

Citation:

A. Smits, Extension of the theory of allotropy. Monotropy and enantiotropy for liquids, in: KNAW, Proceedings, 15 I, 1912, 1912, pp. 361-369

Chemistry. — “*Extension of the theory of allotropy. Monotropy and enantiotropy for liquids.*” By Prof. A. SMITS. (Communicated by Prof. A. F. HOLLEMAN).

The extension meant above concerns the case that the pseudo-binary system exhibits the phenomenon of unmixing in the liquid state.

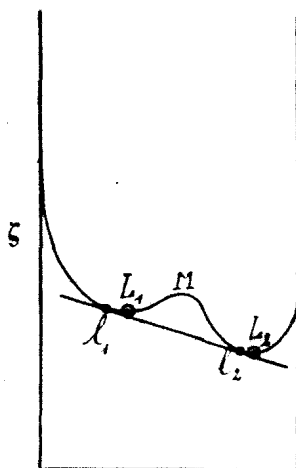


Fig. 1 X.

Let the ζ, x -line be schematically represented by fig. 1 at the temperature and pressure at which the phenomenon of unmixing takes place. Then in the first place it is noteworthy that l_1 and l_2 are the coexisting liquid phases of the pseudo-binary system, and that moreover there exist two minimum points L_1 and L_2 representing the liquid phases which may be formed when the system gets in internal equilibrium, and consequently behaves as a unary substance.

The two liquid phases are not miscible, and when they are brought into contact the metastable liquid L_1 will pass into the stable liquid phase L_2 , so that this operation means the same thing as seeding the metastable liquid. As fig. 1 shows the *metastable* unary liquid point L_1 lies inside, and the *stable* unary liquid point L_2 outside the region of incomplete miscibility, and now it is of importance to examine what happens when we move toward such a temperature that the critical phenomenon of mixing occurs in the pseudo-binary system. The coexisting phases l_1 and l_2 have drawn nearer and nearer to each other, and finally coincided in the critical mixing-point, and the ζ, x -line has then changed into a curve with only one minimum, as fig. 2 shows.

It is now, however, of importance for our purpose to consider the way in which the ζ, x -line has changed its form from that of fig. 1 to that of fig. 2.

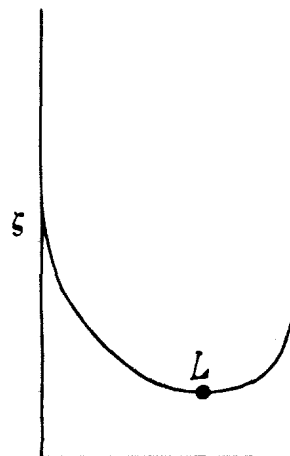


Fig. 2 X.

It is known that before the points l_1 and l_2 coincide, the maximum

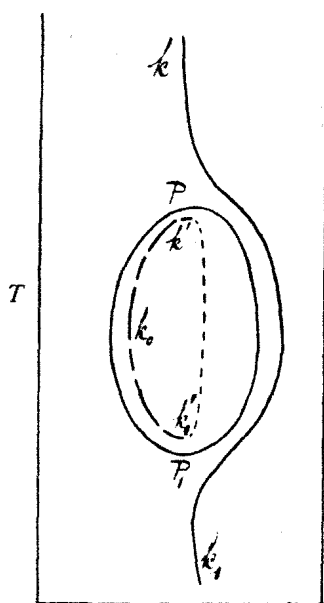


Fig. 3 x.

M vanishes in consequence of the coincidence of this point with the minimum L_1 , at which moment a point of inflection appears with horizontal tangent. At this moment the possibility of the existence of a metastable unary liquid ceases, so that this condition has already become impossible before the critical mixing point has been reached in the pseudo-system. This consideration is in itself already sufficient to indicate in a Tx -diagram the situation of the liquid lines in the unary system with respect to those in the pseudo-binary one. If we assume that the pseudo-system, just as the system *nicotine-water*, presents an upper and a lower critical mixing point, fig. 3. is formed.

