenomenon already predicted by one of us (Smits),
that when the melting-point lines under constant pressure are deter-

mined, a point where $\left(\dfrac{dx}{dT}\right)_P = 0$ can occur twice.

From van der Waals' differential equation

$$v_{sf}\, dp = (x_s - x_f)\left(\frac{\partial^2 \zeta}{\partial x^2_f}\right)_{PT} dx_f + \eta_{sf}\, dT$$

follows for constant pressure:

$$\left(\frac{dx}{dT}\right)_P = -\frac{\eta_{sf}}{(x_s - x_f)\left(\dfrac{\partial^2 \zeta}{\partial x^2_f}\right)_{PT}}$$

or

$$T\left(\frac{dx}{dT}\right)_P = -\frac{w_{sf}}{(x_s - x_f)\left(\dfrac{\partial^2 \zeta}{\partial x^2_f}\right)_{PT}}.$$

Now it follows from this relation that when in the stable region
two lines for *solid-fluid* touch a plane for constant pressure projected
in the P,T,X-figure of the system *ether-anthraquinone*, which contact
must take place in its maximum for the line for small anthraquinone-
concentrations, and in its minimum for that for greater concentra-
tions, the melting-point line will have to possess two remarkable
points, because in the said points of contact w_{sf} must be $= 0$, so

$T\left(\dfrac{dx}{dT}\right)_P = 0$, and so the tangent must be vertical.

Now it follows from the shape of the found (PT_{sf})-lines that the
melting-point line will not present this particularity for all pressures,
but that this phenomenon remains restricted to a certain region of
pressure, outside which only the lower, resp. the upper point will
still possess a vertical tangent in the stable region for some time,
while for greater, resp. smaller pressure it will vanish from the
stable region.

In the annexed T-x-fig. the projection of the liquid and the vapour
line of the two parts of the interrupted three-phase region, and

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fuither some T,x-sections corresponding to different constant pressures have been indicated.

When we consider the melting-point line for the pressure of 45 atmospheres (in the figure the pressure has been given for every melting-point line), we observe that this melting-point line really possesses two vertical tangents, and that it runs strongly back between the two points where the tangent is vertical. Below the first, and above the second point the direction of the melting-point line is normal, however, so at higher temperature it runs to the side of the component with the highest melting point.

It is easy to prove that this is in perfect harmony with the theory, for below and above the points where w_{sf} is zero, w_{sf} must be negative (this follows from the intersection of the $(PT_{sf})_x$-lines with the plane for constant pressure), so that $T\left(\dfrac{dx}{dT}\right)_P$ is positive. Between the said points, on the other hand, w_{sf} is positive, from which follows that $T\left(\dfrac{dx}{dT}\right)$ is negative.

If we now proceed to higher pressures, we see that at 50 and 52.8 atms. the melting-point line has still the same shape in the main; two points may, namely, be indicated where the tangent is vertical, but in concentration these points lie further apart than for lower pressure.

At 54,3 atms. the melting-point line presents this peculiarity that the upper point, where the tangent is vertical, lies exactly on the vapour line of the three-phase region, from which accordingly follows that there $w_{sf} = 0$.

The melting-point line under the pressure of 59 atms. shows that the vapour line of the three-phase region is already met at a place where w_{sf} is positive, so that the melting-point line now possesses only one vertical tangent.

