

Citation:

A. Smits, The course of the solubility curve in the region of critical temperatures of binary mixtures, in: KNAW, Proceedings, 6, 1903-1904, Amsterdam, 1904, pp. 484-497

Now let us consider only what happens for the vasomotor nerves. If these are excited by frequent shocks of the induced current, they react by a vasoconstriction followed by vasodilatation. If the shocks of the current are following one another very slowly, only dilatation is obtained. And finally, if a peripheral motor nerve innervating both striped muscle-fibres and vascular muscles, is stimulated, it may occur sometimes, that after one single shock of the current only contraction of the voluntary fibres follows. If several elementary stimuli, following one another in an appropriate rhythm, are applied, first a contraction of the striped muscles, may be observed, next of the vasoconstrictor, and finally of the vasodilatator fibres.

As soon as we suppose in the retina or in the skin the presence of more than one species of end-organs the possibility may be assumed that only one of these species reacts on stimuli of short duration, whilst other organs react on stimuli of longer duration. If stimuli of definite duration and intensity are made use of, both organs will react, each after its own latent period, in the same way as happens for muscles, vasoconstrictors and vasodilatators, so that we will obtain two sensations subsequent to each other. In cases, where three excitable organs coexist, even three separate sensations may be felt, as in the case of stimulation of the skin and of the retina.

Chemistry. — *“The course of the solubility curve in the region of critical temperatures of binary mixtures.”* (Second communication). By Dr. A. SMITS. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM.

(Communicated in the meeting of December 19, 1903).

In my preceding communication ¹⁾ on this subject I have represented in the figures 3 and 4 the p - x -sections for different temperatures, starting with the critical temperature of A and finishing at the melting point of B . Fig. 3 holds for the case that the three-phase-curve lies entirely below the plaitpoint-curve, and Fig. 4 applied to the case that the three-phase-curve cuts the plaitpoint-curve. In order to obtain the T - x -projection from the combination of the different p - x -sections, the variations of pressure were left out of account.

To complete what precedes the actual succession of the p - x -sections for different temperatures will be represented here.

¹⁾ These Proc. Oct. 27th 1903, p. 171.

Fig. 1.

