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

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday September 26, 1903.

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CONTENTS.

The following papers were read:

Chemistry. — "*The course of the solubility curve in the region of critical temperatures of binary mixtures*" [1]). By Dr. A. SMITS. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

The results of the experiments on critical temperatures of binary mixtures, which have been suggested by the theory of VAN DER WAALS, and the completion of the pressure-temperature-concentration-diagram for the equilibrium of *solid* phases with liquid and vapour lately given by BAKHUIS ROOZEBOOM [2]), made it probable that the pending

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[1]) My first communication on this subject appeared in Zeitschr. f. Elektroch. 33, 663 (1903).

[2]) Proc. Royal Academy Amsterdam 1902, 276.

12

problem of the course of the solubility curve of a solid in the region of critical temperatures was-now capable of solution.

It follows namely from the combination of the two conceptions mentioned above, that the course of the solubility curve cannot show anything remarkable, unless the least volatile substance (*B*) occurs as a solid phase and its melting point lies higher than the critical temperature of the more volatile substance (*A*), which for the sake of brevity we shall call solvent.

We will now consider only the case when the two substances in the liquid state are miscible in all proportions. Then there is in the p, t, x-diagram a continued critical curve, connecting the critical points of the two components. Three different cases may now occur.
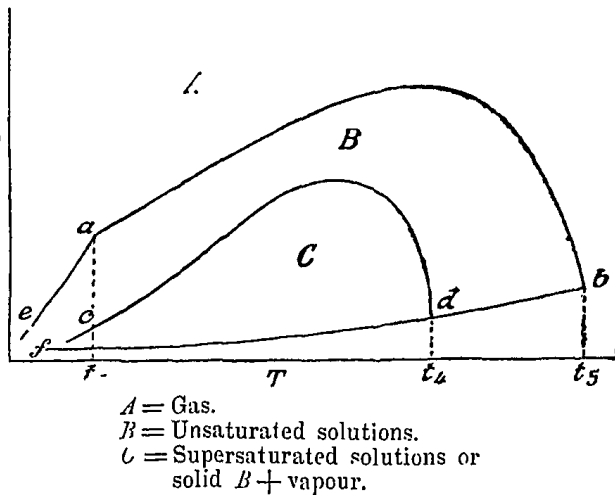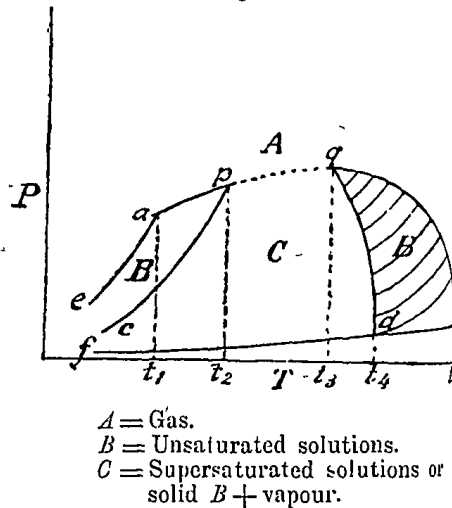
Fig. 1.   Fig. 2.

A = Gas.
B = Unsaturated solutions.
C = Supersaturated solutions or solid B + vapour.

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Fig. 1 and 2 are p, t-projections of the representation in space, a is the critical point of A, b of B, while d represents the melting point of solid B. The line ab is the critical curve and cd the p, t-line for the three-phases equilibrium: solid B+solution+vapour. Further ea is the vapour-tension line of liquid A, fb that of liquid B.

Now the case of fig. 1 will occur when the solubility of solid B in A is comparatively great. In this case the vapour-tensions of the saturated solutions are rather small and so the curve cd lies totally below the critical curve.

The line cd runs on uninterruptedly as far as the melting point of B; the series of the saturated solutions of B is not interrupted by the critical phenomena of the solution; the solubility curve shows nothing remarkable. On the other hand the critical curve also goes on uninterruptedly, the critical phenomena being only those of solutions which are *unsaturated* of solid B.

In the second case, fig. 2, I supposed the solubility of B in A, even at the critical temperature of A, to be still so small, that just a little above it the line cd intersects the critical curve. Then such an intersection takes place in two points p and q.

