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Chemistry. — *"The metastable continuation of the mixed crystal series of pseudo components in connection with the phenomenon of allotropy"*. By Prof A. SMITS (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of March 28, 1914).

1. For the case that a unary system is built up of two pseudo-components the relation between the unary and the pseudo-binary system has been derived by me by making use of GIBBS's principle of equilibrium, which states that a system at constant temperature and pressure tends to pass to such a state that the thermodynamic potential (ζ-function) is a minimum. [1])

In this it has been assumed that when heterogeneous allotropy occurs in the solid state, the ζ-x-curve has a shape as indicated in fig. 1. This assumption comes to this that there exists continuity in the unstable region between the two mixed crystal series, which

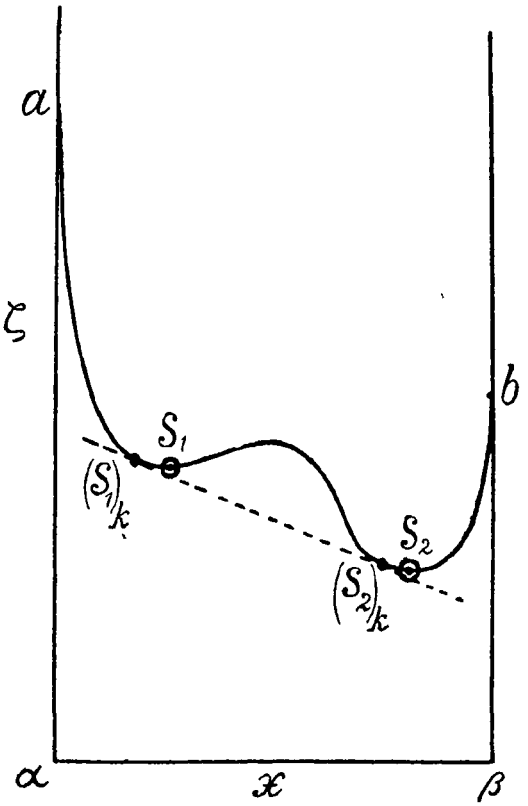

Fig. 1.

[1]) Z. f. phys. Chem.: **76**, 421 (1911).

start from the α and the β-side, and in general possess a different crystalline form.

As HERBETTE [1]) has demonstrated by an experimental way that such a continuous transition between mixed crystals of different crystalline forms occurs for *potassium* and *thallium tartrate* even in the stable region, it must be admitted that the continuity in the unstable region given in fig, 1, is a possibility, especially for mixed crystals whose systems of crystallisation are closely allied to each other.

On the other hand it should be pointed out, that it is very probable, that in many cases the continuity assumed here, does *not* exist, and the two halves of the ζ-x-line, which refer to mixed crystals of different forms, are *not* related. We might imagine that in this case two ζ-x-lines occur, which proceed continuously from one axis to another, as fig. 2 shows. The ζ-x-line cd would then relate to mixed-crystals of one kind, and ab to those of the second kind. The ζ-x-line cd then indicates the ζ-values of different mixed crystals, in which the pseudo-component α is compelled by β to crystallize in

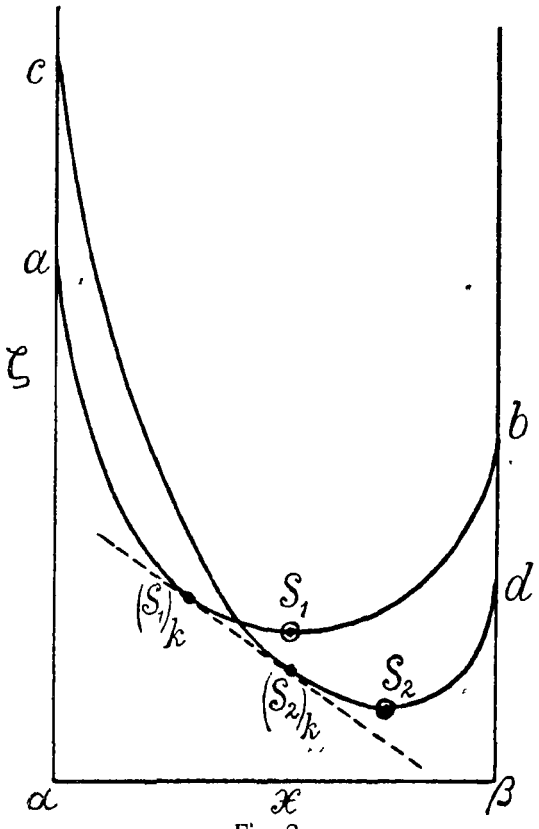

Fig. 2.

