

Citation:

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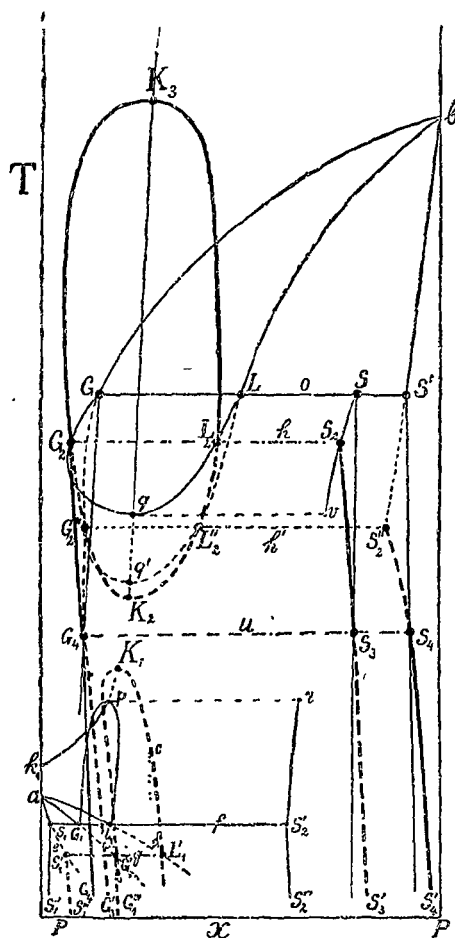


Fig. 3.

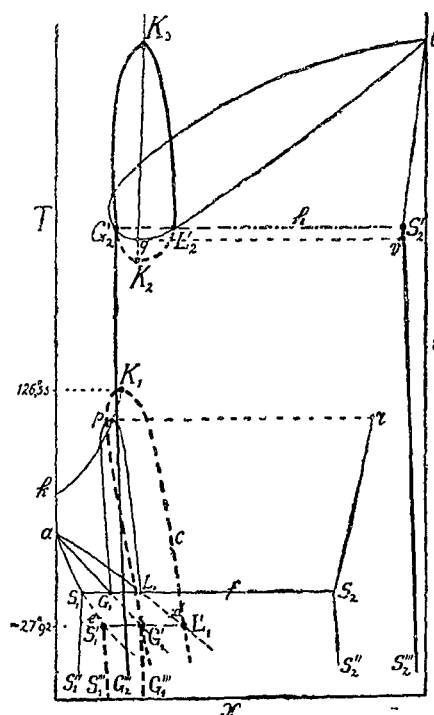


Fig. 4.

tions are given in the figures 3 and 4, and they are easy to understand if we compare what was published before about the system ether-anthraquinone and the system phosphorus.

Anorg. Chem. Laboratory of the University.

Amsterdam, May 30, 1913.

Chemistry. — “*On the pseudo system Methylrhodanide — Methyl-mustard oil.*” By Prof. A. SMITS and H. VIXSEBOXSE. (Communicated by Prof. A. F. HOLLEMAN).

In 1906 ¹⁾ WALDEN stated the fact that different salts dissolved in methylrhodanide CH_3SCN do not bring about a rise of the boiling point, but a lowering of the boiling point.

It appears from the following table that this phenomenon is brought about by the salts $\text{N}(\text{C}_2\text{H}_5)_4\text{I}$, $\text{N}(\text{C}_2\text{H}_5)_4\text{I}$, CdI_2 , and NH_4CNS .

¹⁾ Zeitschr. f. phys. Chem. 55, 297 (1906).

	L	S	Δ
N (C ₃ H ₇) ₄ I	15.57	0.506	—0.369°
N (C ₂ H ₅) ₄ I	»	0.078	—0.221°
Cd I ₂	13.13	0.0798	—0.100°
	»	0.1448	—0.164
	»	0.2058	—0.164
	»	0.2280	—0.164
NH ₄ CNS	14.20	0.050	—0.334
			upto—0.404 during 25 min.
	»	0.107	—0.704
			upto—0.744 during 25 min.

L denotes the number of grams of solvent.

S " " " " " " solved substance.

Δ „ „ rise of the boiling point.

WALDEN has not succeeded in finding an explanation of this peculiar phenomenon. In the first place it occurred to him that it might possibly be owing to the influence of traces of moisture, but the phenomenon remained the same when both the solvent and the solid substance were carefully dried. Further WALDEN considered the possibility of a change of the solvent, a splitting up or an isomerisation, but he thought he had also to reject this possibility for "das reine Lösungsmittel wies im Siedeapparat eine ganze Stunde lang eine konstante Kochtemperatur auf; die von den Salzlösungen abdestillierten Proben des Lösungsmittels ergaben den normalen Siedepunkt des Methylrhodanids."

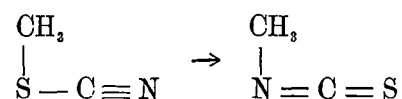
If the latter were correct it would really be a futile attempt to try and find an explanation for the phenomenon of the lowering of the boiling point observed here, but this statement is founded on an inaccurate observation.