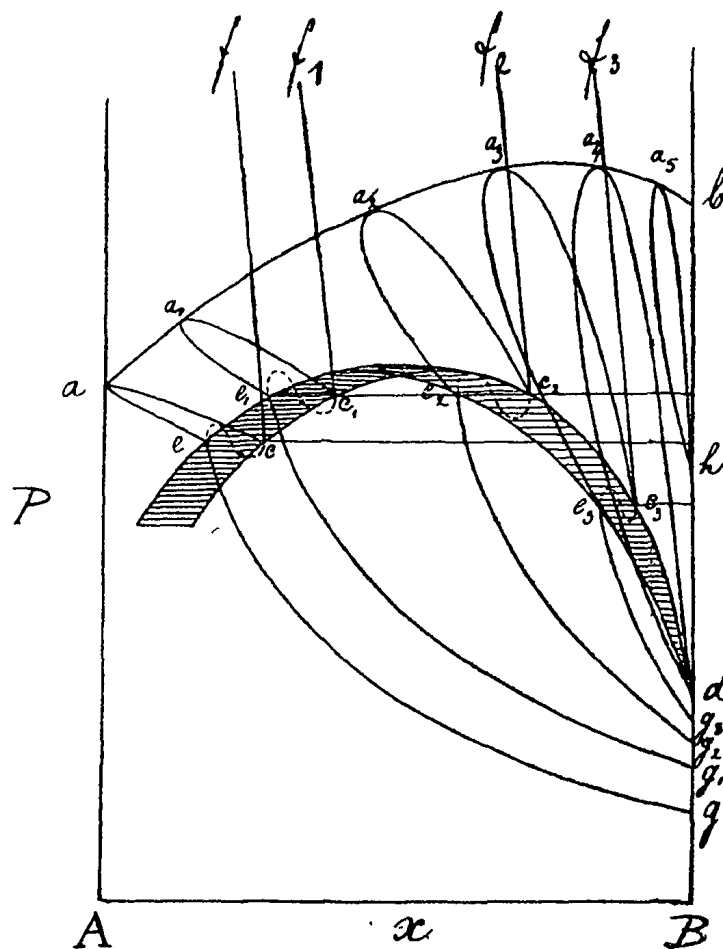


Fig 1 holds for the case that the whole of the three-phase-curve lies under the plaitpoint-curve. $c c_1 c_2 c_3 d$ is the curve of the solutions saturated with solid B ; $e e_1 e_2 e_3 d$ is the curve of the vapours coexisting with these saturated solutions. Both these curves terminate in the point d , the melting point of B . The hatched streak $e e_1 e_2 e_3 d c_3 c_2 c_1 c$ first ascends coming from lower temperatures; it reaches a maximum, and then descends again.

The curve $a a_1 a_2 a_3 a_4 a_5 b$ is the apparent outline of the p - x - t -surface on the p - x -plane, or the M -curve, $a a_1 a_2 a_3 b$ was the apparent outline of the p - x - t -surface on the T - x -plane or the R -curve.

As has been proved by VAN DER WAALS the curves $g e$ and $c f$ are two parts of one continuous curve with an intervening piece which is partly not realisable, and with two vertical tangents.

Fig. 2 represents the case, that the three-phase-curve cuts the plaitpoint-curve.

with the liquid mixtures, for which the line de represents the molecular volumes.

The point b indicates the mol. vol. of the vapour saturated with B and e the mol. vol. of the liquid saturated with B . $abcd$ is the region of the phase-complexes $L + G$, the nodal lines drawn in it connect coexisting phases.

The mol. vols. of the vapours coexisting with solid B lie on the curve bc , and the triangle bcf is the region for the phase-complexes $S_B + G$.

The coexisting phases lie in this case on lines traced from f to the curve bc . The triangle bfe is the three-phase-triangle and therefore the region for $S_B + L + G$.

The line eh , which divides the space under def into two parts, represents the mol. vols. of the liquids coexisting with solid B . For smaller volumes this line runs to the left, because in normal cases the solubility of B in A diminishes with decrease of volume.

The quadrangle $efhi$ is the region of the phase-complexes $S_B + L$, the coexisting phases are indicated by the small lines drawn in the figure. Inside $dehg$ we have only *one* phase, viz. liquid, and above abc only gas.

The lines cb and eh are two portions of a continuous curve with an intermediate portion, which will have two vertical tangents in normal cases. It is easy to prove this with the aid of the theory of VAN DER WAALS, and this can be done in a way analogous to that, in which VAN DER WAALS¹⁾ has proved the existence of two vertical tangents to the p - x -curve for solid-liquid.

We start then from the differential equation of v when x and T vary. (Cont., II pag. 104).

Let us denote the concentration and the mol. vol. of the solid phase by x_s and v_s and that of the coexisting gas phase and liquid phase by x_f and v_f , the equation is then :

$$(v_s - v_f) \left[\frac{\partial^2 \psi}{\partial v_f^2} dv_f + \frac{\partial^2 \psi}{\partial v_f \partial x_f} dx_f \right] + (x_s - x_f) \left[\frac{\partial^2 \psi}{\partial v_f \partial x_f} dv_f + \frac{\partial^2 \psi}{\partial x_f^2} dx_f \right] + \frac{(\epsilon_2 \cdot 1)_v}{T} dT = 0.$$