The closed line PP , indicates the coexisting liquid phases in the pseudo-binary system. Outside the region enclosed within this continuous curve, runs the line kk_1 , on which the stable internal liquid equilibria are found, and inside this region lie the metastable internal liquid equilibria on the line k', k_0, k''). In the points k' and k'' this line passes continuously into the locus of the maximum points M of the ξ - x -lines, and as in these points $\left(\frac{\partial \xi}{\partial x}\right)_{P,T} = 0$, just as for the stable and metastable unary equilibria, but $\left(\frac{\partial^2 \xi}{\partial x^2}\right)_{P,T} < 0$, we may call the locus of the maximum points M the line of the *unstable* internal equilibria.

The theory of *allotropy* attributes the phenomena of monotropy and enantiotropy to the occurrence of different kinds of molecules of one substance, and says that when there exist two or more solid states of a substance, the differences in properties are owing to the situation of the internal equilibrium which will be different in the two solid states.

Now we saw just now that when a substance occurs in two different liquid states, this phenomenon must also be ascribed by the theory to the existence of two different internal equilibria between different kinds of molecules of the same substance. So according to

¹⁾ The lines of the internal equilibria have here a very peculiar shape, which is dependent on the phenomenon of unmixing. I shall return to this subject later on.

this new view there is no essential difference between the occurrence of different solid and different liquid phases of one substance and as in the case considered here we have two liquid phases, one of which is *always* stable with respect to the other, we are justified in speaking here of the phenomenon of *monotropy for a liquid*.

Now it is of importance to examine what will take place when the region of incomplete miscibility comes into contact with one of the melting-point lines of the pseudo-binary system.

Beforehand I will, however, remark that Dr. SCHOEVERS¹⁾, who undertook the same problem at BAKHUIS ROOZEBOOM's instigation, but took no notice of the ξ - x -lines, could only draw by chance a line for the stable unary liquid equilibrium, as shown in fig. 4.

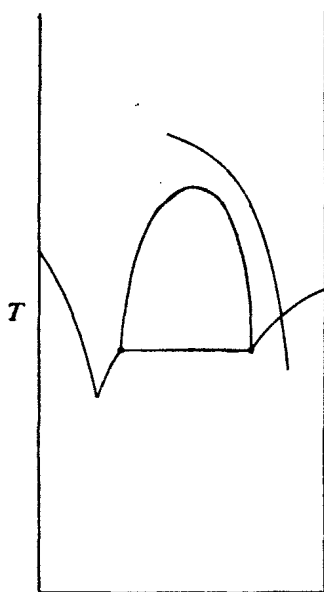


Fig. 4 X.

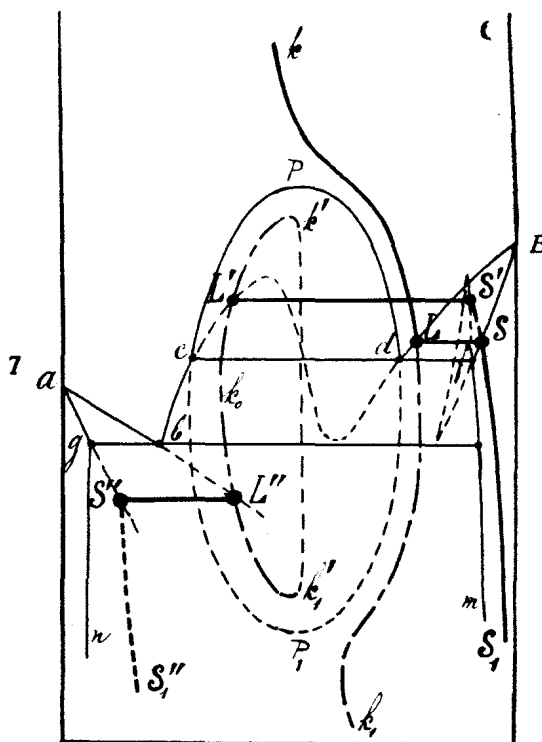


Fig 5 X.

If we suppose that the region of incomplete miscibility comes in contact with the melting-point line of the component with the higher melting-point, we get the T, x -figure 5.