At the pressure of 61 atms. the melting-point line no longer possesses a vertical tangent in the stable region, for where it meets the vapour branch of the three-phase region, w_{sf} is negative. So it appears from this too, that the quantity w_{sf} on the vapour branch passes from negative through zero, and becomes positive, after which it soon passes through zero for the second time and assumes again a negative value. As was already set forth in the communication on the $(PT_{sf})_x$-lines, this is to be ascribed to this that the locus for $w_{sf} = 0$ gets outside the vapour branch on its approach of the plait, but not outside the liquid branch.
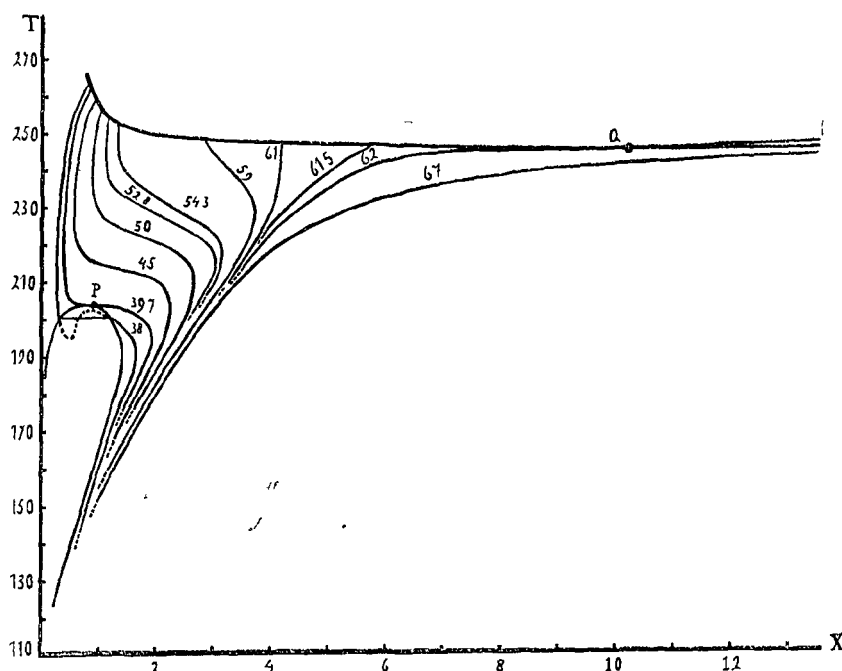
At the pressure of 61,5 atms. the melting-point line runs strongly to the right, because w_{xf} is pretty strongly negative here.

Finally it is still worthy of note that there are two pressures for which the melting-point line presents another, not yet mentioned, peculiarity ; they are the pressures of the two critical end-points p and q.

The melting-point line corresponding to the pressure of the first critical end-point p (39,7 atms.) touches the continuous liquid-vapour branch of the first part of the three-phase region in p, and the melting-point line for the pressure of the second critical end-point q (62 atms.) touches the continuous liquid-vapour line of the second part of the three-phase region in q. In these points $\left(\dfrac{\partial^2 \zeta}{\partial x^2}\right) = 0$, from which it follows that the melting-point line must possess an horizontal tangent there, which VAN DER WAALS SR. [1] already pointed out. So the melting-point line at the pressure of the critical end-point p not only possesses two vertical tangents, but moreover a point of inflection with horizontal tangent.

The melting-point line at the pressure of the second critical end-point q, however, only possesses a point of inflection with horizontal

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[1] These Proc. June 1905, p. 193.

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tangent, but no vertical tangents, but it may still be remarked of this melting-point line that it is the first that pursues its course undisturbed up to the melting-point of anthraquinone. The melting-point lines corresponding to higher pressures also proceed uninterruptedly from the eutectic point to the melting-point of anthraquinone, but they present a point of inflection as sole peculiarity.

Amsterdam, June 1911.

Anorg. Chem. Laboratory of the University.

Chemistry. — *"On the system water-phenol."* By Prof. A. SMITS and J. MAARSE. (Communicated by Prof. A. F. HOLLEMAN.)

Though the system water-phenol has already several times been the subject of investigation, and already many peculiarities of the mutual conduct of these substances have been revealed, it yet seemed worth while once more to take this system in hand, and determine the melting-point figure, the more so as we had come across a hydrate of phenol that had drawn CALVERT's[1] attention already long before, but had not been met with by PATERNO and AMPOLA[2] in their determination of the melting-point line of phenol in the system water-phenol.

In his paper entitled *" Ueber ein krystallisirtes Hydrat? des Phenols"* CALVERT writes as follows: "Schüttelt man 4 Theile Phenol mit 1 Theil Wasser gut durch einander und kuhlt man das Gemenge auf 4° ab, so bedecken sich die Wände des Gefässes mit feinen sechsseitigen rhombischen Prismen. — Dieser neue Körper löst sich in Wasser, Alkohol und Aether und schmilzt bei 16°. Die Analyse der zwischen Fliesspapier abgepressten Krystalle führte zur Formel $C_2H_6O_2 + HO$"[3].

After all CALVERT, however, seems not to have been perfectly convinced of the existence of this hydrate, for in the title he placed a note of interrogation after the word *Hydrat*. — Now it will appear from what follows, that CALVERT really had come across a hydrate of phenol and that PATERNO and AMPOLA have quite overlooked this compound in consequence of the circumstance that the formation of this hydrate very often does not take place, so that very easily metastable states

[1] Zeitschr. f. Chemie *1*, 530 (1865).

[2] Gazz. Chim. ital. **27**, 523 (1897)

[3] RINKES (Thesis for the doctorate Amsterdam 1910 and Rc. *30*) has availed himself of this circumstance for the preparation of perfectly pure phenol, as the homologues of phenol do not give hydrates, as far as we know.