If T is kept constant, the last term of the first member becomes zero and we get after an unimportant transposition :

$$\left[(v_s - v_f) \frac{\partial^2 \psi}{\partial v_f^2} + (x_s - x_f) \frac{\partial^2 \psi}{\partial v_f \partial x_f} \right] dv_f = - \left[(v_s - v_f) \frac{\partial^2 \psi}{\partial v_f \partial x_f} + (x_s - x_f) \frac{\partial^2 \psi}{\partial x_f^2} \right] dx_f$$

or

$$\frac{\partial^2 \psi}{\partial v_f^2} \left[(v_s - v_f) - (x_s - x_f) \left(\frac{\partial v_f}{\partial x_f} \right)_{v,T} \right] dv_f = - \left[(v_s - v_f) \frac{\partial^2 \psi}{\partial v \partial x_f} + (x_s - x_f) \frac{\partial^2 \psi}{\partial x_f^2} \right] dx_f.$$

¹⁾ loc. cit.

We have :

$$(v_s - v_f) - (x_s - x_f) \left(\frac{\partial v_f}{\partial x_f} \right)_{p,T} = v_{sf}.$$

v_{sf} denotes the decrease of volume per molecular quantity, when an infinitely small quantity of the solid phase passes into the co-existing phase at constant pressure and constant temperature.

By substitution we get:

$$\frac{\partial^2 \psi}{\partial v_f^2} \cdot v_{sf} \cdot dv_f = - \left[(v_s - v_f) \frac{\partial^2 \psi}{\partial v_f \partial x_f} + (x_s - x_f) \frac{\partial^2 \psi}{\partial x_f^2} \right] dx_f$$

or

$$\frac{dv_f}{dx_f} = - \frac{\left[(v_s - v_f) \frac{\partial^2 \psi}{\partial v_f \partial x_f} + (x_s - x_f) \frac{\partial^2 \psi}{\partial x_f^2} \right]}{\frac{\partial^2 \psi}{\partial v_f^2} \cdot v_{sf}}.$$

VAN DER WAALS has lately demonstrated that v_{sf} can twice become zero when v_s is smaller than v_f , in consequence of which $\frac{dv_f}{dx_f}$ becomes twice infinitely large.

Further $\frac{\partial^2 \psi}{\partial v_f^2}$ can also twice become zero, but this does not give rise to an infinitely large value for $\frac{dv_f}{dx_f}$, as, $\frac{\partial^2 \psi}{\partial v_f^2}$ being zero, and we being therefore in D or D' (Fig. 2 VAN DER WAALS), $v_{sf} = \infty$ and $\frac{dv_f}{dx_f}$ has therefore a finite value.

If v_s is larger than v_f , which may also occur, then only one vertical tangent is possible. This is attended by a change also in the course of the lower part of the line $cbch$. In the above figure ch runs to the left for smaller volumes, but then this curve must directly run to the right, which means that the solubility of B in A increases for smaller volumes (larger pressures), a behaviour which may also be expected theoretically for smaller volumes when initially $v_f > v_s$, whereas the reverse, so the usual course is found for larger volumes. If, however, $v_s > v_f$ the course must be the abnormal one from the beginning.

For the better understanding of fig. 3 I shall add a few words about each of the different regions.

Let us assume that we have a mixture of the concentration x_1 for a volume $x_1 v_1$; we are then in the region of $L + G$. If we draw the nodal line $n v_1 n_1$ through v_1 , n denotes the mol. vols. and

the concentration of the liquid and n_1 those for the vapour coexisting with this liquid. In addition the relation between the volumes of liquid and vapour may be read from the pieces, into which the point v_1 divides the nodal line; it is viz. $\frac{\text{liquid}}{\text{vapour}} = \frac{n_1 v_1}{n v_1}$.

With a concentration x_2 and volume $x_2 v_2$ we are in the region $S_B + G$; the mol. vols. and the concentration of the vapour coexisting with solid B , are denoted by v_2 ; the relation of the volumes by $\frac{\text{solid}}{\text{vapour}} = \frac{n_2 v_2}{f v_2}$.