Now the critical-temperatures and pressures between a and p and between q and b refer to *unsaturated* solutions. At p and q, however where the p, t-line of the solutions and vapours saturated of solid B and the critical curve meet, the case occurs, when the saturated solution is found at its critical temperature; for here the vapour-tension of the saturated solution is quite equal to the critical pres-sure and so *saturation temperature and critical temperature must coincide*.

If we were to prolong the critical curve from p to q, we should pass through the region of solutions and vapours *supersaturated* of solid B. Hence critical phenomena will be possible here only provided that the solid phase B does not occur. So this part of the critical curve is *metastable*.

To prolong the three-phases-line between p and q, on the other hand, is impossible, as will soon be evident.

A third case forming a transition between fig. 1 and 2 would be the following: the curve cd would touch the inside of the critical curve in one point. The points p and q would coincide at this point. Hence the chance that such a case should occur is extremely small.

A better insight than by the p, t-projections of the representation in space is, however, given by the p, x-projections, especially when these are combined for different temperatures as in fig. 3 and 4, which has already been indicated by Prof. BAKHUIS ROOZEBOOM [1]). That is why I here add p, x-projections both for case 1 and for case 2 and in order to be able to construct from these projections the entire t, x-diagrams also, I have given the projections starting from the critical temperature of A up to the melting point of B.

The preceding px-diagrams 3 and 4 correspond with the p, t-dia-grams 1 and 2. Let us first confine ourselves to fig. 3. At the critical temperature t of the substance A, ae and ac are the p, x-curves for coexisting vapours and liquids (unsaturated solutions). The points c and e indicate the *saturated* solution and the vapour in equilibrium with it. Further for the same temperature ge is the p, x-curve for the *vapours* and cf the p, x-curve for the *solutions* coexisting with solid B. According to the theory of VAN DER WAALS ge and cf are at bottom two portions of a *continuous curve*, which

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[1]) Zeitschr. f. Elektroch. **33**, 605, (1903).
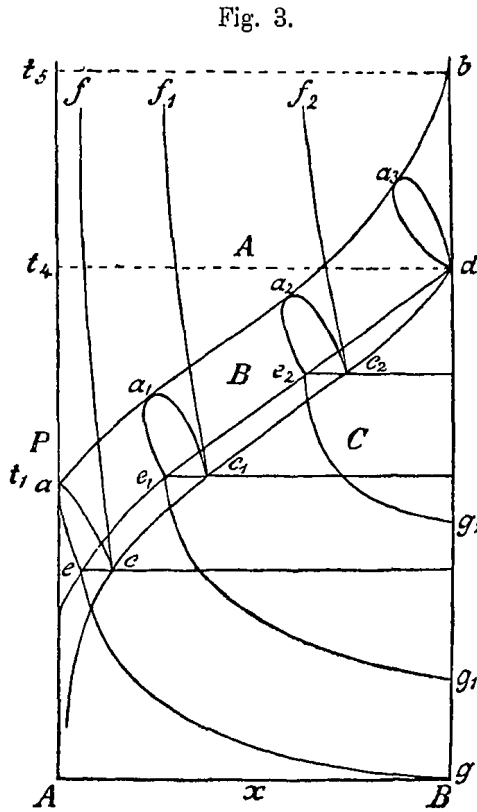
Fig. 4.

Fig. 3.

A = Gas.
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    solid B + vapour.
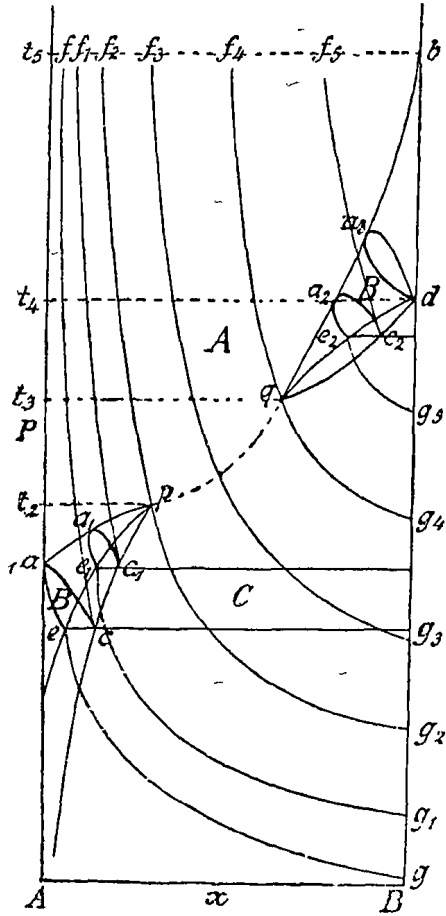
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has between c and e a part only partly to be realized with a maximum and a minimum.

