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Chemistry. — “Critical terminating points in three-phase lines with solid phases in binary systems which present two liquid layers.”

By Prof. H. W. BAKHUIS ROOZEBOOM and Mr. E. H. BÜCHNER.

(Communicated in the meeting of January 28, 1905).

Up to the present only one critical terminating point has been found in systems of one component, namely in the equilibrium liquid-vapour. If this is represented by a p, t -line this suddenly terminates in the point where liquid and vapour have become identical. There exist at the moment no well-founded reasons to assume critical terminating points also in the equilibria solid-liquid and solid-vapour. We will not further consider these here.

In systems of two components we get instead of a critical point

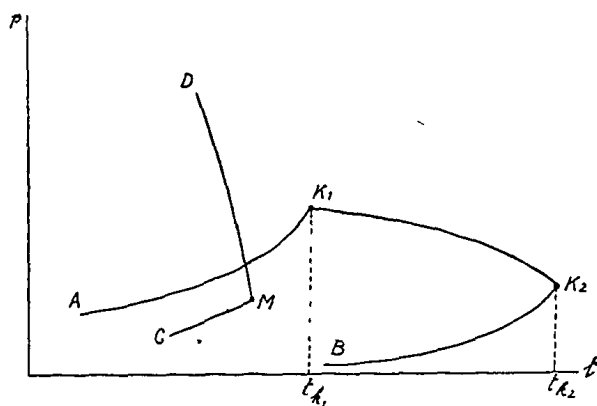


Fig. 1.

liquid-vapour, a critical line K_1K_2 , which connects the critical points of the components. In a p, t, x -diagram this line runs in space, here its p, t -projection is only indicated. (AK_1 and BK_2 are then the equilibria-lines liquid-vapour for the components A and B). If

there is a homogeneous mixing for all concentrations in the liquid phase, this will then be the *only* critical line.

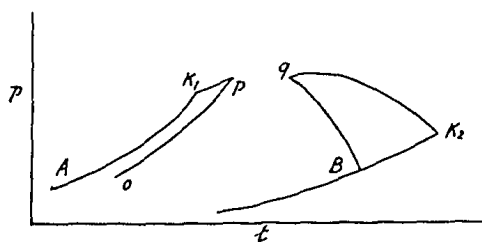


Fig. 2.

are then two such meeting-points p and q with the two parts $o p$ and $q B$ of the three-phase line. This line therefore acquires two critical terminating points owing to its meeting the critical line liquid-vapour. Between p and q both lines cease to exist.

¹⁾ These Proceedings 1904.

Other cases of similar critical terminating points through the meeting of three-phase lines in binary mixtures might be conceived when no homogeneous mixing in all concentrations is possible in the liquid phase and when, therefore, two liquid layers are possible. It was of great importance for the knowledge of the conditions of existence of solid phases at high temperatures and pressures to also trace the critical terminating points in similar cases. If we indicate the two liquid layers by L_1 and L_2 , the vapour by G and the one or other component in the solid state by S , then besides the three-phase line SLG , two other three-phase lines SL_1L_2 and L_1L_2G will be possible. In order to trace the critical terminating points of these lines we

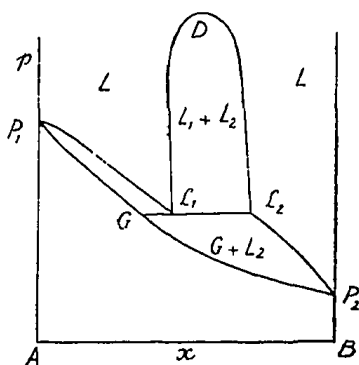


Fig. 3.

first consider the line L_1L_2G . Here we first take exclusively the cases where the p, x -diagram has the form of Fig. 3, in which G, L_1 and L_2 indicate pressure and concentration of coexisting vapour with two liquid layers. The three-phase pressure for this system lies, therefore, between the vapour pressure of liquid A and B (P_1 and P_2)¹⁾.