If we now take a concentration x_3 with a volume $x_3 v_3$, we are in the three-phase-triangle. The mol. vols. of the three phases are indicated by the three angles; the relative volumes are found by drawing a line from f through v_3 , till it intersects the line bc . The relation $\frac{\text{solid}}{\text{liquid} + \text{vapour}} = \frac{n_3 v_3}{f v_3}$ and the relation $\frac{\text{liquid}}{\text{vapour}} = \frac{bn_3}{en_3}$. If finally we have a concentration x_4 with a volume $x_4 v_4$, we are in the region $L + S_B$; the mol. vols. of the coexisting phases are now expressed by n_4 and n'_4 , the relative quantities being indicated by $\frac{\text{liquid}}{\text{solid } B} = \frac{v_4 n'_4}{v_4 n_4}$.

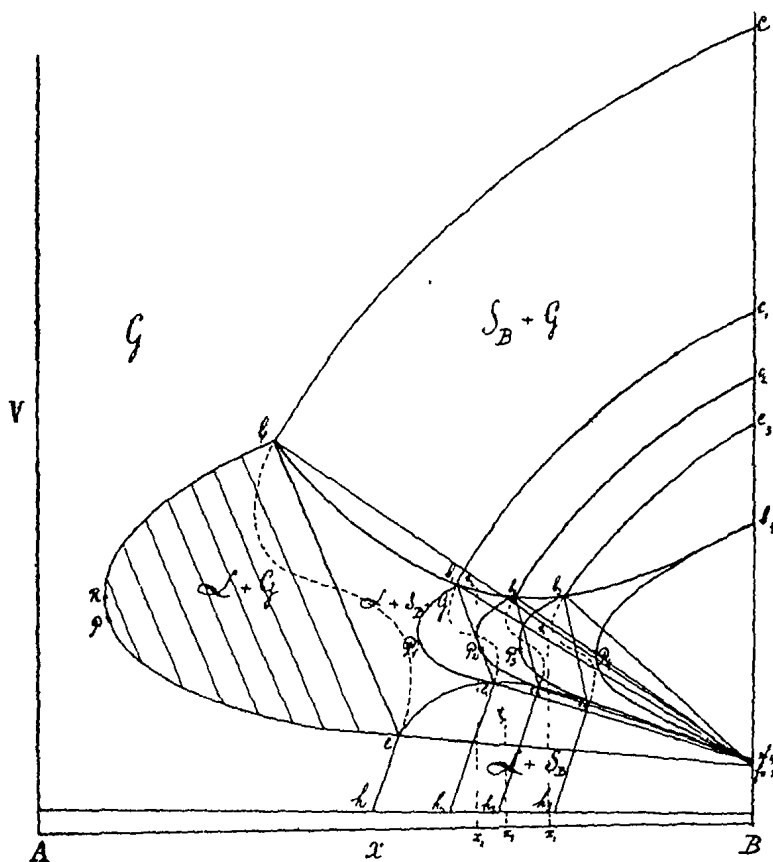
When the temperature rises, this vv -section suffers a change; in the first place the curves ab and bc are moved lower and the curves de and ef are moved upward. The displacement of the point f however is very small compared with the other displacements. The points b and e are also moved to the right, because the solubility of B in A is supposed to increase with rise of temperature.

These are the changes for the case that we are still below the critical temperature of A ; when we have reached this temperature, the curves ba and ed pass without a break into each other and with rise of temperature up to the melting point of B we get a series of conditions represented in Fig. 4. (p. 491).

The binodal curves bPe with the plaitpoints in P lie all inside each other; they cannot be prolonged to the B side below the melting temperature of B , because the substances A and B become miscible in all proportions only at the melting point of B . Just above the critical temperature of A the nodal lines for the saturated vapours and liquids have a strongly slanting position; at higher temperatures, however, they slant less, because the difference in concentration between b and e becomes smaller.

