

Citation:

A. Smits, On critical endpoints in ternary systems. II, in:
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it is possible to determine by the *electro-optic method* a *transition temperature* of the two modifications of the sal-ammoniac fogs, which we have discovered. Other examples will be tried also.

(To be continued).

Chemistry. — "*On critical end-points in ternary systems*. II. By Prof. A. SMITS. (Communicated by Prof. A. F. HOLLEMAN).

In two previous communications I already discussed some particularities which may occur in ternary systems obtained by the addition to a system of the type ether-anthraquinone of a third substance which presents critical end-points neither with anthraquinone, nor with ether¹⁾. An example of this was *naphthaline-ether-anthraquinone*, which was examined by Dr. ADA PRINS²⁾.

Though some more cases were afterwards theoretically examined by me, the publication was postponed not to anticipate too much on the experimental investigation, which was greatly delayed by want of time.

Now however just recently we have met with the very welcome circumstance that the petrographer-mineralogist NIGGLI not only has seen that the phenomena which are found for the said systems, are of fundamental significance for *petrography* and particularly for the *chemistry of the magna*, but that moreover he has had the courage to enter upon an investigation of this territory, which is so comparatively difficult to explore³⁾.

In virtue of this it seemed desirable to publish our results already now, the more so as I may cherish the hope to facilitate the experimental study of others somewhat in this way.

Having discussed one of the possible types pretty fully in my last communication on this subject, a more general discussion of the classification of the different cases which might be distinguished for ternary systems with critical end-points may suffice here.

1st Case. In the first place I will mention the case that critical end-points occur for only one of the three binary systems; this case was discussed by me before, and tested by an example by Dr. ADA PRINS.

If we call the components *A*, *B*, and *C*, and if critical end-points occur only in the system *A—C*, we know that the ternary system

¹⁾ These Proc. 25 Sept. 1909. 182.

" " 24 Sept. 1910. 342.

²⁾ These Proc. 24 Sept. 1910. 353.

³⁾ Zeitschr. f. Anorg. chem. 75. (1912).

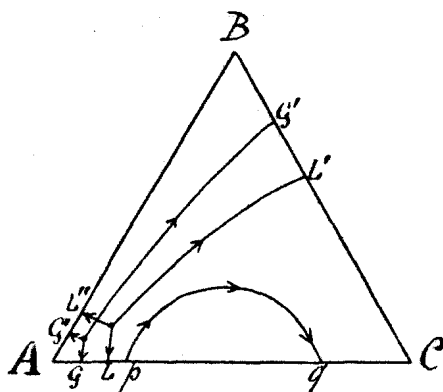


Fig. 1.

will possess a *critical end-point curve* pq , which projected on the concentration triangle can have a shape as indicated in fig. 1 by the curve pq , the temperature of which rises in the direction indicated by the arrows.

If in the same triangle we draw the projection of the eutectic vapour and liquid lines, along which the temperature also rises in the direction indicated by the arrows, we

see that in the case considered here none of the eutectic lines comes into contact with the critical end-point curve pq .

2nd Case. In the second place we shall suppose that in two of the binary systems critical end-points occur, but in such a way that in the symbol for the critical end-point $S + (G=I)$, the solid phase S is the same in the two binary systems. Let the component C be here this solid phase, then we get the following simple projection on the supposition that the system AB does not possess either a minimum or a maximum critical temperature.

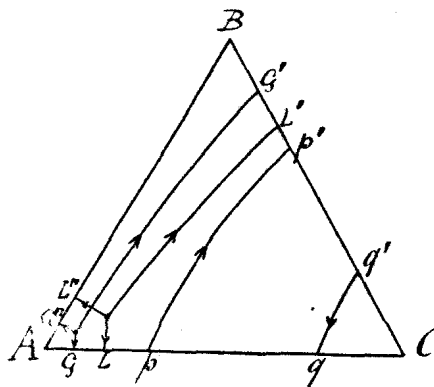


Fig. 2.

Let us consider the case that B possesses a much higher critical temperature than A , then the temperature of the critical end-point p' will probably be higher than that of p , and hence the temperature will continually rise from p to p' . In this case the temperature along the q -line may rise from q' to q , but the reverse is also very well possible; the former has been assumed in the figure. If the system AB had a minimum critical temperature, the critical end-point lines might get a greater distance, and in the case of a maximum critical temperature depressions can occur which may even give rise to a closed portion, so that a region is formed where no critical end-points occur any more.