Now it is of importance to determine the continuity between the two pieces ed and cb of the interrupted melting-point line of the pseudo-component B , and also the continuity which is connected with it, between the mixed crystal lines ef and mf . Now it is the question where the liquid lines of the unary system will meet those

¹⁾ Thesis for the doctorate.

of the pseudo-binary system. In the first place we see that the stable unary liquid line meets the melting-point line of the pseudo-system in L , so that there a total solidification will take place, at least if phenomena of retardation fail to appear.

The solid states, which are in internal equilibrium below this temperature, and so belong likewise to the unary system, lie on the line SS_1 . It is further noteworthy that one of the two metastable parts of the melting-point line of the pseudo-component B , intersects the metastable liquid line of the unary system in L' .

At the temperature of this point of intersection an intersection must also take place of the metastable produced parts of the mixed crystal line mf' and of the line for the solid internal equilibrium S_1S , which intersection is denoted by the point S' .

It follows from this that when the metastable unary liquid is cooled down, and no retardation takes place, at L' total solidification to the metastable unary solid phase S' will set in, which, however, becomes stable at S . So what is remarkable about this, is that the metastable point of solidification lies *higher* than the stable one, and this is due to this that here there is no monotropy in the solid state but monotropy in the liquid state, in consequence of which we get the reverse of what we are accustomed to, as is immediately clear, when we draw the P, T -fig. Our T, X -fig. 5, however, reveals more. We see namely from it that when the metastable part of the region of incomplete miscibility extends far enough below the eutectic point of the pseudo-system, the metastable unary liquid line can also be cut by the metastable prolongation of the melting-point line of the pseudo-component A , so that the possibility also exists that in L'' total solidification of the metastable unary liquid to the metastable unary solid substance S'' sets in, which solid phase will then follow the line $S''S_1''$ at lower temperatures. So one of the peculiarities of this case consists in this that the metastable unary liquid possesses *two* metastable points of solidification, and that when this liquid is not converted to a stable one, it can solidify to a solid substance which is at first metastable and at lower temperatures stable when it is first heated above a definite temperature, and then cooled down. If the temperature is not raised so high, the metastable unary liquid solidifies to another solid substance, which remains metastable, at least when no transition equilibrium occurs in the solid state.

Now it should, however, be pointed out that the two mentioned points of solidification of the metastable unary liquid need not necessarily exist. The upper point of solidification may be absent, in con-

sequence of the partially metastable, partially unstable middle portion of the melting-point line of the pseudo-component *B* no longer intersecting the metastable unary liquid line, but running round this curve. And the lower point of solidification may be absent, when the same curve lies entirely above the metastable prolongation of the melting-point line of the pseudo-component *A*.

When the question is considered in what way in case of liquid monotropy, the metastable phase can be obtained from the stable one, one arrives at the conclusion that this will have to take place by rapid condensation of the vapour, which in concentration is nearer the metastable than the stable liquid.

Whether substances have already been found which belong to the above-described type, is still open to doubt, though in the literature statements are found, which might lead us to suppose so.

As is known, it was believed for a long time that the pseudo-system of sulphur had to possess a region of unmixing, because it was thought that some phenomena observed in the investigation furnished indubitable indications in this direction. This view was first pronounced by BAKHUIS ROOZEBOOM, and supported by KRUYT, on the ground of his own observations¹⁾. After SMITH c.s.²⁾ had made it probable that the quasi-unmixing was to be ascribed to a difference of temperature, I succeeded last year in conjunction with Dr. DE LEEUW³⁾ in ascertaining with perfect certainty that the phenomenon in question has nothing to do with a phenomenon of unmixing, and is really brought about by a difference of temperature, which gives rise to a quasi-unmixing when tubes with more than a certain inner diameter are used.

Moreover it appeared that the point of solidification of states of sulphur fixed at higher temperatures could not give support to the old view, so that not a single reliable experimental datum is now known that speaks in favour of the existence of a region of incomplete miscibility in the pseudo-system.

