

Citation:

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The *general symmetrical cubic equation* can be brought by an *affine transformation* into the form $\psi(x) + \psi(y) = 2k$ only when condition (25) is satisfied.

This condition expresses that the three asymptotes of the cubic curve represented by the given equation pass through *one* point.

In connection with this we might have obtained equation (25) also in a geometrical way. Of a cubic curve which has as equation

$$A\xi^3 + B\xi^2 + C\xi + A\eta^3 + B\eta^2 + C\eta = 2D,$$

the three asymptotes pass namely through *one* point, a property which can stand an affine transformation.

Chemistry. — “*On the appearance of a maximum and minimum pressure with heterogeneous equilibria at a constant temperature*”.

By Dr. F. E. C. SCHEFFER. (Communicated by Prof. A. F. HOLLEMAN.)

(Communicated in the meeting of April 29, 1910).

In the spacial figure of a binary system in which occurs a complete miscibility in the liquid condition, a complete separation in the solid condition and where the vapour pressures of the liquid fall continuously from $x=0$ to $x=1$, two three-phase lines appear at the place where one of the two components in the solid condition coexists with liquid and vapour. Whereas the pressure values on the three-phase line of the first component increase continuously with the temperature, this is not the case with the line of the second component; ROOZEBOOM suspected that the latter in its P - T -projection always possessed a maximum¹⁾ Later, KOHNSTAMM²⁾ showed that this maximum need not appear always; from the equation of the three-phase line deduced in 1897 by VAN DER WAALS³⁾, the condition could be deduced when a maximum appeared and when not, because in the former case the value of $(\eta_v - \eta_s) - \frac{v_v}{v_l}(\eta_l - \eta_s)$ must be 0. This condition, however, may point to the appearance of a minimum as well as that of a maximum.

The appearance of a minimum pressure on the three-phase line of the second component becomes even very probable when a minimum occurs in the P - x -lines of the liquid-vapour plane. For this case the

¹⁾ BAKHUIS ROOZEBOOM, Heterogene Gleichgewichte. II. 331.

²⁾ KOHNSTAMM, Proc. 1907, Febr. 23.

³⁾ VAN DER WAALS, Proc. 1897, April 21.

P - T -projection of the spacial figure has been indicated in fig. 1 and the T - x -projection of the two three-phase lines in fig. 2. The three-phase line $O_A E$ is always situated above the sublimation line of A ; the line $O_B E$ always above that of B ; in point R the minimum line meets the three-phase line; liquid and vapour, under three-phase pressure, get here the same composition which, in fig. 2, amounts to an intersection of liquid- and vapour branches of the three-phase line of the second component. If we arrange the three phases according to their B -content, the order in which they follow at temperatures above that of R is LGS_B , below R , GLS_B . We now see that at temperatures below R the above condition may be fulfilled ($x_v > x_l$ where these values relate to the first component), so that the value of $\frac{dp}{dt}$ becomes 0, which, therefore, in our case causes the appearance of a minimum.

The condition for the appearance of a minimum is, however, not dependent on the presence of a minimum pressure line on the liquid-vapour plane; of this it is totally independent, so that there exists the possibility that a minimum pressure may appear in the P - T -projection of the three-phase line of the second component while the liquid-vapour plane is still falling continuously from $x = 0$ to $x = 1$.

In the case of a line of maximum pressure occurring on the liquid-vapour plane, this line will, in quite an analogous manner, come in contact with the three-phase line of the first component (fig. 3 and 4). In point R the value of $\frac{dp}{dt}$ is positive $\left(= \frac{Q_{lv}}{V_v - V_l} \right)$; between R and O_A there is now a possibility of the appearance of a maximum which has been mentioned previously by KOHNSTAMM. In this case two maxima may therefore occur, although neither of them need necessarily appear at all. It appears from the T - x -projection that at temperatures between R and O_A (fig. 4) the condition $x_v > x_l$ is complied with and that the value of $\frac{dp}{dt}$ may become nought.