Convinced of the universality of the phenomenon that a substance that behaves like a unary one is in internal equilibrium¹⁾ we were

¹⁾ We speak of internal equilibrium when different kinds of molecules of *one* and the same substance are in equilibrium.

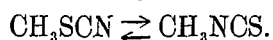
naturally led to expect the same for methylrhodanide, and it was now naturally supposed that the methylrhodanide, as it is obtained in the preparation, is not yet in internal equilibrium, and that the lowering of the boiling point or the increase of the vapour tension which occur, are a consequence of the setting in of the internal equilibrium which is possibly reached with appreciable velocity under the influence of the said salts. These salts would therefore be catalysts.

Now it is known that in sealed tubes heated to 180° methylrhodanide is partly converted to the isomer methyl mustard oil¹⁾. We have here an intramolecular atomic shifting



As methylrhodanide boils at 130,5° and the isomer, the mustard oil at 119°, this conversion when accelerated by the said salts, might give rise to a lowering of the boiling point resp. increase of vapour tension.

This consideration led us to the supposition that the internal equilibrium which was mentioned just now, might be an equilibrium between the isomer molecules CH_3SCN and CH_3NCS :



Before we now proceeded to test this supposition, the difference of vapour tension between pure methylrhodanide and a saturate solution of CdI_2 in methylrhodanide was examined at different temperatures in a small tensimeter, in which mercury was used as the liquid measuring the tensions.

It was remarkable to see that in the first moments the saturate CdI_2 -solution possessed a smaller vapour-tension, but soon the difference of vapour tension passed through zero, and then obtained the opposite sign. At 25° the position of the mercury manometer appeared not to change any more after a fortnight, and the increase of vapour tension amounted to 11,2 mm. Hg. The same experiments were also made at higher temperatures, and, as was expected, they gave a greater difference of vapour tension as result. These were, however, less reliable quantitatively, because mercury seems to have analysing power at higher temperatures. Accordingly glass-spring manometers will be used to obtain more accurate results when the investigation is continued.

After it had thus appeared that by the addition of CdI_2 after a transient decrease of vapour tension actually an *increase of vapour*

¹⁾ For allylrhodanide conversion to mustard oil already takes place after distillation under atmospheric pressure.

tension takes place, the following experiment was undertaken. A glass vessel filled with methylrhodanide and an excess of CdI_2 was exhausted, and then kept for 6 weeks in a thermostat of 20° . Then the vessel was opened and the liquid investigated, in the first place as to its boiling point, and in the second place as to the formation of mustard oil.

Before we proceeded to the determination of the boiling point of this liquid the boiling-point of the pure methylrhodanide used by

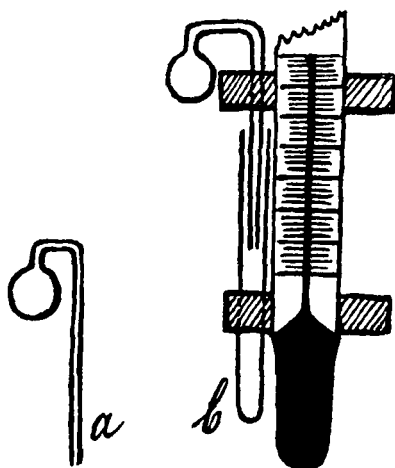


Fig. 1.

Fig. 2.

us, was examined, by the exceedingly convenient method of SMITH¹⁾, which enables us to investigate extremely small quantities of substance. A tube of the shape indicated in fig. 1, is filled with the liquid which is to be examined, then fastened to a thermometer (fig. 2), and placed in a suitable liquid bath, which is slowly heated, and vigorously stirred. At the boiling-point a continuous stream of vapour bubbles escapes from the open end. If then the temperature is again slowly lowered, the escaping of the vapour bubbles will suddenly cease as soon as the temperature has fallen somewhat below the boiling-point. This point can be sharply observed, and the experiment may be so often repeated till all the substance has evaporated.

As we used an oil-bath, and CH_3SCN easily dissolves in oil at 130° , we made the narrow tube *a* of the boiling bulb open into a tube *b* which was ± 2 mm. wider. In this way we succeeded in making the escaping vapour bubbles very clearly visible and prevented that they immediately dissolved in the rapidly moving oil.

When the experiment was repeated till almost all the liquid was evaporated, the pure methylrhodanide gave the following result:

1st bulb	2nd bulb
130.9°	130.9°
131.4	131.1
131.5	131.3
131.5	131.4 almost all the liquid has disappeared

¹⁾ Americ. Chem. Soc. 32, 897 (1910).

from which appears that it was *not* perfectly pure, but that it contained a trace of a more volatile component which pretty quickly disappears when the liquid is boiled, so that after $\pm \frac{1}{4}$ has evaporated a boiling-point is found which is constant within the errors of observation, viz. $\pm 131.3^\circ$.