The p, t -line CM for the three-phase equilibrium L_1L_2G is situated accordingly in Fig. 1 between AK_1 and BK_2 .

On elevation of temperature L_1 and L_2 may approach each other, or recede. If the first happens and if they still coincide below the line K_1K_2 , for instance in M , then the two layers become identical, a case of which many instances have been found by ALEXEJEV and ROTHMUND. This point has been quite properly called a critical point. This critical terminating point of the line for L_1L_2G must of course necessarily be a point of intersection with a critical line. The said critical line is the line DM in Fig. 1.

If the liquids L_1 and L_2 can be made to mix more completely by an increase of pressure a mixing point D will be found to exist in Fig. 3 at a sufficiently high pressure. If now L_1, L_2 approach each other at a higher t , D will then be situated at a lower pressure whilst the concentration in the mixing point may differ. In this way is obtained the critical line DM for the phases L_1L_2 . Its one terminating point lies at the meeting point M where G occurs together with L_1L_2 and where consequently the lowest possible pressure is

¹⁾ The other case where the three-phase pressure is higher than those two does not lead to materially different results:

attained. In the upper direction a terminating point would only be conceivable in the case of the occurrence of a solid phase. If an increase of pressure promotes the separation of the two layers, DM would then run from the point M to the right instead of to the left.

In the case, therefore, in which the two liquid layers possess an upper mixing point M which lies below K_1K_2 , the critical lines K_1K_2 , for GL and DM for L_1L_2 , are quite independent of each other.

If, however, the upper mixing point is not yet reached below K_1K_2 , CM will continue up to a meeting point with K_1K_2 . As the phases occur in the order GL_1L_2 , G will then become identical with L_2 in O , Fig 4.

The critical line K_1O is here at the same time broken off. From a consideration of a series of p, x -diagrams for successive temperatures we may, according to Mr. BÜCHNER, easily demonstrate graphically that the other end of the critical line GL , which commences in K_2 , now amalgamates with the upper part of the critical line L_1L_2 , the lower continuation of which is not realisable owing to the absence of M . In this way is formed the critical line K_2PD whose upper part may eventually also run to the right.

A junction of the three-phase line GL_1L_2 , with the critical line GL in O will, secondly, always take place when L_1 and L_2 diverge by an elevation of temperature. This may frequently occur with two liquid layers which have a lower mixing point M^1 . The three-phase line GL_1L_2 then terminates in O by intersection with the critical line GL and in M^1 by intersection with the critical line M^1P for $L_1 = L_2$. From the p, x -diagrams we may now again deduce that the upper continuation of this line is not now realisable because the lower part coincides with the second part of the critical line GL which proceeds from K_2 . In this way the critical line M^1PK_2 originates.

Lately, KUENEN has found instances of the cases represented by Figs. 4 and 5.

The figures 1, 4 and 5 exhibit the three main types of the manner in which the three-phase line meets either the critical line GL or the critical line L_1L_2 , and then finds 1 or 2 terminating

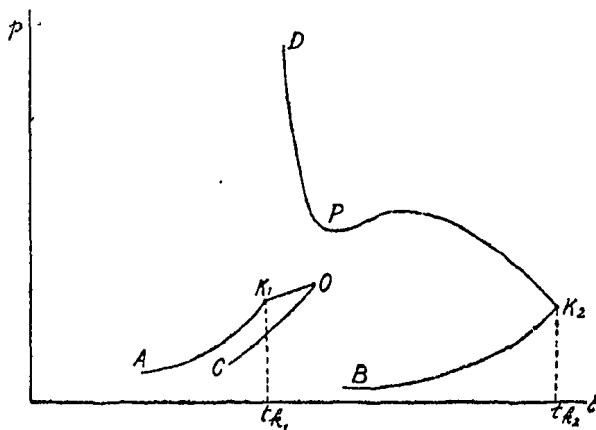


Fig. 4.