Now whereas in the spacial figure of the above mentioned form only maximum and minimum pressure lines can appear on the liquid-vapour plane, because the concentration of the solid matter never differs from 1 or 0, it becomes possible that maximum and minimum pressure lines for the coexistence of solid and liquid and of solid and gas also appear when the concentration of the solid matter is not limited to 1 and 0,

In the first place this may happen when one or more compounds occur in the spacial figure; as to the presence of minimum pressure lines on the SG and SL planes, which come in contact with the maximum sublimation point and minimum melting point on the three-phase line, several communications have appeared in these Proceedings from VAN DER WAAALS, BAKHUIS ROOZEBOOM, SMITS and others.

In the second place similar lines may occur in systems where the solid matter is a mixture of the components in varying proportions (mixed crystals). If we suppose that complete mixing takes place in the solid condition we can readily observe the possible cases from fig. 5. In this figure is drawn a circular curve of which the three-phase line forms a part; this gives us a simple means for observing all the possibilities. We conclude from this figure that six types are possible in which one line of maximum or minimum pressure comes in contact with the three-phase line (ab , bc , cd , de , ef , fa , where these letters indicate each time the triple points of the components). We can also distinguish six cases where two contacts occur ($a(b)c$, $b(c)d$, $c(d)e$, $d(e)f$, $e(f)a$, $f(a)b$) and six, where three of the said lines have a point in common with the three-phase line ($a(bc)d$, $b(cd)e$, $c(de)f$, $d(ef)a$, $e(fa)b$, $f(ab)c$)¹⁾.

The other conclusions may, I think, be passed over, but it should be pointed out that it is shown, from fig. 5, in the plainest manner that when on the three-phase line occurs a point in which $x_s = x_l$ and another in which $x_l = x_g$, there must also occur on the three-phase line a point in which solid and gas have the same composition, a condition which we notice occurs in quite an analogous manner in the appearance of a dissociating compound.

Let us consider more particularly the case in which three lines of minimum pressure occur in the spacial figure (fig. 6). We then obtain a P, T projection which exhibits a great analogy with that of a dissociating compound which is less volatile than both components. The line where S and L have the same composition meets the three-phase line in R_1 , the one where S and G have the same composition does so in R_2 ; in analogy with the corresponding remarkable points of a dissociating compound we may call these points the minimum melting point and maximum sublimation point of the mixtures behaving as a simple substance; both these points which in a dissociating compound exhibit one composition in their positions occur here with different x . This causes also the P, T line for the constant x to pass

¹⁾ In this communication it has been assumed that the solid matter, on melting, always increases in volume.

through R_1 (which therefore, possesses a cusp) and not through R_2 and reversedly, so that the two cusps of the P, T line of the compound occur in our case no longer on one but on two different lines ¹⁾.

The T, x -projection of the three-phase line represented in Fig. 7 exhibits the intersections of the liquid and solid branch in R_1 , of the solid and gas branch in R_2 , of the liquid and gas branch in R_3 ; the three said points correspond with the homonymous ones in the P, T -projection (fig. 6).

Finally, it should be mentioned that the appearance of a maximum or a minimal pressure on the three-phase line may be readily ascertained from the equations given by VAN DER WAALS in 1897.

$$\frac{dp}{dt} = \frac{(\eta_v - \eta_s) - \frac{x_v - x_s}{x_l - x_s} (\eta_l - \eta_s)}{(v_v - v_s) - \frac{x_v - x_s}{x_l - x_s} (v_l - v_s)}$$

has the value 0 when the numerator becomes 0, for this we require $x_v - x_s > x_l - x_s$; this condition is fulfilled on the three-phase line between O_A and R_1 where, consequently, a maximum pressure may appear, whilst between O_B and R_3 a minimum pressure may occur.