The curve $b b_1 b_2 b_3$ is the v - t -curve for the saturated vapours, the

Fig. 4.



curve $e e_1 e_2 f_1$ is the v - t -curve for the saturated liquids. The former curve has a minimum, the second a maximum¹⁾.

That the v - t -curve of the saturated vapour must have a minimum can be easily proved for the system $\text{AgNO}_3\text{—H}_2\text{O}$ ²⁾. In this case the matter is so simple, first because the vapour consists only of water and secondly because the maximum of the pressure is still below $1\frac{1}{2}$ atmosphere and therefore the law of BOYLE-GAY-LUSSAC may be applied for an approximation.

The vapour tensions of the saturated AgNO_3 -solutions are not yet accurately known, but this is of no importance here. We may assume here for the moment, that the values are perfectly accurate and then see what the position of the v - t -curve for the vapour must be.

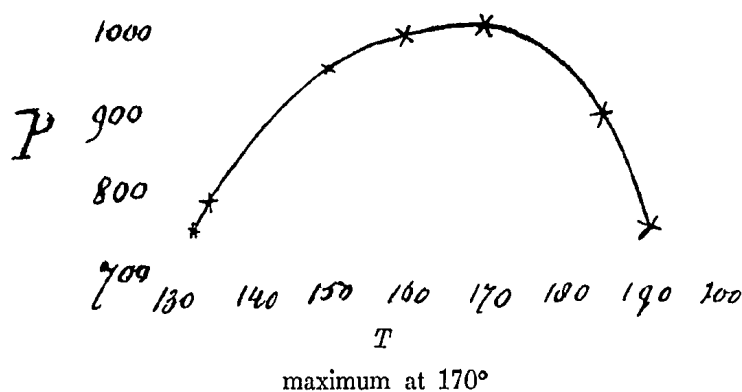
We get the following result :

1) Probably this need not always be the case.

2) These Proc. IV, 371. Dec. 28, 1901.

Temp.	Vapour tension in m.m. Hg.	Mol. vols. of the vapour in liters
133	760	33.35
135	800	31.82
150	960	27.49
160	1000	27.02
170	1010	27.37
185	900	31.75
191	760	38.09

Fig. 5.



The figures 5 and 6 are graphical representations of the pt - and the vt -curves.

We see, that the maximum in the pt -curve lies at about 170°, and that the minimum in the vt -curve lies at 161°. The maximum in fig. 5 is therefore not found at the same temperature as the minimum in fig. 6. (p. 493).

That this must be the case can be easily proved by applying the equation $PV = RT$. If we differentiate this equation, we get :