[1]) Compt. rend. **140**, 1649 (1905).

the crystalline form of β, whereas the line ab refers to mixed crystals in which β is forced by α to crystallize in the crystalline form of α.

These states would certainly be realisable when the pseudo components presented the phenomenon of isodimorphy, but then we should have to assume that the pseudo components can occur in different crystalline forms, merely in consequence of a different arrangement in the "Raumgitter" of a same kind of molecules.

Without the slightest doubt such a case is conceivable, but it is by no means probable. We can hardly assume that when the pseudo-components in the solid stable state are miscible to a limited extent, the phenomenon of *isodimorphy* always occurs. *Besides it is in my opinion highly probable that a difference in composition is the cause of the difference in crystalline form.* It is now the question whether another view is possible, which obviates the difficulty mentioned here.

It is clear that the stability of the "Raumgitter" of the pseudo component α becomes smaller as there has been dissolved more of the pseudo component β, and thus it will be possible that at a certain concentration the "Raumgitter" has become so unstable that it can

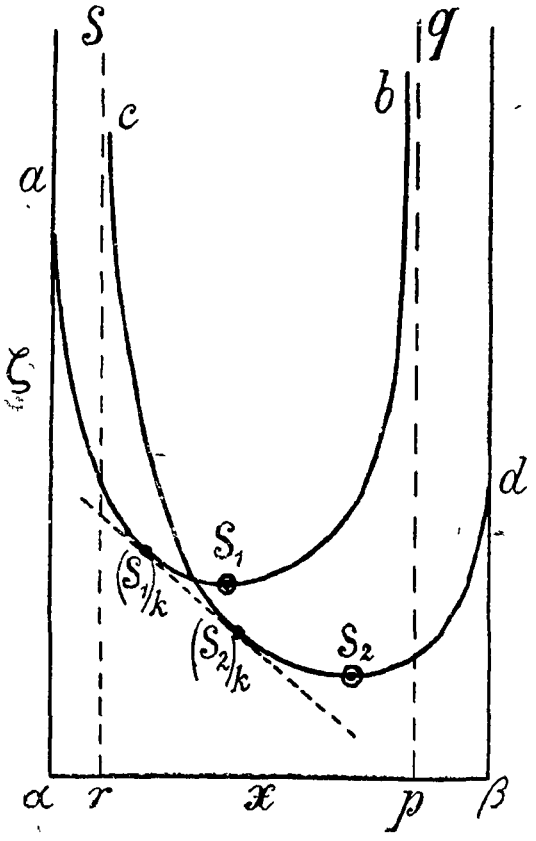

Fig. 3.

no longer maintain itself. It is now the question how this has to be expressed in the ζ-x-figure.

There exist here two possibilities. It is possible that as fig. 3 indicates, the ζ-x-line $a\,b$ starting from the α-axis, approaches the line $p\,q$ asymptotically instead of running to the other axis, which means that a mixed crystal of the concentration p is impossible, as this mixed crystal would require an infinitely large value of ζ.

In the same way the ζ-x-line $d\,c$ would then approach asymptotically to $r\,s$.

Then the expression $\left(\frac{\partial \zeta}{dx}\right)_{PT} = MRT\ log\ \frac{x}{1-x} + \int_v^{\infty} \left(\frac{dp}{dx}\right)_{v,T} dv$ becomes infinite at a definite value of x, because then the second term of the second member becomes $= \infty$.

Another possibility is this, that the ζ-x-line ends suddenly in the figure, as fig. 4 shows. So this figure expresses that the possibility

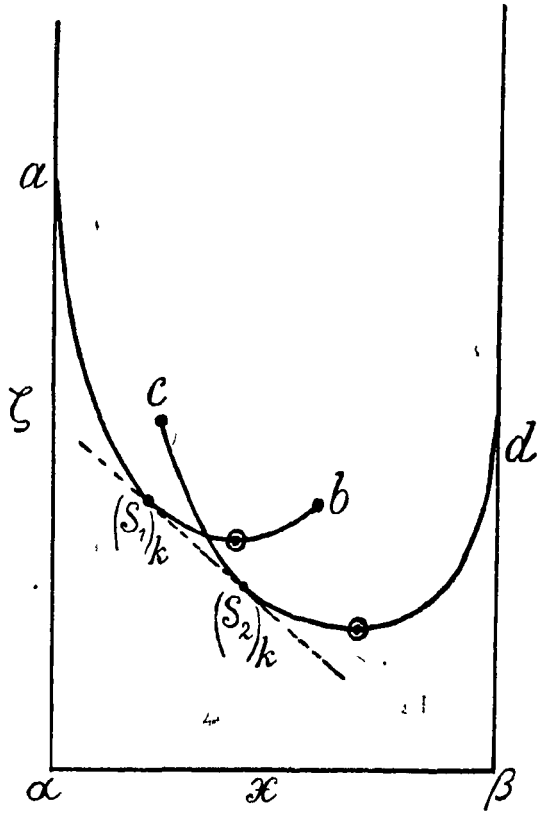

Fig. 4.