For a somewhat higher temperature the diagram is a little different, because now the vapour- and liquid curve continuously pass into each other with a critical point in a_2, the vapour-line $g_1 e_1$ being shorter than at the former temperature. At rise of temperature this vapour-line continually decreases in length, until at the melting point of B in the point d it has disappeared altogether. Above the melting point a saturated solution is no longer possible and so there we get only a liquid- and a vapour-line with a critical point in a_3. If we draw a line through the points a, a_1, a_2, a_3 and b, a second through the points c, c_1, c_2 and d and a third through the points

e, e_1, e_2 and d, these lines indicate the said t, x-projections; ab is the critical curve, cd the curve of the saturated solutions and ed that of the vapours saturated with B. In accordance with fig. 1 the whole of the critical curve lies above the solubility curve; above the critical curve lies the gas-region and below the solubility curve the region of solid $B +$ vapour or of the *supersaturated* solutions.

After what precedes the connection between the fig. 2 and 4 is easy to see.

The solubility of B in A at the temperature t_1 being small, the vapour and liquid-lines ae and ac are short. Above t_1 ae and ac again fluently pass into each other and have already approached nearer to each other, because the saturated solution c_1 and the coexisting vapour e_1 differ less from each other; a consequence of this is that the lines $g_1 e_1$ and $c_1 f_1$ have also approached to each other. At t_2, the first critical temperature of the saturated solution, the solubility curve $cc_1 p$, the vapour-line $ee_1 p$ and the critical curve $aa_1 p$ concur. This implies that at this temperature the curve $g_2 p$ for the vapour coexisting with solid B is the prolongation of the curve pf_2 for the solution coexisting with solid B. The same occurs at a great many higher temperatures.

That a continuation of the lines cp and ep is *imaginary*, clearly appears from this diagram, as the vapour- and the liquid-line, if both were prolonged, would change places, which is impossible. [1]

Whereas from t_2 to t_3 *saturated* solutions are absolutely impossible, at t_3 the same phenomenon occurs as at t_2; here also the solubility curve $dc_2 q$, the vapour-line $de_2 q$ and the critical curve $ba_3 a_2 q$ converge and the critical phenomenon is observed with a *saturated* solution.

At higher temperatures a convergence of the three curves can no longer occur and in consequence all critical temperatures between t_3 and t_5, just as between t_1 and t_2, are critical temperatures of *unsaturated* solutions. If between p and q solution $+$ vapour $+$ solid B be impossible, it is conceivable, as suggested before, that we may succeed in getting *supersaturated* solutions and observing their critical phenomena. In such a case the dotted critical curve if prolonged might be realized between p and q, so this dotted line is *metastable*.

For a thorough knowledge of the phenomenon a p, x, t-diagram is most desirable and a v, x, t-diagram indispensable. Both space-

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[1] In the first communication, Zeitschr. f. Elektr. 33, 663, this point was not sufficiently cleared up.

representation I hope to communicate after some time and now I want to point out only the fact, -that the point p, which is bound to a certain concentration can be reached at only one very definite volume, which holds true for q also.

By means of the v, x, t-diagram it can also be made clear, that no line can be drawn of a definite limitation between the region for solid $B +$ vapour and the region of unsaturated vapours. In the region for solid $B +$ vapour we have namely a system consisting of two components in two phases, therefore a bivariant system wherein there are numberless ways in which with rise of temperature the pressure can be changed. Consequently it depends altogether on the volume what course we follow at increase of temperature.

In order to test the discussed phenomena by an example I chose for the substances A and B ether and anthrachinon. The critical temperature of ether is 190°, hence it is rather low, nor is the critical pressure high, namely $\pm$ 36 atmospheres. It is obvious that these two circumstances make the experiment much easier. Anthrachinon was chosen because this substance is very little soluble in ether, its melting point lies 283° above the critical temperature of ether and it is still very stable at its melting point.