$$\frac{dv}{v} = \frac{dT}{T} - \frac{dp}{p}$$

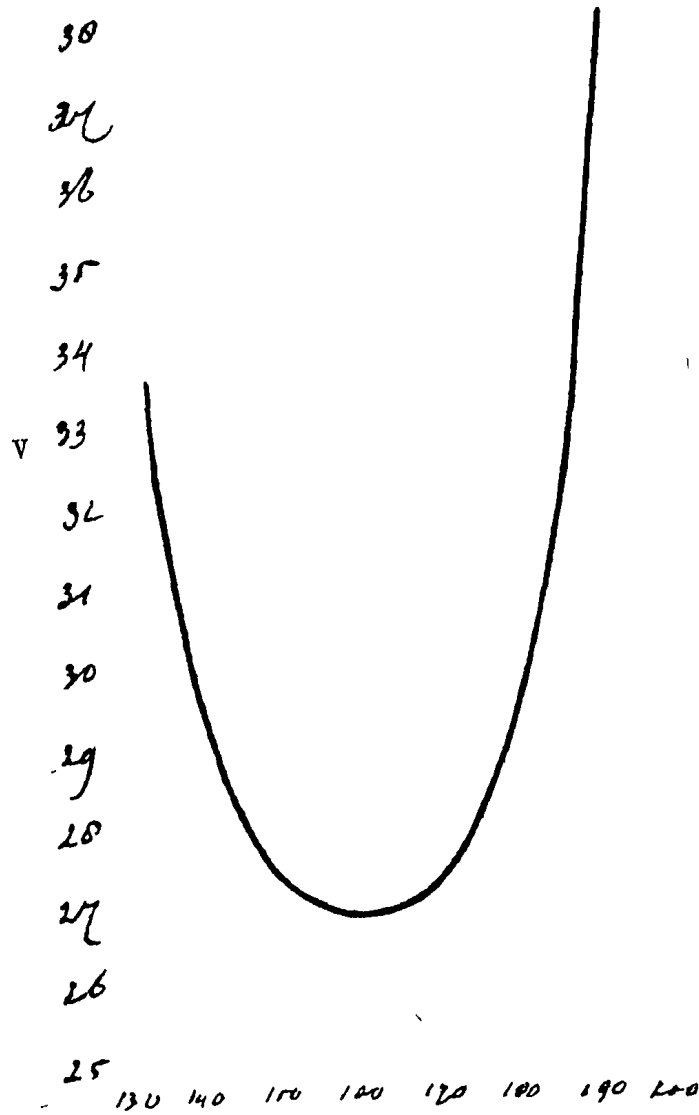
or

$$\frac{dv}{dT} = \frac{v}{T} \left(1 - \frac{T}{p} \frac{dp}{dT} \right)$$

For the minimum in the vt -curve $\frac{dv}{dT} = 0$ is therefore :

(493)

Fig. 6



minimum at 161° .

$$1 - \frac{T}{p} \frac{dp}{dT} = 0$$

or

$$\frac{dp}{dT} = \frac{p}{T}$$

So when $\frac{dv}{dT} = 0$, $\frac{dp}{dT}$ has a positive value. In the maximum of the vapour tension curve we have :

$$\frac{dp}{dT} = 0 \text{ hence } \frac{dv}{dT} = \frac{v}{T}.$$

So for the temperature, at which the vapour tension curve has reached its maximum, the v - t -curve is ascending.

Finally I shall briefly point out that the value for $\frac{dp}{dT}$ at 161° , calculated from the vapour tension curve harmonizes well with the theoretical value $\frac{p}{T}$. For the range of temperature between 150° — 170° , p may be found from the following interpolation formula

$$p = p_{150} + 5,5 (t-150) - 0,15 (t-150)^2$$

For 161° follows from this

$$\frac{dp}{dT} = 2,2$$

and

$$\frac{p}{T} = \frac{1001}{434} = 2,3.$$

It follows from the construction that the v - t -curve for the saturated solutions can have a maximum, but it is not easy to deduce this theoretically.

We shall now continue the discussion of fig. 4.

If we take a concentration x_1 with a volume $x_1 v_1$ and at the temperature for which the first v - x -section holds, we are in the three-phase-triangle bfe , and so we have side by side $S_B + L + G$. At the temperature for which the second v - x -section is drawn, the point v_1 is no longer in the three-phase-triangle, but in the region for $S_B + G$; the liquid has therefore disappeared, and only solid $B +$ vapour is left.

At the temperature corresponding to the third v - x -section the point v_1 has returned to the three-phase-triangle and solid $B +$ vapour has therefore been partly converted into a liquid. At the temperature corresponding to the fourth v - x -section the point v_1 is found in the region of the unsaturated liquids with their vapours and at the melting point of the substance B , v_1 lies in the region of the vapour and so everything has evaporated.

If on the other hand we had started from the concentration x_2 with a volume $x_2 v_2$, we should have left the three-phase-triangle with increase of temperature and we should have reached the region for $S_B + G$, and have passed from there straight into the gas-region. As v_2 is situated above the v - t -curve bb_4 , there is here nothing retrograde as in the case discussed above. It is obvious that the retrograde phenomenon will occur for conditions lying above the tangent drawn to the v - t -curve bb_4 from a certain point f' (between

f_0 and f_4), and below that part of the curve bb_4 that lies between the point of contact and the point b_4 ¹⁾.