of the existence of mixed crystals of the same crystalline form suddenly ceases at b resp. c, and that the prolongations of the lines

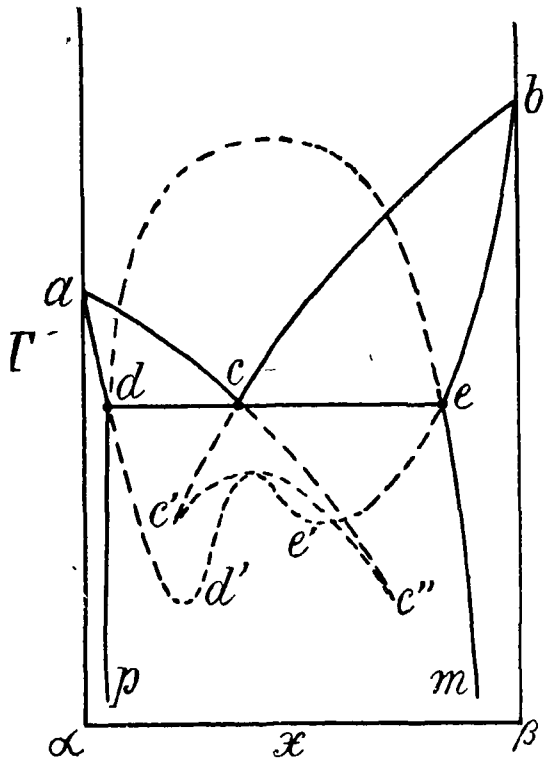

Fig 5.

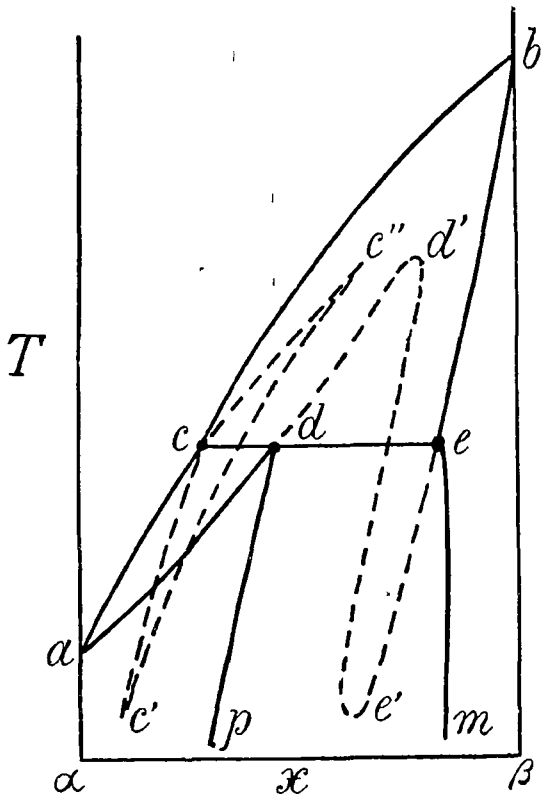

Fig. 6.

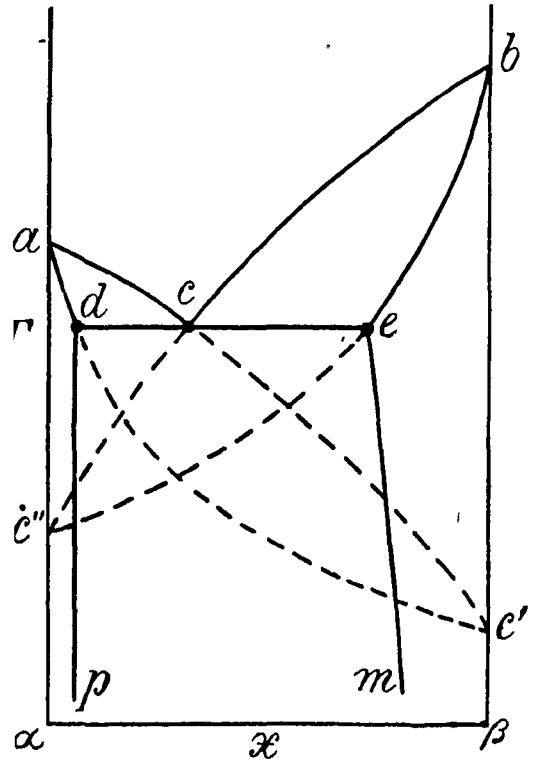

Fig. 7.

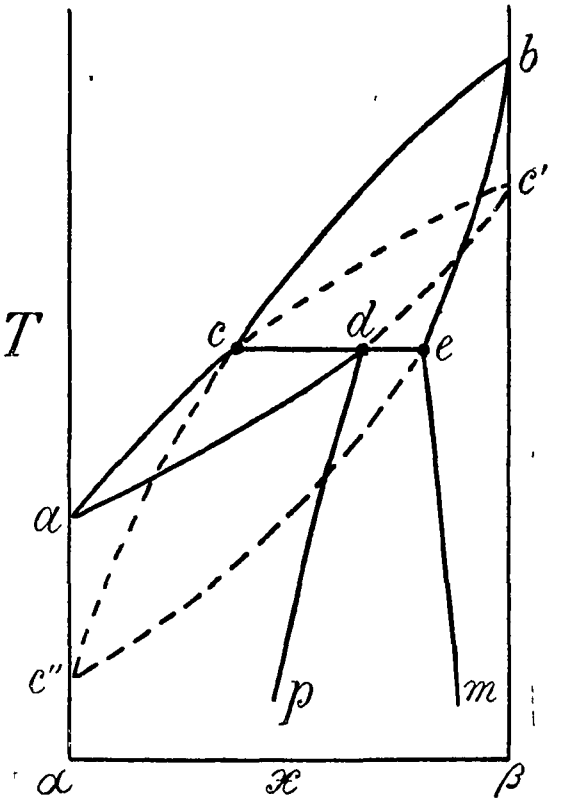

Fig. 8.

which might be imagined, have thermodynamically absolutely no sense any more.

2. It is clear that as far as the metastable and unstable equilibria are concerned, the pseudo T-x-figure will be different according as one view or the other is held.

The assumption of continuity in the unstable region would lead to the T, x-figures 5 and 6.

In Fig. 6 the lines pd and me pass continuously into each other, in the same way as in Fig. 5.

The assumption of isodimorphy of the pseudo components, which is less probable than the two following, yields the figures 7 and 8.

The assumption of an asymptotic course of the ζ-x-lines leads to the figures 9 and 10.

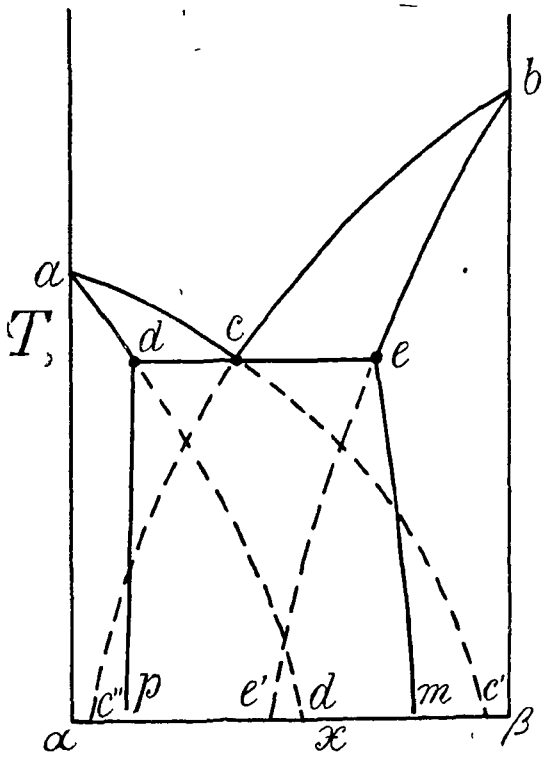

Fig. 9.

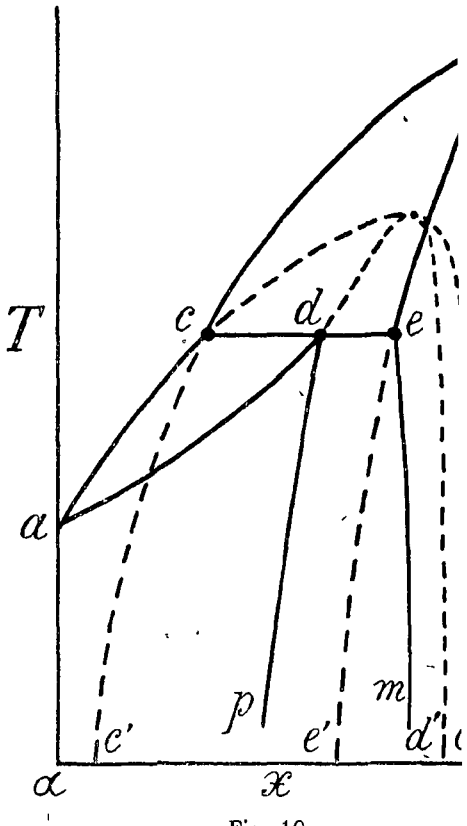

Fig. 10.

$\left(\frac{\partial^2\zeta}{\partial x^2}\right)_{\substack{PT \\ L}}$ becoming $= \infty$ for a definite value of x, and

$$T\left(\frac{dx}{dT}\right)_P = -\frac{\eta_{SL}}{\left(x_s - x_L\right)\left(\frac{\partial^2\zeta}{\partial x^2}\right)_{\substack{PT \\ L}}}$$

$\left(\frac{dv}{dT}\right)_P$ assumes the value *zero* for that definite value of x.

It appears at the same time from these figures that when the temperature of the three phase equilibrium lies between the meltingpoint temperatures of the pseudo-components, one of the metastably produced meltingpoint lines must possess a maximum temperature.

When in conclusion we consider the case that the ζ-x-lines for solid suddenly terminate in the ζ, x-figures, we find what follows for the corresponding T,x-figures.

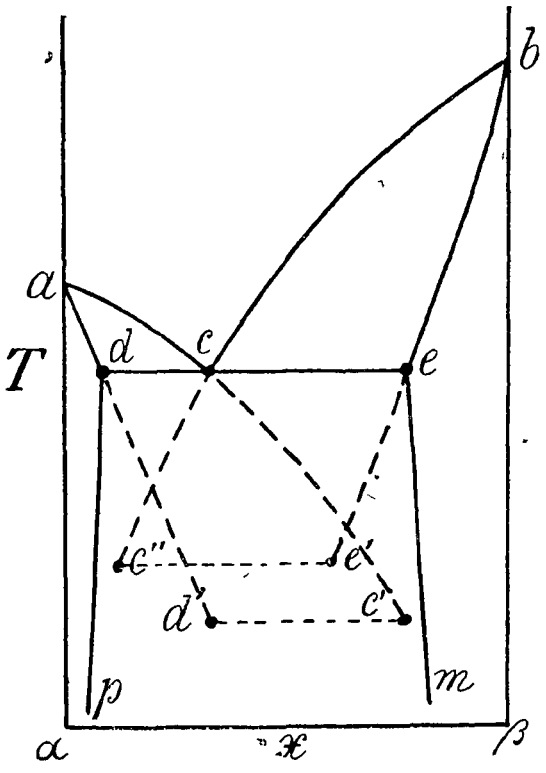

Fig. 11.

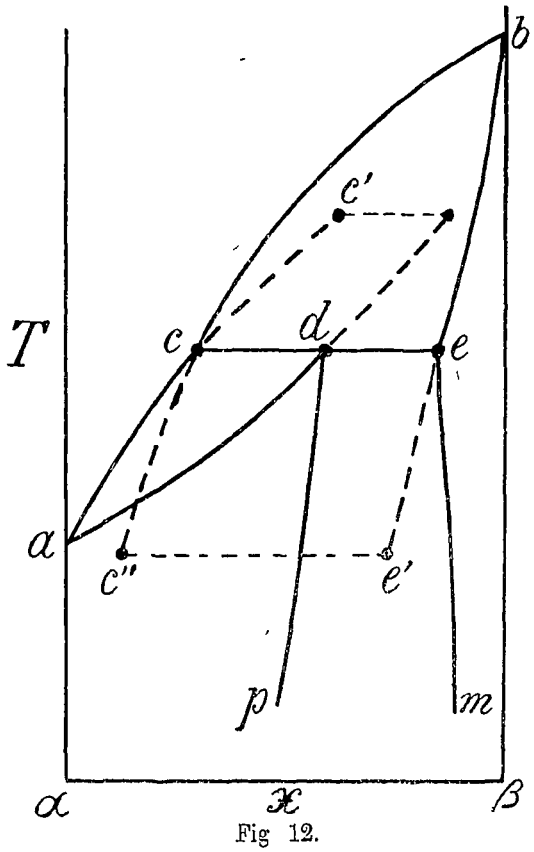

Fig 12.

We have treated here systems of two pseudo-components α and β, but it is clear, that the same holds also for any other binary system.

Amsterdam, 20 March 1914.

Anorg. Chem. Laboratory of the University.

(To be continued.)