The experiments were carried out in thick-walled tubes of 5 c.m. length filled with weighed quantities of ether and anthrachinon. The ether was free from alcohol and water; the anthrachinon was crystallized from icevinegar. The tubes filled with ether and anthrachinon were closed by melting while in a bath of — 80° (solid $CO_2 +$ alcohol) and then hanged up in an air-bath with little mica windows. This air-bath had been supplied with an apparatus, driven by a motor, for keeping the tubes constantly swinging. The temperature of the bath could be kept constant within 1°.

In order to determine the solubility curve the temperature was observed at which all the anthrachinon had been dissolved. In order to determine the critical curve at very slow decrease or increase of temperature this was noted down when formation of nebula occurred, resp. the liquid phase disappeared. The average of the two temperatures was noted down in the graphical representation. If possible the volume of the liquid was chosen in such a way, that on reaching the critical temperature the tube was nearly filled with liquid. Only saturation- and critical temperatures for mixtures of definite concentration being determined by these experiments, only a t, x-diagram can of course be constructed from them, which is given in fig. 5.

From a comparison with fig. 4 it is easy to see that the direction of the two pieces of the critical line and that of the line for the

Fig 5.
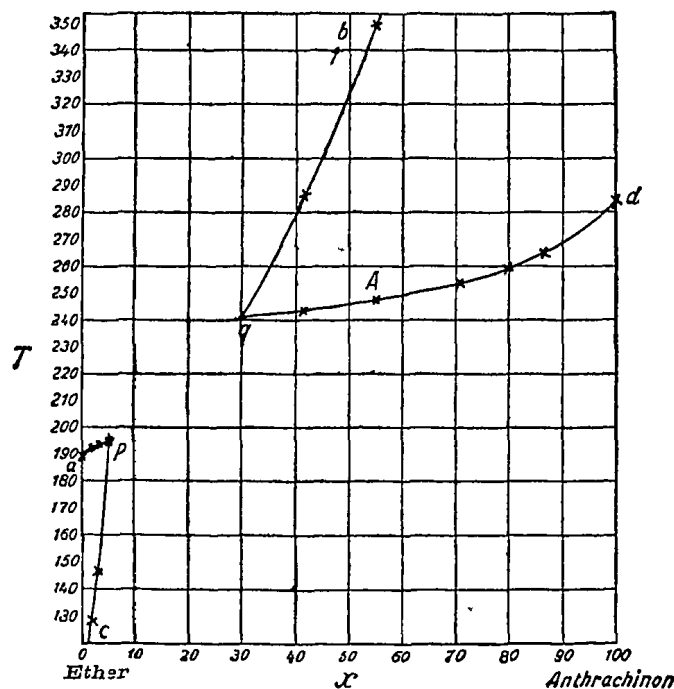
solutions saturated with solid B is quite conformable with the t, x-projection in fig. 4. The point p lies at 195°, 95 °/₀ ether and 5 °/₀ anthrachinon. The point q has, as regards the concentration, not yet exactly been determined; I estimate it at 70 °/₀ ether and 30 °/₀ anthrachinon, the temperature lies at 241°.

In order to elucidate the very remarkable phenomena we found, I shall more closely consider the case that we start from a mixture of ether and anthrachinon composed of 45°/₀ ether and 55°/₀ anthrachinon (A fig. 5) and slowly heat this mixture. The quantity of anthrachinon being so great and the volume rather small, we always have below 195° excess of solid anthrachinon together with a saturated solution and vapour. The concentration of the saturated solution at rise of temperature moves along the line cp. At about 195° we reach the first critical temperature of the saturated solution, when more heat is added the solution disappears and we get solid anthrachinon + vapour. Apart from the continually increasing evaporation of anthrachinon all remains unchanged up to about 241°. At this temperature the critical phenomenon occurs again; whereas at p the liquidphase *disappeared*, here it is *formed* again [1]). On further rise of temperature more anthrachinon is continually dissolving and along

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[1]) The points p and q can never be accurately reached in one experiment, a very definite volume being required for every concentration.

qd we go to the point A, where at 247° all anthrachinon has exactly been dissolved. If we now increase the temperature still more we come into the region of *unsaturated* solutions; from A therefore, we go parallel to the T-axis upwards to the temperature 350°, where the *unsaturated* solution has reached its critical temperature and all passes into the gaseous state.

The influence, which greatly diminishes the accuracy of the results, is the dependency of the volume; the error created by it, is small for the critical curve ap and for the solubility curve bq, because these curves have a rather slight curvature. For the critical curve bq and especially for the lower part the possible error in the concentration is rather great, so that the point q is pretty uncertain.

It seemed very interesting to me to investigate, whether or not it would be possible to determine points of the metastable part of the critical curve. I indeed succeeded to get between the temperatures t_2 and t_3 a solution, which, as discussed before, was supersaturated. A tube filled with 6°/₀ anthrachinon and 94°/₀ ether was heated in the air-bath. The solution saturated at the first critical temperature containing only 5°/₀ anthrachinon, some solid anthrachinon was still left above the critical temperature of 195°. At increase of temperature always more anthrachinon passed into vapour and at last all had become gas. Now, if I made the temperature fall rather quickly, no solid anthrachinon was deposited, which would have been normal, but at 211° a nebula appeared and a *supersaturated solution* was formed. Then, when I made the temperature fall slowly, the solution remained over a range of temperature of 9°. At 202° suddenly a transformation appeared by which the solution passed into solid anthrachinon and vapour and the metastable phase disappeared. On subtracting more heat the formation of nebula once more appeared at ±195°, the first critical temperature of the saturated solution, and for the second time a liquid was formed, but now this liquid was a stable phase. This phenomenon shows, that vapours are also possible, which are *supersaturated of solid* and for their transition into the stable phase choose a round-about way by another metastable phase, viz. a supersaturated solution.

I repeated the same experiment with a greater anthrachinon-concentration; now the formation of nebula appeared at 216°, it is true, but before a visible quantity of liquid had been formed, solid anthrachinon already was deposited. These two temperatures could not serve to determine the metastable part of the critical curve, because the vapour-space in the tube happened to be too large. So the temperatures under observation were not critical temperatures.

The results obtained enable me to somewhat elucidate a few dark points occurring in literature. From the experiments of WALDEN and CENTNERSZWER [1]) on the solubility of KJ in liquid SO_2 up to 96°, it is obvious that after one of the two liquid layers, which are coexistent between 77°.3- and 88°, have disappeared, the solubility decreases and at 96° amounts to no more than 0,58 mol. % KJ.

On account of this in their diagram they make the solubility curve below 100° terminate into the t-axis, as indicated in fig. 6. It is obvious, that this is not compatible with the theory given above, the prolonging of the solubility curve as far as the t-axis is certainly wrong. Most probably the same phenomenon appears with SO_2 and KJ as with ether and anthrachinon; the diagram may be somewhat different, the type, however, will be the same [2]). Hence it is not improbable, that on prolonging the solubility curve up to higher temperatures we should again observe an increase of the solubility, so that the direction up to the first critical temperature of the saturated solution will be somewhat like that indicated in fig. 7.
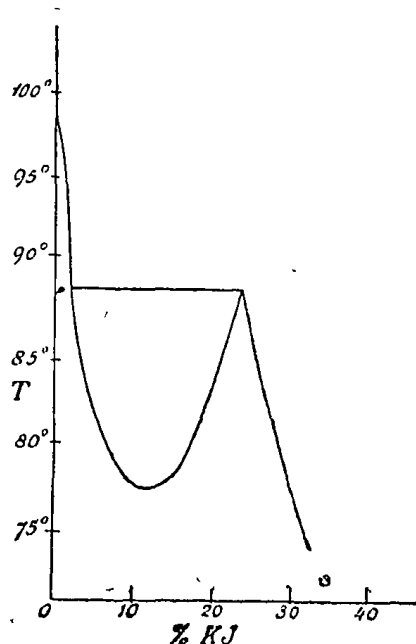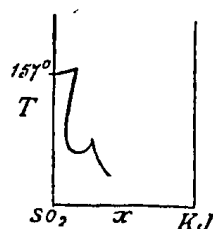
Fig. 6.

Fig. 7.

Since 1880 many more experiments have been made which point to the fact, that gases above their critical state are able to dissolve

[1]) Zeitschr. f. physik. Chem. 42, 456 (1903)

[2]) For the systems $SO_2 + Rb J$ and $SO_2 + Na J$ the same holds true. Zeitschr f. physik. Chem. 39, 552 (1902).

liquids and *solids* [1]). VILLARD e. g. found, that when he compressed oxygen at the usual temperature (17°) to ± ˙200 atmospheres in a tube with bromine, this evaporated in a much higher degree than corresponded with the vapour-tension at the temperature of observation. This could be observed because, while the oxygen was being compressed, the colour of the vapour grew darker and darker and because bromine on decrease of pressure was deposited against the wall in the form of little drops.