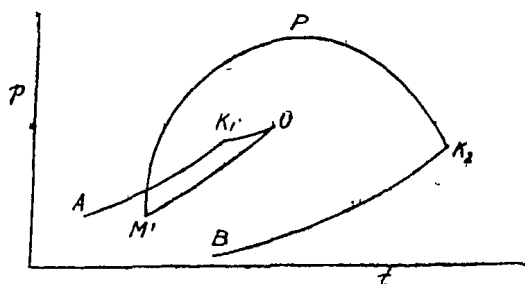


Fig. 5.

ourselves to the case where *B* occurs as a solid phase as no critical phenomena can occur in presence of solid *A*.

In many cases where the line GL_1L_2 proceeds to lower temperatures the solid phase will occur in a point *Q*. According to previous research by myself, 4 three-phase lines then meet in the quadruple point *Q*. If we take the case of Fig. 1 we obtain in Fig. 6 *QM* for GL_1L_2 , *QB* for GL_2S , *EQ* for GL_1S , whilst *QN* indicates the equilibrium of the solid phase *S* with the liquid layers L_1L_2 .

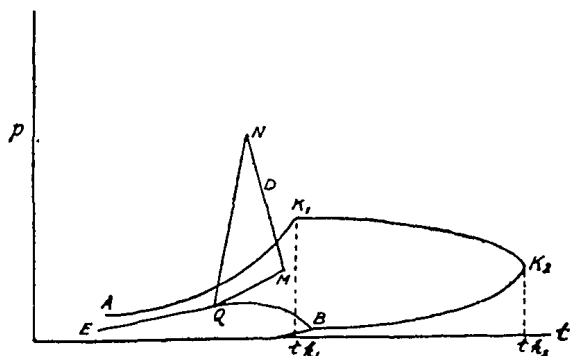


Fig. 6.

either to the right or the left according to the volume differences of the phases.

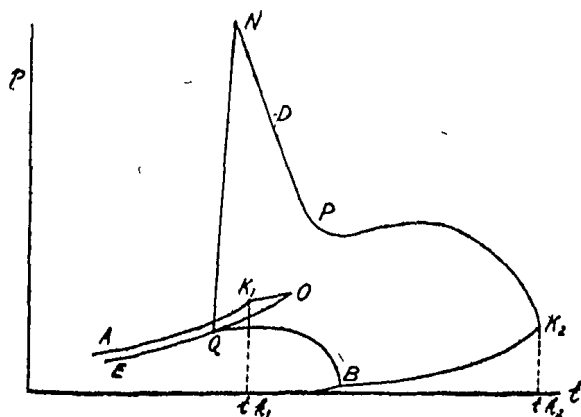


Fig. 7.

pressure only exist when *Q* and *M* do not differ too much in temperature.

points, also of the fusion of parts of the one critical line with those of the other.

In the second place we will now consider the occurrence of critical terminating points on those three-phase lines where one of the phases is solid. We may then limit

lines have been formerly studied by me in cases where hydrates of SO_2 , HBr , HCl occurred as solid phases. For the component *B* as solid phase their courses will be analogous, and like all ordinary melting lines the direction will diverge only a little from the vertical

If the line runs to the right and the critical line *MD* to the left there might be a possibility of their meeting in a critical terminating point *N* as the two liquid layers might here become identical in presence of solid *B*. The chances that this will occur with an attainable

Fig. 7 represents a similar meeting point N for the case corresponding with Fig. 4. Far greater chance of attaining a critical terminating point of the line L_1L_2S is offered by the case of Fig 5 which would lead to Fig. 8. The line OQ is here supposed not to proceed as far as the lower mixing point M' because the solid phase occurs previously at Q . For this reason the downward continuation of the critical line $L_1 = L_2$ is wanting.

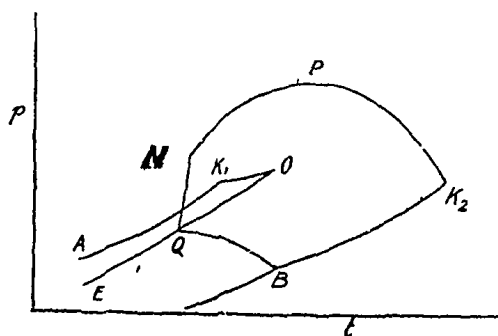


Fig. 8.

which on being dissolved in liquid CO_2 give rise to two layers.