3rd case. The phenomena become much more interesting when the critical end-point curve comes in contact with a eutectic line. This case may be found when in two of the three binary systems critical end-points occur, but so that the solid substance S in the symbol

of the critical end-point $S + (G=L)$ is different in the two binary systems.

So we suppose now that in the two binary systems AB and AC critical end-points occur, in such a way that the critical phenomenon appears by the side of solid B in the system AB , and by the side of solid C in the system AC . A meeting of a eutectic line with a critical end-point curve of course means this that the critical phenomenon occurs at the temperature of the meeting by the side of *two* solid substances, and so it is clear that a eutectic line must always meet *two* critical end-point curves *simultaneously*, namely the critical end-point curves which belong to the solid substances to which the eutectic line refers.

Let us now assume for the sake of simplicity that the melting-point figure of the system BC possesses a eutectec point. We can then state at once that by the side of the conglomerate of solid $B + \text{solid } C$ critical phenomena can appear only when the eutectic temperature of the system BC lies *above* the critical temperature of the component A , and the greater this difference is the greater will be the chance that the case in question can be realized.

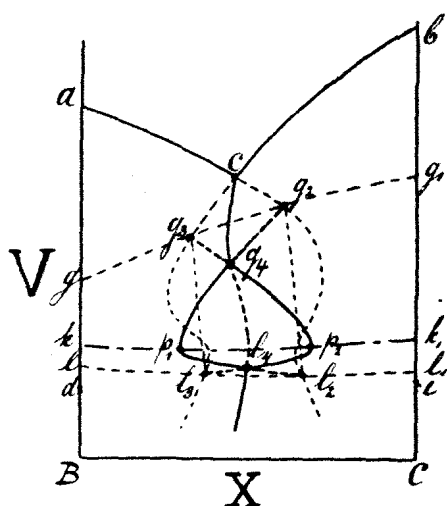


Fig. 3.

To get a better insight into the peculiarities of such a system it is necessary to make use of a ternary V, X -figure, as was used by me before.

This V, X -figure is pretty simple so that it is possible to give at once the projection of the principal lines of equilibrium on the V, X -plane of the binary system $B-C$.

Below the eutectic temperature the V, X -figure of the system B, C consists of two lines ac and bc , which indicate the mol. volumes and the concentrations of the

vapours, which can coexist with solid B resp. solid C .

Now it is of importance to show what equilibria would appear when as we proceed along the isotherm ac resp. bc the deposition of solid C resp. of solid B did not take place.

This case I examined before in the p, x -section for another purpose, and the sections discussed then quite agreed with the V, X -fig. of the system B, C drawn above¹⁾.

¹⁾ These Proc. 30 Dec. 1905. 568.

If on compression the deposition of solid C failed to appear in the vapour coexisting with solid B , the solubility-isotherm acg_2l_2 shows that in this case a metastable three-phase equilibrium between vapour, liquid, and solid B might occur, the coexisting phases of which are indicated by the points g_2 , l_2 , and d .

The figure also shows that if the vapour that coexists with solid C could be compressed without solid B being formed, a metastable three-phase equilibrium between vapour, liquid, and solid c might appear, indicated by the points g_3 , l_3 , and e .

If we now think the third component A added, and placed in the third angle of the base of the trilateral prism, and if we assume that the chosen temperature lies above that of the first critical end-points in the systems AB and AC , it is possible that the stable ternary V, X -figure simply consists of two isothermal solubility surfaces which intersect along a line which originates in the point c . Along this ternary solubility isotherm solid $B + \text{solid } C + \text{vapour}$ coexist. Now it is clear that a two-sheet liquid-vapour surface extends within the said solubility surfaces, which begins on the binodal vapour and liquid line in the plane for BC . The two sheets of this liquid-vapour-surface will continuously merge into each other in space, and this continuous transition takes place on the critical isotherm, the projection of which on the BC -plane is indicated by the line kk_1 .

When the said liquid-vapour-surface lies entirely inside the two isothermal solubility surfaces, no critical phenomena can occur in stable condition, and in this case no particularities occur. Now we know that at temperatures lower than those assumed here stable liquid equilibria must occur, and this must also happen when we raise the temperature, and in this way approach the eutectic temperature of the system $B-C$. With decrease of temperature we shall see liquid appear as stable phase, because then the liquid-vapour-surface extends more quickly in space than the solubility surfaces. The consequence of this is that at a certain temperature the three-phase solubility isotherm for $S_B + S_C + G$ just touches the liquid-vapour-surface. So at this moment $S_B + S_C + L + G$ must be able to coexist for the first time, from which follows that this contact must take place in a point of the critical isotherm of the liquid-vapour surface so that liquid and vapour are identical there, and a critical phenomenon makes its appearance.