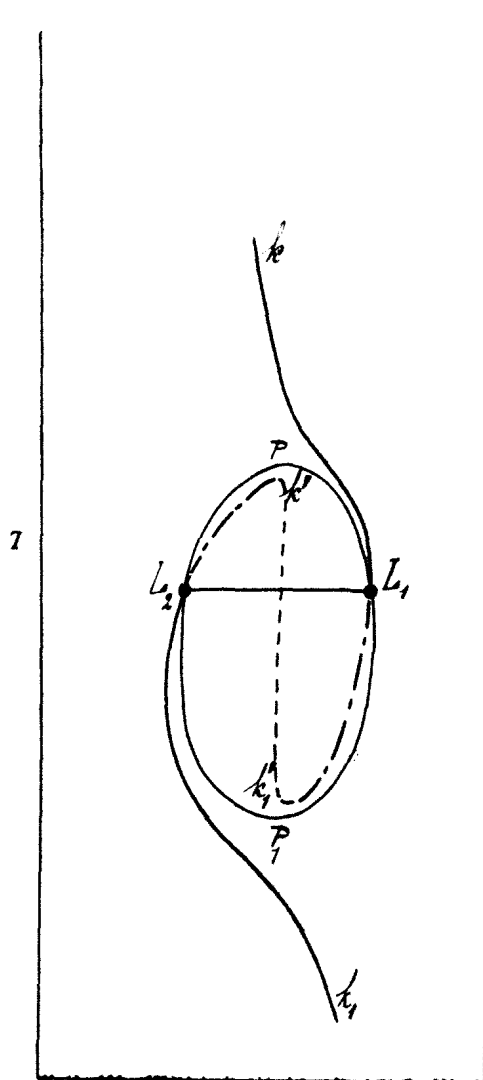
That the shape of the line for the stable unary liquid equilibrium resembles that of the line *kL* in Fig. 5, is of course, of not the slightest importance, for also when the pseudo system possesses no region of incomplete miscibility in the liquid state, the said line can have such a shape. Besides, the system sulphur, as I already stated, is at least pseudo-ternary, which view is in harmony with the

¹⁾ Z. f. phys. Chem. **64**, 513 (1908).

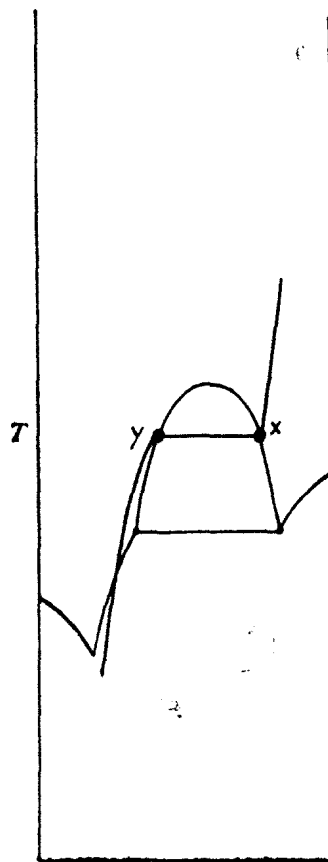
²⁾ " " " " **57**, 685 (1907).

³⁾ These Proc. Oct. 1911, p. 461.

results of the investigations of ROTENJANZ ¹⁾ and ATEN ²⁾. In a more complicated case, in which a line of equilibrium is the resultant of three or more lines of equilibrium a line of equilibrium with a clearly marked point of inflection will of course exceedingly easily arise, as is, indeed, the case for the aldehydes ³⁾.



X
Fig. 6.



X
Fig. 7.

2. Let us suppose in the second place that above the temperature of the three-phase equilibrium $S_B + L_1 + L_2$ the ζ - x -line of fig. 1

¹⁾ Z. phys. f. Chem. **62**, 609 (1908).

²⁾ See Versl. Kon. Ak. 28 Sept. 1912, p. 396. This paper will shortly appear in These Proceedings

³⁾ Z. f. phys. Chem. **77**, 269 (1911).

plete miscibility in the pseudo system comes in contact with one of the melting-point lines, we may distinguish different cases. In his Thesis for the Doctorate SCHOEVEERS gives the following figure 7, adding that when on loss of heat the phase x has been entirely converted to y , the ordinary phenomena will occur at lower temperatures.