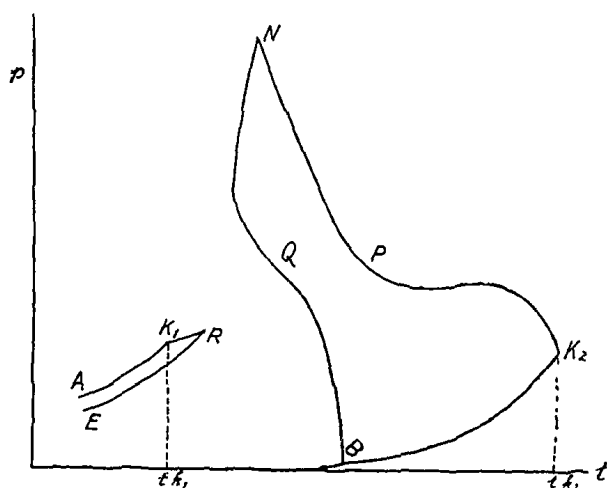


Fig. 9.

of the solid phase. ER then intersects the critical line liquid-vapour in a critical point R which quite corresponds with the point p of SMITS (fig. 2). The line QO is now wanting, namely, below R we notice nothing of a second liquid. Mr. BÜCHNER has here again graphically deduced that in this case the line QB , for the second series of liquids in presence of solid B and vapour, fuses with QN to a single line BQN where the one fluid phase has the character of vapour on the lower part and of liquid on the upper part, whilst these however, gradually pass into each other.

In this case, like in fig. 4 the lower part of the critical line GL

If, however, the mixing point M' should lie but very little below Q (metastable) the point of intersection N might be found at a comparatively low pressure. Mr. BÜCHNER has frequently noticed a similar proximity of M' and Q in systems of all kinds of organic substances

Besides the three cases fig. 6, 7, 8 in which there exists a critical terminating point of the line QN a fourth type is possible. This occurs when the liquid on the line EQ already becomes critical with the vapour before Q has been reached, that is before the second liquid occurs in presence of

fuses with the upper part of the critical line L_1L_2, K, P, N , and we have here again the possibility that the line BQN also possesses a critical terminating point N . This point bears some resemblance to the second critical terminating point found by SMITS in *q* fig. 2. That we are dealing in fig. 9 with a region of two liquid layers could only be made plainly visible, if, owing to the non-appearance of the solid phase, two liquids, in presence of vapour (metastable), occurred below R . Otherwise it is only the peculiar course of BQN , which shows that we have this type.

Mr. BUCHNER has succeeded in finding a case where this course could be indicated (although N remained unattainable). Fig. 10 gives