If we further consider the case that the composition is x_3 and the volume v_3 , we have the case that with rise of temperature we get from the three-phase-triangle into the region for $L + S_B$ and so that the vapour disappears. With further increase of temperature we pass directly from the region $L + S_B$ into the gas-region, just as for the condition x_2, v_2 we passed from the region $S_B + G$ into the gas-region. In the remaining cases nothing noteworthy takes place; we must only point out, that for systems of the type of fig. 4 the critical phenomenon can only be observed for *unsaturated* solutions.

Fig. 7 applies to systems of the type of ether-anthraquinone. The difference between this figure and the preceding one lies in the fact

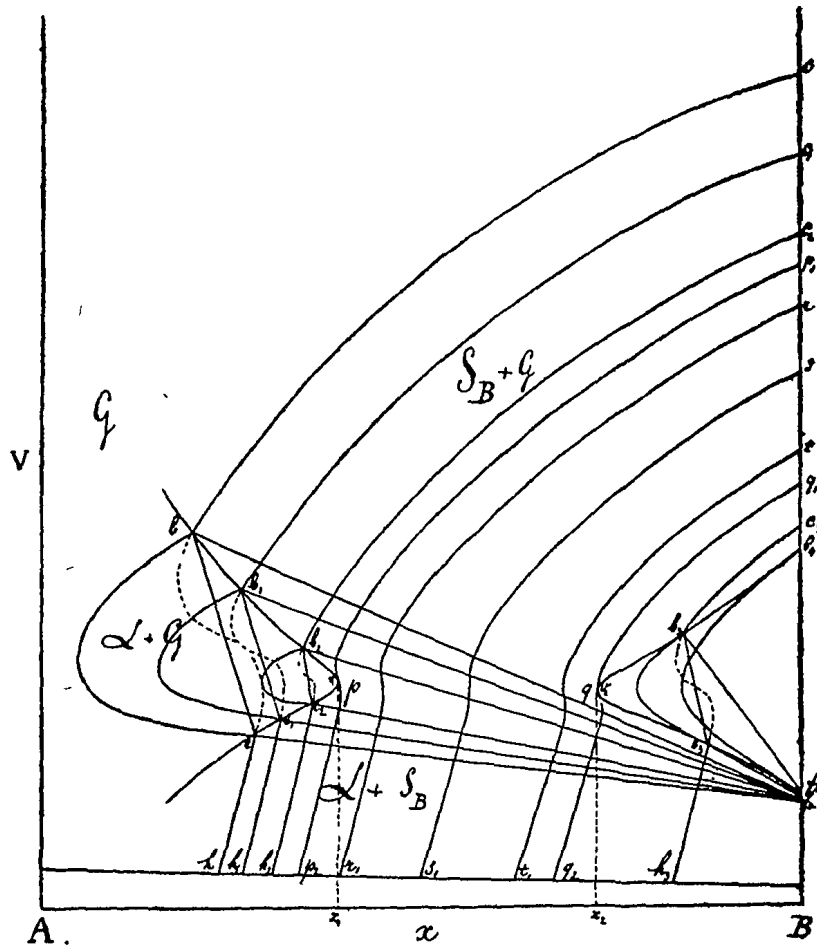


Fig. 7.

¹⁾ CENTNERSZWER (Zeitschr. f. Elektrochem. N^o. 40 S. 799 (1903) has lately drawn attention to this retrograde phenomenon.

that if we come from low temperatures the v - t -curve for the saturated vapour and that for the saturated liquid approach each other more and more, and finally pass without a break into each other. At q we get a repetition of what precedes in reversed order. On the left of p and on the right of q we have the same thing as in fig. 4; at p and q however, we see something special, viz. that here the critical phenomenon can be observed for a just *saturated* solution.