By ordinary phenomena SCHOEVEERS understands the deposition of one of the two components in pure state. The theory of allotropy, however, says that from the liquid which is in internal equilibrium, a solid substance will deposit, which is also in internal equilibrium, so that this solid phase will contain the two pseudo-components. If we express this in a drawing, we may get among others fig. 8, which is at once clear without any further elucidation. It is, however, necessary to point out that it is also possible that the line for the internal liquid equilibrium $L, LL'L''$ does not intersect the stable part of the melting-point line of the pseudo-component B , but that of the pseudo-component A . Besides it is possible that coming from higher temperatures the line for the internal liquid equilibrium does not meet the region of incomplete miscibility for the first time on

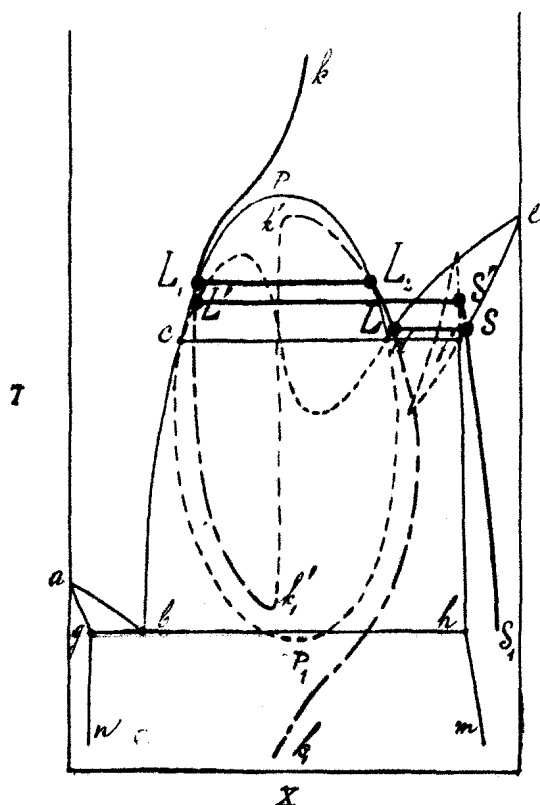


Fig. 9.

the righthand side, but on the lefthand side, in which case fig. 9 gives one of the possible situations. The region of incomplete miscibility lies too high here to give the second lower metastable unary point of solidification.

All these T,x -figures can be accurately determined by means of the ζ - x -lines, which has been omitted here for want of space.

It may finally be remarked that the phenomenon of enantiotropy for liquids has never been observed as yet, but the possibility of this phenomenon is beyond all doubt.

Anorg. chem. laboratory of the University.

Amsterdam, Sept. 20, 1912.

Chemistry. — “*The application of the theory of allotropy to the system sulphur*”. II. By Prof. A. SMITS. (Communicated by Prof. A. F. HOLLEMAN).

In a preceding communication ¹⁾ I already pointed out that the theory of allotropy requires that the system sulphur must be considered to be at least *pseudo-ternary*.

On that occasion a T,x -figure was projected by me, which as I stated already then, had still to undergo a simplification by the omission of the region of incomplete miscibility ²⁾. But the figure had to be modified also in another respect, for in the meantime SMITH and CARSON ³⁾ had determined the melting-point line of a third crystallised modification of the sulphur, the so-called *soufre nacré* (mother-of-pearl sulphur), which had been discovered by GERNEZ ⁴⁾.

To keep the representation as simple as possible for the present, the modification required to insert this third crystallised condition of sulphur into our figure, has been accomplished by assuming in the pseudo binary system $S_R—S_M$ and $S_M—S_\mu$ ⁵⁾ above the eutectic point a discontinuity in the monoclinic mixed crystals. In consequence of this the line for the internal liquid equilibrium in the plane for the pseudo-binary system $S_R—S_M$ meets the stable melting-point line of one kind of monoclinic mixed crystals in l_2 , and the metastable branch of the melting-point line of the other kind of monoclinic mixed crystals in l_0 , the same line of equilibrium cutting the metastable part of the

¹⁾ These Proc. XIV 263.

²⁾ „ „ XIV 461.

³⁾ Zeitschr. f. phys. Chem. 77, 661 (1912).

⁴⁾ Journ. de phys. 3, 76 (1884).

⁵⁾ By S_R , S_M , S_μ the pseudocomponents are meant here.