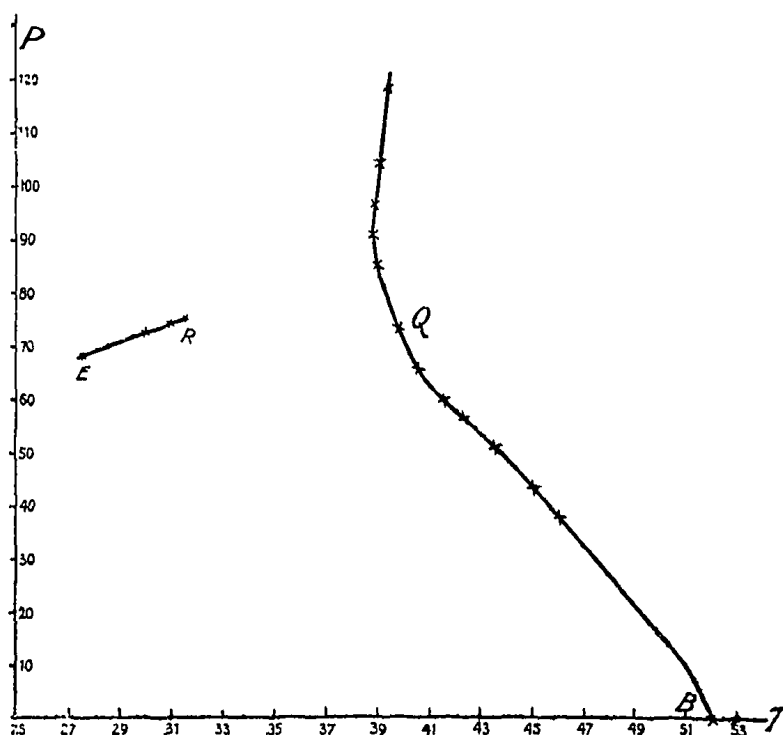


Fig. 10.

a correct representation of the p, t -lines ER and BQ for solid diphenylamine in presence of solution in liquid CO_2 , and in vapour very rich in CO_2 , on ER , and in presence of a much more diphenylamine-containing second liquid phase on BQ . The point R is situated only 0.6° above the critical point of pure CO_2 , consequently diphenylamine is but very sparingly soluble in CO_2 at that temperature.

Between 31.6° and 38.8° two liquid phases are not capable of existing in presence of solid diphenylamine; above these we again find the second three-phase line with two fluid phases now much

richer in diphenylamine. This line was determined up to 120 atm. pressure. The significance of all the regions in which three-phase lines are absent can only be expressed by a series of p, x -diagrams.

The above considerations foreshadow the possibility of enunciating in general terms the conditions for the existence of a solid phase in presence of one or two fluid ones, when traversing the region of the critical phenomena of those latter ones, also for those binary mixtures which in the liquid state are not miscible in all proportions.

Mathematics. — “*On non-linear systems of spherical spaces touching one another.*” By Prof. P. H. SCHOOTE.

1. Before passing to our real investigation it is necessary to find how many spherical spaces touch $n + 1$ spherical spaces given arbitrarily in the n -dimensional space S_n . And in its turn the answer to this question demands a knowledge of the situation of the centres of similitude of those given spherical spaces. So we start with a study of these centres of similitude. To this end we represent the spherical space, which is in S_n again the locus of the points situated at a distance r from the centre M , by the symbol $Sp_n(M, r)$.

2. Just as is the case with two circles lying in the same plane, two spherical spaces $Sp(M_1, r_1)$ and $Sp(M_2, r_2)$ lying in S_n admit of two centres of similitude on the line M_1M_2 connecting the centres, an external one U_{12} and an internal one I_{12} ; through U_{12} pass the lines P_1P_2 connecting the extremities P_1, P_2 of direct parallel rays, through I_{12} pass the lines $P_1P'_2$ connecting the extremities P_1, P'_2 of opposite parallel rays.

Supposing that in S_n a number of $n + 1$ spherical spaces $Sp(M_k, r_k)$, ($k = 1, 2, \dots, n + 1$) is given arbitrarily, we shall now investigate the situation of the $(n + 1)_2$ pairs of centres of similitude ($U_{p,q}, I_{p,q}$) with respect to each other. To this end we first notice that the three pairs of centres of similitude of the three spherical spaces $Sp_n(M_i, r_i)$, ($i = 1, 2, 3$) form the three pairs of opposite vertices of a complete quadrilateral, each of the four triplets of points

$$(U_{12} U_{13} U_{23}), (U_{12} I_{13} I_{23}), (I_{12} U_{13} I_{23}), (I_{12} I_{13} U_{23})$$

consisting of three points of a right line; we indicate these lines in the given order by

$$l_{123} \quad , \quad l_{12}^{(3)} \quad , \quad l_{13}^{(2)} \quad , \quad l_{23}^{(1)}$$

If we now further regard the $n - 1$ pairs of lines ($l_{12\mu}, l_{12}^{(p)}$) through