It will be a simple matter to deduce also the possible forms for the other cases; the collection of facts at our disposal, is as yet too incomplete for us to be certain as to the occurrence of the above cases. However, the melting point lines of the system $\text{HgI}_2 - \text{HgBr}_2$,²⁾ *d*- and *l*-carvoxime³⁾, monochlore-monobromohydrochinondiacetate⁴⁾, *p*-azoxyphenetol-*p*-methoxycinnamic acid⁵⁾, *p*-azoxyphenetol-cholesteryl benzoate⁵⁾ and of many others point to the appearance of maximum and minimum lines on the SL -plane and a good many examples are already known of maximum and minimum lines on the LG -plane, although in the latter cases there is generally no complete certainty as to the nature of the solid phase.

¹⁾ SMITS, Proc. 1906 April 27.

²⁾ REINDERS, Dissertation, Amsterdam 1899.

³⁾ ADRIANI, " " 1900.

⁴⁾ KÜSTER, Zeitschr. f. Physik. Chemie 8. 583.

⁵⁾ A. PRINS, Dissertation, Amsterdam 1908.

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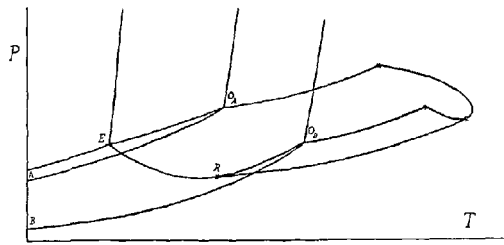


Fig. 1.

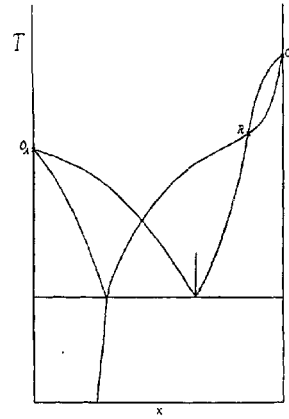


Fig. 2.

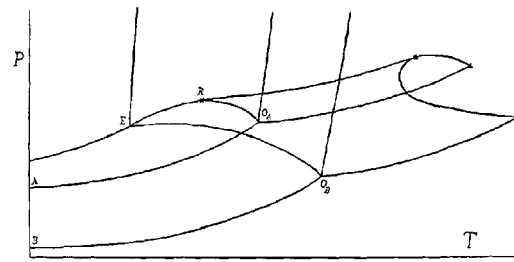


Fig. 3.

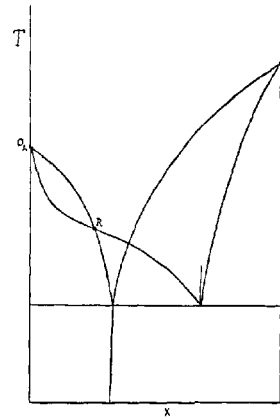


Fig. 4.

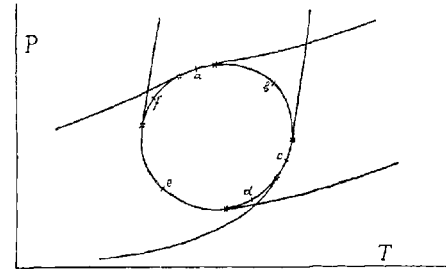


Fig. 5.

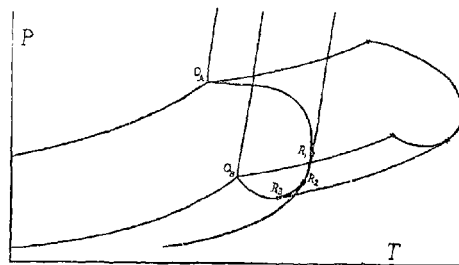


Fig. 6.

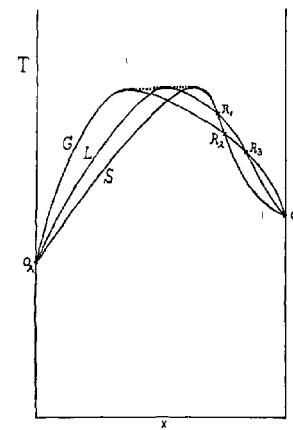


Fig. 7.