In connection with this the following things may be remarked. Starting from the pairs of points g_2, l_2 and g_3, l_3 two continuous curves pass over the liquid-vapour-surface, the former of which indicates the vapours and liquids coexisting with solid B , and the

latter of which contains the vapours and liquids which can be in equilibrium with solid C .

If the liquid-vapour-surface touches the solubility isotherm of $S_B + S_C$, it is clear that also the lines starting from the nodes g_2, l_2 and g_1, l_1 must touch, which accordingly takes place on the critical isotherm.

If we now think the temperature still a little lower, the just mentioned contact will change into an intersection, and so two points of intersection will occur, one of which indicates the vapour phase, and the other the liquid phase of the four phase equilibrium $S_B + S_C + L + G$.

The intersection of these lines, which are indicated in projection by g_1, g_2, p_1, l_1, l_2 and g_1, g_2, p_2, l_1, l_2 , means of course that the liquid-vapour surface intersects the solubility surfaces, in consequence of which the liquid-vapour equilibria get partly into the stable region. These stable liquid-vapour equilibria lie within the two intersecting lines g_1, p_1, l_1 and g_2, p_2, l_2 . The first intersection line, which refers to the liquid and vapour phases which coexist with solid B , possesses a critical end-point in p_1 , and the second intersection line, which indicates the liquid and vapour phases which can be in equilibrium with solid C , possesses a critical end-point in p_2 . The points g_1 and l_1 denote, as was already said, the vapour and liquid coexisting with $S_B + S_C$, and so it is evident that through these two points the line must pass which has its origin in C , and indicates the coexistence of a fluid phase with a conglomerate of S_B and S_C .

If we lower the temperature still more, the points g_1 and l_1 , and also p_1 and p_2 move more and more apart, whereas on rise of temperature they draw nearer and nearer together, and coincide in the *double critical end-point*, for which the symbol is $S_B + S_C + (L=G)$. At temperatures above this *double critical end-point* there will exist only fluid phases or coexistence between fluid phases with solid B resp. with solid C , or with the two solid substances at the same time. It is, however, clear that as was already observed, liquid will have to appear again in the ternary system before the eutectic temperature of the system $B-C$ is reached, and so we see that when at lower temperature a *double critical end-point* has appeared, a second *double critical end-point* will occur at higher temperature, so that then at rise of temperature a repetition will take place of what has happened at lower temperature, but in the reversed order. So after the second double critical end-point has appeared, the stable part of the liquid-vapour-surface will continually increase in extent. To this is added

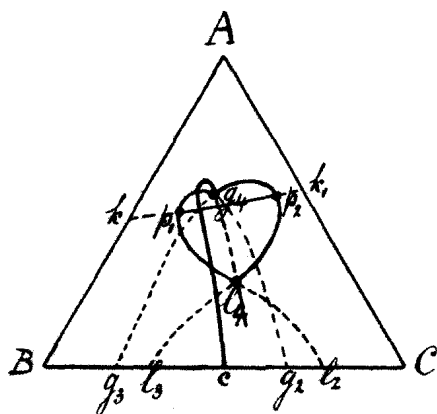


Fig. 4.

lines of the two three-phase equilibria $S_B + L + G$ and $S_C + L + G$, indicated by the letters g, g, p, l , resp. g_2, g_2, p_1, l_2 intersect in two points g_4 and l_4 , where four-phase equilibrium prevails, and where accordingly also the fluid line of the three-phase equilibrium $S_B + S_C + F$ runs, which is denoted by the symbols cg, l_4 . It is further noteworthy that the liquid branches of the three-phase equilibria $S_B + L + G$ and $S_C + L + G$ are cut by the critical isotherm kk_1 , so that p_1 and p_2 are two critical end-points.