We have further seen in fig. 4 that the succession of conditions $L + S_B + G \rightarrow S_B + G \rightarrow G$ could occur there for conditions lying above the curve bb_4 . In fig. 7 this takes place, besides above the curves bp and qb_4 , also between the concentrations x_1 and x_2 , corresponding with the points p and q , for any *arbitrarily* chosen volume, because the region for $S_B + G$ between p and q passes continuously into the region for $S_B + L$. Hence this phenomenon will occur much more frequently for the type of fig. 7 than for the type of fig. 4.

The usual succession $L + S_B + G \rightarrow L + G \rightarrow G$ is here only possible for conditions lying within the v - t -curve $ee_1e_2pb_2b_1b$.

The retrograde phenomenon discussed above will here be observed for all conditions lying below the branch b_4b_3q of the second v - t -curve and above the tangent drawn to the branch qe_3f_4 from a point f (between f_0 and f_4). A very essential point of difference with the case of fig. 4 is further to be found, first in the circumstance that with a concentration x_1 and a volume x_1v_1 we pass here suddenly from the region $L + S_B + G$ into the gas region and secondly that for a composition *slightly* richer in B than x_2 , and with a volume x_2v_2 , just at the moment at which all the solid B would evaporate, a *saturated* solution is formed, which reaches its critical temperature immediately after its formation.

From fig. 7 follows that if we started from a concentration x_2 with a volume x_2v_2 , with which therefore the point q can be reached, the transition $L + S_B + G \rightarrow S_B + G$ takes place at a temperature lower than that corresponding to the point p , so that the points p and q can never be determined by one experiment, which it is practically superfluous to mention.

The curves p_1pp_2 , rr_1 , tt_1 and q_1qq_2 , which denote the mol. vols. and the concentrations of the "fluide" phases coexisting with solid B , have still two vertical tangents, as they are in the immediate neighbourhood of p and q , from which the retrograde solidification follows. For the curve SS_1 , drawn halfway between p and q , the two vertical tangents coincide in accordance with the px -curve in Fig. 2, which means, that there retrograde solidification is no longer possible.

We shall conclude with some remarks on the determination of the plaitpoint- or critical temperature.

As is known, the critical phenomenon for binary mixtures can only be observed, when before the region $L+G$ is left, there is exactly the same quantity of liquid as of vapour, or in other words, when the volume is exactly the same as the plaitpoint volume (see fig. 4). In this case we enter the gas region at the plaitpoint P . In general every concentration requires then another volume. If the volume is greater or smaller than the plaitpoint volume, we do not observe a critical phenomenon. In the first case we come to the gas branch of the binodal curve, and consequently total evaporation of the liquid takes place when the temperature rises slowly; the liquid mass decreases more and more and disappears in the lower part of the tube. In the second case we reach the liquid branch of the binodal curve and the whole tube is finally filled with liquid.

A sudden transition from the region $L+G$ into the gas region, in consequence of the fact that the liquid and the gas phase become *identical* is only observed for a volume equal to the plaitpoint volume, also when the temperature rises very slowly. Yet for other volumes phenomena may be observed, closely resembling the critical ones, but this is only to be attributed to the fact that the temperature rises too quickly for the equilibrium to be established.

For a simple substance the plaitpoint temperature is the highest, but this is not the case for binary mixtures. The highest temperature for a binary system will be observed for the volume of the critical tangent R , so for a volume larger than the plaitpoint volume (see fig. 4). For still larger volumes the liquid will again disappear at lower temperatures, so that from the plaitpoint volume to larger volumes the temperature, at which all the liquid has disappeared, and which we might also call condensation temperature, passes through a maximum value. If the volume is smaller than the plaitpoint volume, the tube is completely filled with liquid, but the temperature at which this takes place, is always lower than the plaitpoint temperature.

Amsterdam, Dec. 1903.

Chemical Laboratory of the University.