After these determinations the liquid was examined which at 20° had been in contact with CdI_2 for six weeks. In the determination of the boiling-point in the way described just now the following result was obtained, the experiment being repeated 18, resp. 19 times with the same filling.

1 ^{ste} bulb	2 nd bulb
123.6°	124.8°
124.5	125.9
125.4	127.0
127.4	128.0
129.3	128.8
130.2	129.6
131.1	130.1
131.7	130.5
131.8	130.9
131.8	131.3
131.9	131.7
132.0	131.8
132.3	131.9
132.6	132.2
132.9	132.6
133.2	133.4
134.0	134.3
almost empty 136.5	135.8
	136.4 almost empty

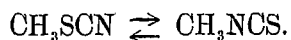
From these experiments it appears with the greatest clearness that by the contact with CdI_2 at 20° the boiling-point of the methylrhodanide is lowered by an amount of at least $7^\circ.7$ (1st bulb), but at the same time the course of the boiling point shows that on conti-

nued evaporation the lowering of the boiling-point becomes smaller and smaller, soon passes through zero, and then becomes a rise of the boiling-point. This phenomenon shows that a more volatile component with lower boiling-point is formed in the methylrhodanide, and that the vapour is much richer in this component than the coexisting liquid, so that this new component can easily be expelled on prolonged evaporation.

That under these circumstances the lowering of the boiling-point of the substance under investigation is finally replaced by a rise of the boiling-point is easy to understand, as the liquid contained dissolved CdI_2 .

That the *first* experiment with the first bulb yielded $123^{\circ}6$, and that with the second bulb $124^{\circ}8$ is owing to this that more vapour escaped from the second bulb than from the first bulb before the first determination was made.

Finally we undertook the chemical investigation of another part of the same liquid. This chemical investigation consisted in this that we examined whether mustard oil had formed in this liquid. In order to do this we boiled the liquid with dilute sulphuric acid in a flask which was closed by means of a pierced cork with a long glass tube. It is known that in the presence of mustard oil H_2S is formed under these circumstances, which can be immediately demonstrated by means of a lead-acetate paper laid on the mouth of the long glass tube. The result was a very clear hydrogen sulphide reaction, which quite failed to appear in the investigation of the "pure" methylrhodanide¹⁾, which was a conclusive proof that the lowering of the boiling point is accompanied with the formation of mustard oil, so that it is all but certain that the peculiar phenomenon which was observed for the first time by WALDEN must be ascribed to the formation of this substance, and that when the substance behaves as a unary one we shall have to do with the following internal equilibrium.



It is clear that if on continued investigation the above equilibrium really appears to exist, we have again a very interesting system here, which urgently calls for further investigation. This will certainly be taken in hand; first of all the pseudo-system methylrhodanide-methyl mustard oil will be examined, and then by means of catalysers the situation of the unary system will be determined in

¹⁾ Probably this contains also a trace of mustard oil, which in the experiment escapes the action of the H_2SO_4 .

this pseudo-system, as well with regard to the gaseous as to the liquid and the solid phase.

The phenomenon, observed here with great probability, of internal equilibrium between structure isomers will be of pretty general occurrence without any doubt, so that it will not be difficult to discover many more interesting examples, which are accessible to experiment.

Anorg. Chem. Lab. of the University.

Amsterdam, May 27, 1913.

Physics. — “*On the point in which the solid state disappears as an answer to the question in how far this point can be compared to the critical point of a liquid. The easiest way to do this is by means of the ψ -curve*”. By Prof. J. D. VAN DER WAALS.

(Communicated in the meeting of February 22, 1913).

If the ψ -curve is drawn at the triple point, the same straight line is touched by: 1. the ψ -curve liquid-vapour, 2. the ψ -curve for the solid substance. Let us put the case that occurs most frequently, in which $v_s < v_l < v_g$. On rise of the temperature the ψ -curves descend, but not in an equal degree. The liquid-vapour curve descends more than the curve for the solid substance. Relatively ψ_s ascends therefore. And accordingly the tangent for the coexisting states liquid-vapour, and that for the coexisting states liquid-solid are separated. The pressure has increased, but that for the coexistence solid-liquid far more than for the coexistence liquid-vapour. When the temperature continues to rise the ψ -curve for the liquid will more and more approach the ψ -curve for the solid substance, and it will reach it at the temperature at which the solid state disappears at infinite pressure. At the critical point liquid-vapour these two states are identical; the solid state on the other hand has been expelled by the liquid state. This, however, takes place at a pressure equal to infinity and so a volume equal to v_o . Above this temperature the solid state no longer exists, but the liquid state does. I have shown elsewhere, however, that then, when the pressure again approaches infinity, and hence the volume to v_o , the viscous-solid state will probably appear.

If we now consider the case, in which, as for water and ice $v_s > v_l$, the p, T -line for the coexisting phases runs from the triple point to lower temperatures. Now two cases are possible, viz. that