If we start from a temperature lying a little above that of the first critical end-points in the systems $B-A$ and $C-A$, we know that on rise of temperature not only the critical end-points p_1 and p_2 , but also the vapour point g_4 and the liquid point l_4 of the four phase equilibrium $S_B + S_C + L + G$ will approach each other till they coincide in the *double critical end-point*. As g_4 is a point of the ternary eutectic vapour-line and l_4 a point of the ternary eutectic liquid-line it follows from what precedes that these two ternary eutectic lines will have to pass continuously into each other in the double critical end-point. In the first double critical end-point P the continuous eutectic line possesses in consequence a *temperature maximum*. At higher temperature the second double critical end-point Q occurs, and from this temperature the liquid and vapour points of the second continuous part of the eutectic line recede more and more from each other, so that the second double critical end-point is at the same time the *temperature minimum* of the second continuous part of

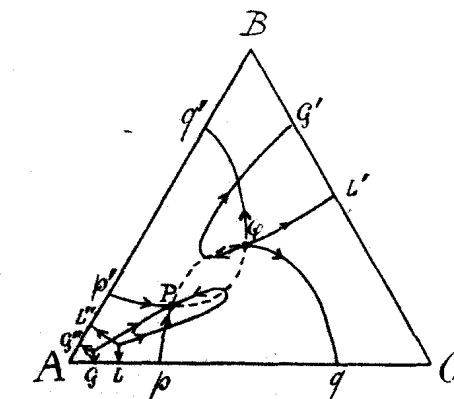


Fig. 5.

the eutectic line. If we represent this in a diagram, i. e. if we draw the projection of the pq -lines and that of the eutectic lines in the concentration triangle, we get fig. 5, in which the arrows again indicate the direction in which the temperature rises.

It is clear, that it is also possible that the two continuous pq -lines do not intersect. In this case there are no double critical end-points, and so the eutectic lines proceed undisturbed up to the ternary eutectic point.

4th case. In the fourth case we might suppose that each of the binary systems presents critical end-points. To realize this case we shall have to choose three substances, the critical temperatures of which lie apart as far as possible, so that in each binary system the triple point of one component lies far above the critical temperature of the other. If then double critical endpoints occur, we get a combination of fig. 2 and fig. 5.

5th Case. It is clear that the appearance of mixed crystals in the system $B-C$ does not bring about any change in the foregoing considerations, when this system has a eutectic point; if this is not the case, modifications appear which are most considerable when the components B and C are miscible in all proportions, as in the system $\text{SO}_2 + \text{HgBr}_2 - \text{HgJ}_2$, examined by NIGGLI¹⁾. The projection of the critical end-point lines runs then as is schematically represented in fig. 6.

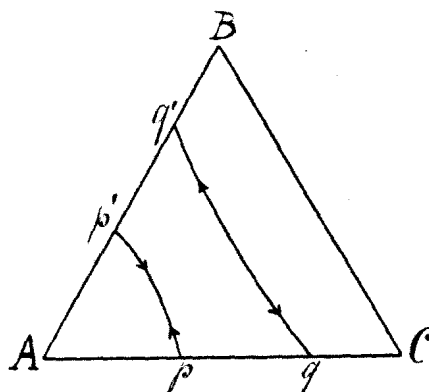


Fig. 6.

Now it should be pointed out, however, that when the melting-point line of the system $B-C$ has a very marked minimum, a closed portion can be formed in the middle of the figure, so that no critical endpoints occur there then. If on the other hand the said continuous melting-point line has a very marked maximum, the special case might be found that though no critical endpoints occur in the binary systems $A-B$ and $A-C$, they do occur in the ternary system. We can imagine that this case arises from the ordinary case fig. 6 by the points p_1 and q_1 , and also p_2 and q_2 , approaching each other and coinciding, in consequence of which the two critical end-point lines merge continuously into one another. If then this continuous curve contracts still further, we have obtained a closed critical end-point curve, which lies quite inside the concentration triangle.

¹⁾ NIGGLI, The projection.

6th Case. If a binary compound appears as a solid phase, different cases may be distinguished, the most interesting of which I will discuss here. In the first place we shall suppose that the components B and C do not give critical end-points either with A , nor with the compound BC , but that this compound gives critical end-points only with the most volatile component A . It is clear that when this case occurs, the triple point temperature of the compound BC will probably lie far above that of the components B and C .

