Chemistry. — "*The boiling points of saturated solutions in binary systems in which a compound occurs*". By Prof. H. W. Bakhuis Roozeboom.

(Communicated in the meeting of November 25, 1905).

In a previous communication [1]) it has been ascertained what branches in the three-phase lines for solid, liquid and vapour may occur in binary systems in which a solid compound appears, namely for the three cases that:

a. the vapour pressure of the liquid mixtures diminishes gradually from the component A to the component B;

b. liquid mixtures occur with a minimum pressure;

c. liquid mixtures occur with a maximum pressure.

For the right understanding of the behaviour of such systems it is particularly desirable to ascertain what is the order of the phenomena which appear with different mixing proportions of the components when these, at a constant pressure, are brought from low to high temperatures.

If those pressures are very low the mixtures, at a sufficiently low temperature, are completely solid, and on elevation of the temperature, they pass gradually and, at last, completely into vapour, therefore simply a sublimation occurs.

If the pressures are sufficiently high (in the case of components which are not too volatile, 1 atm. is quite sufficient), the solid substances pass gradually and, at last, completely into liquid and these liquids evaporate at still higher temperatures. In this case, fusion takes place first and evaporation afterwards.

With moderate pressures, however, the melting and evaporation phenomena partly coïncide, namely when pressures are chosen which occur on the three-phase lines of the components or the compound.

What cases may be distinguished when no solid compound appears has been fully investigated previously, by me. [2])

Particular attention has been called to the fact that the three-phase line of the component B may be sometimes intersected twice at the same pressure, which is possible when this line exhibits the branches Ia and Ib, described in the previous communication. (See line BD' in fig. 1 and 6). In such a case two separate boiling

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[1]) These Proc. VIII, p. 455. I learned that Dr. Smits had also come to the conclusion that the minimum on the three-phase line did not coincide with point H.

[2]) Heterogene Gleichgewichte. Heft 2. p. 338, et seq.

points of solutions saturated with solid B occur, one on branch $1b$ and another on branch $1a$. At the last point, boiling does not take place on heating but on cooling. The t, x-figures at a constant pressure have been deduced by me, and the phenomena, in solutions of salts in water and of sulphur in carbon disulphide, have been demonstrated by SMITS and DE KOCK.

The figures 1, 3, 5, 6 show at once that this same case may also occur in solutions saturated with a compound of the two components as soon as their three-phase line shows branch $1b$ as well as $1a$. Examples of two boiling points of the saturated solution have not thus far been noticed in binary compounds although they should be far from rare.

In compounds where, among the saturated solutions, there is present one with a minimum pressure (Fig. 3), a second boiling point of the saturated solution might occur with solutions either richer in A or in B; in fact a third boiling point at the side of the solution richer in B would be possible if the point D in fig. 3 were situated so low that, at the same pressure, the branches DT_2, T_2T_1 and T_1H could be intersected in succession. The saturated solution would then in succession first disappear, then reappear to finally disappear once more. Examples belonging to this case have thus far not been sufficiently studied.

If branch 3 of the three-phase line exists for the solutions richer in B (GD in Fig. 1 and 6, GH in Fig. 3 and 5), then if this line is crossed, there occurs at a constant pressure a boiling point of the saturated solution of a different nature from that on branch 1. The t, x-figure of such a case is quite analogous to that derived by me [1] for saturated solutions of the component A whose three-phase line in Fig. 1, 3, 5 always indicates branch 3. On boiling the solution saturated with A the following transformation takes place :

$$\text{solid} + \text{liquid} \rightarrow \text{vapour.}$$
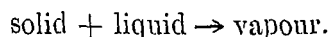
As solid and liquid now pass together into vapour in a definite proportion, it now depends on the quantity of those two phases which of the two disappears at the boiling point. This case occurs for instance on the three-phase line for ice in systems of water and little volatile substances as salts, also on the three-phase line for solid CO_2 in mixtures of CO_2 with less volatile substances such as alcohol.

The same must now also serve for compounds in so far branch 3 occurs therein. Among the binary systems whose liquid-vapour pres-

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[1] Heter. Gleichg. II. 341 et seq.

sure always diminishes from A to B, the branch 3 has thus far only been found with ICl_3 and ICl, as observed in the previous communication. From STORTENBEKER's experiments, it may be deduced that for ICl_3 the branch 3 extends from 34° at 100 mm. to 22°7 at 42 mm., for ICl from 22° at 24 mM. to 8° at 11 mM. The peculiar boiling phenomenon is, therefore, only possible between these temperatures and pressures, but has not been expressly stated in the solutions saturated with ICl_3 or ICl.

In binary systems in which a liquid with a minimum pressure occurs on the three-phase line of the compound, branch 3 must *always* appear as shown in fig. 3 or 5. Among the examples cited in the previous communication, there are sure to be found some where the simultaneous boiling of the solid phase and the solution may take place at 1 atm. pressure.

Another kind of boiling-phenomenon may, finally, take place on branch 2 of the three-phase line of a compound. This branch cannot occur with the components, for the peculiarity of the branch consists in this that the saturated solution contains an excess of the component B, whilst the saturated vapour contains an excess of A; the compound is, therefore, the phase whose composition is situated between those of the two others. This is, of course, only possible with a compound and not with one of the components.

According to Fig. 1, 3, 5, 6 of the previous communication branch 2 must occur with all compounds where coexisting liquids with an excess of B are possible, for it commences immediately at the melting point.

Now, this is possible with a number of hydrated salts which, below their melting point, yield saturated solutions with excess of salt; but the appertaining pressures are then generally so small that the boiling phenomenon cannot be readily observed. In the case of salt-hydrates which occur at a higher temperature so that the equilibrium-pressure on their three-phase line might amount to 1 atm., the solutions richer in salt seem to be very rare and no example is known to me.

An example is, however, known if H_2O is replaced by NH_3. With the compound $NH_4Br . 3NH_3$, branch 2 appears and the pressures are even greater than 1 atm. In this case the boiling phenomenon has been observed by me.

Branch 2 has, however, been met repeatedly in my previous researches on gas-hydrates where water is then the component B. If we now take those hydrates near solutions with more water the

vapour generally contains but little water, and we are dealing with branch 2.

The conversion now taking place with heat supply at a constant pressure is:

$$\text{solid} \rightarrow \text{liquid} + \text{vapour.}$$
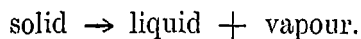
In all those cases it is, therefore, not the liquid which boils but the compound. The gas is very plainly seen to emanate from the crystals lying in the liquid, whilst the latter does not diminish but increases. The phenomenon has been very plainly observed with the two hydrates of HCl and of H Br and with those of SO_2 and Cl_2. With the last two and with $HCl.H_2O$ it could be observed at 1 atm. pressure.

It must also exist with I Cl but limited between 27° at 39 mm., and 22° at 24 mm., much more plainly with ICl_3 where it may appear between the melting point 101° at 16 atm. and 34° at 100 mm. Between this a three-phase pressure of 760 mm. occurs at 64°, and at the said temperature it may, therefore, be observed in an open apparatus. Solid ICl_3 breaks up into a liquid with 63 and into a vapour with 89 atom-percent of chlorine.

That similar phenomena may also appear in compounds which are very stable at a lower temperature, has recently been demonstrated by ATEN in the case of Bi_2S_3. This sulphide breaks up at 760° into a liquid containing 55 atom-percent of S and a vapour consisting almost exclusively of S. Therefore, the actual melting point of the sulphide cannot be determined at 1 atm. pressure. A similar behaviour may be expected of many compounds having a melting point situated much higher than the boiling point of one of its components, such as in the case of oxides, sulphides, phosphides etc.

We must point out another peculiarity which distinguishes the boiling phenomena on branch 2 from those on branches 1 and 3. The liquids and vapours belonging to the latter are both either richer in A or richer in B than the compound : consequently the boiling phenomena concerned are observed in systems consisting of the compound with a smaller or larger excess of one of the components. On branch 2 however the vapour is richer in A and the liquid richer in B, therefore the boiling phenomenon can occur in mixtures of the compound with A as well as with B. In the first case such a system, below the boiling point at the existing pressure, consists of compound + vapour and the liquid appears only at the boiling point, in the second case, the system below the boiling point consists of compound + liquid and the vapour appears at the boiling

point. In the particular case that the compound was perfectly pure, liquid and vapour should appear both together at the boiling point.

This may be made plain by the example of ICl_3. The whole t, x-figure at 1 atm. is schematically represented by fig. 7.
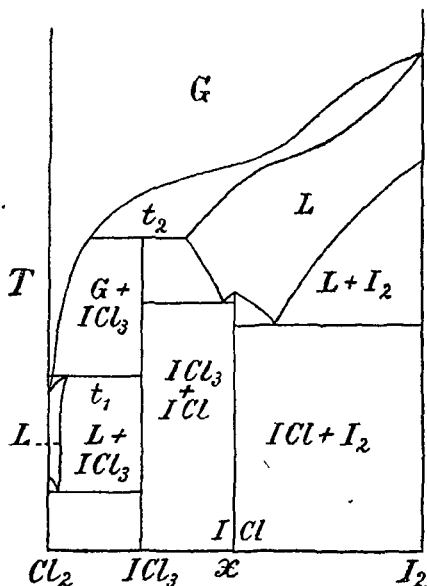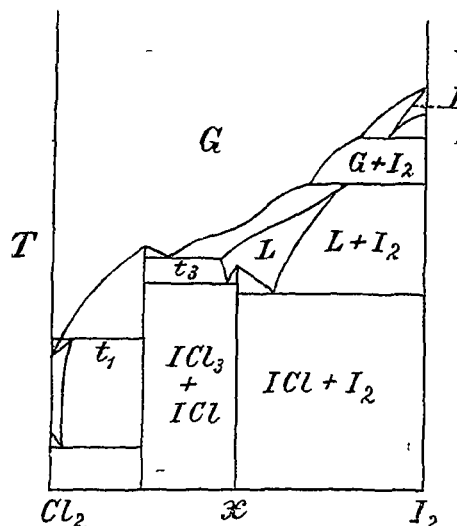

Fig. 7.   Fig. 8.

in which t_2 represents the temperature (64°) in question. In the different regions G represents vapour and L liquid. The further parts of the figure are entirely dominated in their relative situation by that of the three-phase lines. On this entirely depends which branches of a particular three-phase line will be intersected at the same pressure. In fig. 1 (previous communication) a simultaneous intersection of the branches Ia and Ib is only possible on the three-phase line of the compound. If, however, as with ICl_3, the melting point F lies at a high pressure, a simultaneous intersection of Ib with 2 or 3 is possible. This is why in Fig. 7, besides the boiling point t_2 on branch 2, t_1 also occurs as boiling point on branch 1b.

The pressure of 1 atm. is also higher for ICl or I than their three-phase line, consequently for these compositions, melting and boiling phenomena occur quite separately and the melting point lines of ICl and I run quite below the boiling point line.

If we take a pressure somewhat lower than 100 mm. we obtain a t, x-figure 8. For ICl_3 we now have again t_1 as boiling point on branch 1b and t_3 as boiling point on branch 3. For ICl, melting and boiling are still quite distinct but at a pressure below 100 mm.

the three-phase line for solid iodine is intersected both on branch 1b and 1a and therefore the complication in the figure occurs at the side of the iodine.

Still greater complications may appear when according to Fig. 3 (previous communication) there exist liquids with a minimum pressure and when consequently the branches 1b, 1a and 1b can also appear at the side of the liquids richer in B, whose intersection at an equal pressure may coincide eventually with those of branch 2 or branch 3. When such systems have been more closely investigated it will not prove difficult to give detailed t, x-figures for the same.

Chemistry. — *"The reduction of acraldehyde and some derivatives of s. divinyl glycol (3.4 dihydroxy 1.5 hexadiene)"*, By Prof. P. VAN ROMBURGH and W. VAN DORSSEN.

(Communicated in the Meeting of November 25, 1905)

The reduction of acraldehyde (acroleïne) with sodium amalgam [1] as well as with zinc and hydrochloric acid [2] has been studied by LINNEMANN, who states that he has obtained in the first case propyl and *iso*propyl alcohol, in the second case *iso*propyl and allyl alcohol, also a substance called acropinacone of the composition $C_6H_{10}O_2$, or rather a product of non-constant boiling point, of which the fractions boiling between 160°—170° and 170°—180° gave, on analysis, values which led to this formula.

CLAUS [3] could not confirm the results of LINNEMANN as regards the formation of *iso*propyl alcohol in the reduction with zinc and hydrochloric acid.

GRINER [4] has also repeated LINNEMANN's experiments with the object of preparing acropinacone (divinylglycol) but only obtained very small quantities of a liquid without constant boiling point which bore no resemblance to the glycol which, however, was obtained by him in fairly large quantity by reduction of acraldehyde in acetic acid solution with a copper-zinc couple. The other products of the reaction have not been further described by the author.

If we consider the formula of acraldehyde in connection with the

[1] Ann. d. Chem. u. Pharm. 125 (1863) S. 315.

[2] Ibid Suppl. III (1864—1865) S. 257.

[3] B. B. III. (1870) S. 404.

[4] Ann. d. Phys. et Chim. [6] 26 (1892). p. 369.