Fig 8.
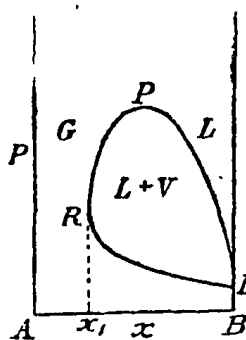
Prof. BAKHUIS ROOZEBOOM [2]) has already given an explanation of this phenomenon by means of the p-x-loop, which applies to the said system of *oxygen—bromine* at 17°, because this temperature lies far above the critical temperature of *oxygen* (— 111ᶜ) and also above the melting point of *bromine* (— 7,3°).

According to HARTMANN [3]) this p-x-loop has the form, given in fig. 8. It follows from the great rise and running back of the vapour-line ERP, that the partial pressure of the vapour of B between R and P must be much greater than the pressure in E. Though increase of pressure alone is sufficient to increase the vapour-tension, the influence of compressed gases is much greater in consequence of the solution of the gas in the liquid.

It is clear that by increase of the oxygen-tension *total* evaporation can be reached here, the region liquid + vapour having for a certain concentration of A' given place to the gas-region.

With the systems $CH_4—C_2H_5Cl$, $CH_4—CS_2$, $CH_4—C_2H_5OH$ VILLARD found the same phenomenon in an even more striking way. Also with *solids* VILLARD could observe an increase of the partial pressure. The partial pressure of iodine was perceptibly increased by an oxygen-pressure of ± 100 atmospheres, whereas with hydrogen a perceptible increase did not occur until at 200 à 300 atmospheres At ± 300 atmospheres methane dissolves very perceptible quantities of camphor and paraffine, even so much that on decrease of pressure the dissolved substances crystallize in visible quantities against the walls of the tube.

At 300 atmospheres acthylene dissolves rather much J, which on

[1]) HANNAY and HOGARTH. Proc. Roy. Soc. 30, 178, (1880).

    VILLARD. Journ. de Phys (3) 5, 453 (1896).

    WOOD. Phyl. Mag. 41, 423, (1896).

[2]) Die Heterogene Gleichgewichte 2, 99.

[3]) Journ, phys. Chem. 5 425 (1901).

decrease of pressure is deposited in crystals. Paraffine strongly dissolves in aethylene; so much so that under a pressure of 150 atmospheres we can make it evaporate *altogether*. Stearine acid also easily dissolves in aethylene, but not to such a high degree as paraffine.

As yet we have not been able to explain the total evaporation of a solid by a gas above its critical state, *without an intermediate liquid phase*; this is owing to the fact, that there was no suspicion of the behaviour shown by the system ether and anthrachinon. If we compare the figures 3 and 4 with each other, it is obvious that if in fig. 3 we start from solid B and by compression of A at a constant temperature we follow a course parallel to the x-axis from right to left, a liquid phase will always appear first before we come into the gas-region. This phenomenon observed by VILLARD in the system camphor-aethylene will also occur in fig. 4 between the temperatures t_1 and t_2 and between t_3 and t_4, so that this behaviour does not decide the type to which the system belongs. Investigations at different temperatures only would enable us to do so.

It is, however, quite different, when the solid evaporates altogether without giving a liquid first. If this be the case we can directly point out the type; then it belongs namely to type fig. 4, *for there only it is possible when coming from the region for solid B+vapour to pass into the gas-region without an intermediate liquid-phase, as long as we work between the temperatures t_2 and t_3.*

Probably the systems alcohol $+$ KI, KBr, $CaCl_2$ and $CS_2 + I_2$ ot HANNAY and HOGARTH, ether$+HgI_2$ of WOOD and CO_2+I_2 of VILLARD belong for the greater part to the type fig. 4. ·

That, as would follow from VILLARD's experiments, also the partial vapour tension of solids would be considerably increased by relatively slight pressures (100 à 200 atmospheres) of an additional gas, seems, however, possible to me only when the vapour-line of the system solid-vapour can get a course similar to that of liquid-vapour, which will probably be the case only when the added gas A dissolves in the solid phase B. This point will soon be investigated by me.

Chemical laboratory of the University.

Amsterdam, September 1903.