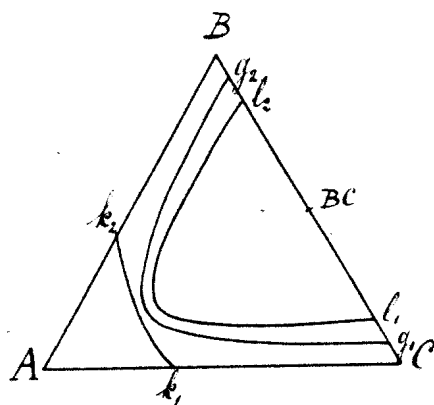


Fig. 7.

seen from A , as it is supposed here that the compound BC is less volatile than the components B and C . When the liquid vapour surface in the ternary v - x -figure recedes more on rise of temperature than the surface of nodes for the liquids and vapour coexisting with solid BC , the critical isotherm will touch this surface of nodes at a given temperature; then the

liquid and the vapour line of this surface of nodes merge continuously into each other. At a still somewhat higher temperature a closed portion is formed in the surface of nodes, in consequence of which two ternary critical end-points have appeared, as fig. 8 shows.

If we think the temperature as gradually rising, the critical end-points will recede from each other in the beginning, and they will also move towards the plane BC , but before the triple point temperature of the compound has been reached the points p_1 and p_2 will approach each other, and they will coincide, because when we approach the triple point temperature, the surface of nodes of the liquids and vapours that coexist with solid BC will have to con-

If we draw the projection of the vapour and the liquid line of the three-phase equilibria $S_{BC} + L + G$ and that of the critical isotherm on the concentration triangle corresponding to a temperature lying above the critical temperature of A and a little above the highest eutectic temperature of the system $B-C$, Fig. 7. is formed.

The isotherm k_1k_2 is convex

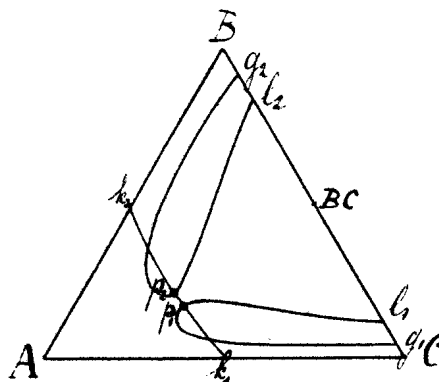


Fig. 8.

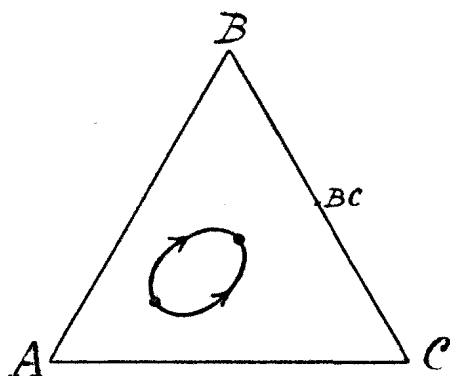


Fig. 9.

or AC or in both, other cases may occur, but they are easy to derive from what precedes. If also ternary compounds are included in our considerations, the cases get somewhat more complicated, as I hope to show on a following occasion.

tract more rapidly than the liquid-vapour surface, for this surface of nodes entirely disappears at the triple point temperature of BC . So if we draw the ternary critical end-point line in this case, we get a closed curve, as is drawn in fig. 9 with a temperature minimum and maximum.

If critical end-points occur also in one of the binary systems AB

Amsterdam, June 27 1912.

Anorg. chemical laboratory
of the University.

Astronomy. — "*Researches on the orbit of the periodic comet Holmes and on the perturbations of its elliptic motion*". V.
By Dr. H. J. ZWIERS. (Communicated by Prof. E. F. VAN DE SANDE BAKHUYZEN).

In January 1906 I communicated to this Academy the most probable elements I had derived for the return of the comet Holmes in 1906—07. In a later paper, November 1906, I discussed the then known three photographic observations of the comet by Prof. MAX WOLF at Heidelberg, and from these derived corrections to the mean longitude, to the inclination and to the longitude of the ascending node of the orbit. The elements obtained were:

Epoch 1906 January 16.0 M. T. Greenw.

$$\begin{aligned}
 M_0 &= 351^\circ 47' 36''.838 \\
 \mu &= 517''.447665 \\
 \log a &= 0.5574268 \\
 \varphi &= 24^\circ 20' 25''.55 \\
 i &= 20\ 49\ 0.62 \\
 \pi &= 346\ 231.63 \\
 \Omega &= 331\ 44\ 37.85
 \end{aligned}
 \left. \vphantom{\begin{aligned} M_0 \\ \mu \\ \log a \\ \varphi \\ i \\ \pi \\ \Omega \end{aligned}} \right\} 1906.0$$

These elements left the following errors O—C in the three observed places: