

Citation:

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But in consequence of the special position of the lines α , the locus (P) now consists of the three hyperboloids $(\alpha_1 \alpha_2 \alpha_3 \alpha_4)$, $(\alpha_1 \alpha_2 \alpha_5 \alpha_6)$ $(\alpha_3 \alpha_1 \alpha_5 \alpha_6)$.

8. Two triplets of planes $\alpha_1, \alpha_2, \alpha_3$ and $\beta_1, \beta_2, \beta_3$ determine a pencil of cubic surfaces of which the nine lines $(\alpha_i \beta_i)$ form the basis. If these surfaces are conjugated projectively to the planes through an arbitrary line l , the surface O^4 , generated by the two pencils contains besides the already mentioned ten lines six lines more of which each of the given six planes furnishes one.

These *sixteen* lines form a configuration, in which each line is intersected by six others; it is identical to the figure which is generated when four arbitrary planes α_i are intersected by four other planes β_i . For, the planes through l , conjugated to the figures $(\alpha_1, \alpha_2, \alpha_3)$ and $(\beta_1, \beta_2, \beta_3)$ can be called successively β_4 and α_4 .

Let t be a transversal of the lines $l, (\alpha_1 \beta_1), (\alpha_2 \beta_2), (\alpha_3 \beta_3)$. The projectivity indicated above can be arranged in such a way that the plane (t) is conjugated to the cubic surface passing through a point of t , hence containing t . In an analogous manner we can deal with two other lines, each of which rests on l and on three not intersecting lines $(\alpha_k \beta_l)$. Then the projectivity is determined and the surface O^4 generated in this way evidently now contains *nineteen* lines.

We finally note that E. TRAYNARD (*Bull. Soc. Mat. de France*, vol. 38, p. 280) has described an O^4 with *thirty* lines.

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

Those who have been occupied with the sulphur problem up to now, have always thought the pseudo system to be binary, i.e. they assumed that they had to deal with two pseudo components or two kinds of molecules, which can be converted into each other, and one of which gives rise to the formation of the well-known crystallized modification, the monoclinic and the rhombic sulphur, whereas the other would produce the amorphous sulphur, called so because attempts to make this form of sulphur crystallize have not been successful as yet.

Though in my opinion the above view is not the correct one, I will begin with treating sulphur as a pseudo-binary system, and show

what relation there would have to exist between the equilibria in the pseudo-binary and the unary system to explain the observed

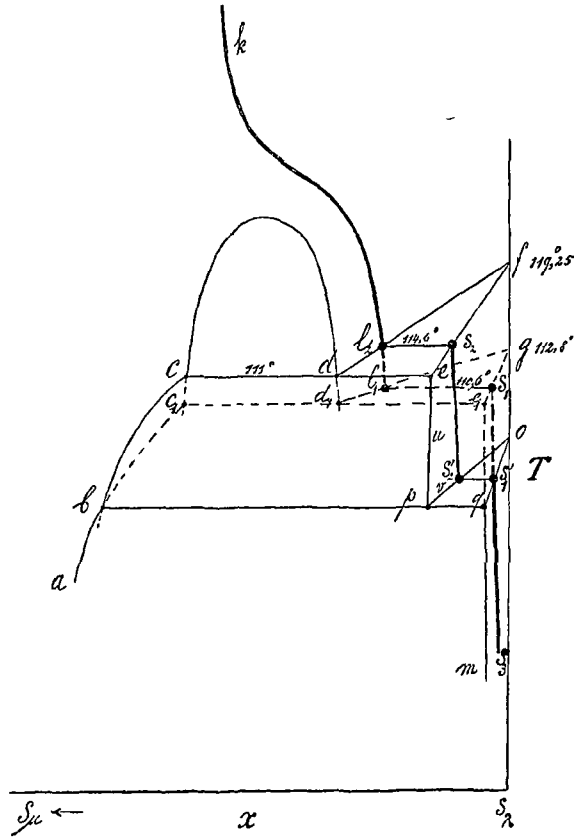


Fig. 1.

phenomena; especially because in this way it appears the more clearly how rational the pseudo-ternary view is.

The $T-X$ -figure, arrived at in this way, has been given schematically in fig. 1.

The lines f_2 and gl_1 are the melting-point lines of the monoclinic and the rhombic sulphur, the former of which is made to meet the region of non-miscibility at 111° and 4% S_ρ , because it was thought that from this concentration of S_ρ the point of solidification did not change any more on addition of S_μ .

The same thing has been assumed in this figure, hence the metastable melting-point line of the rhombic modification meets the metastable region of non-miscibility at d_1 .

As in accordance with the theory mixed crystals had to be assumed, to which also some experimental data point, as I already demon-

strated, the mixed crystal lines fe and ge_1 , corresponding to the melting-point lines have been drawn.

The existence of the latter mixed crystal line, which at e_1 passes into the line e,m with a break, involves the necessity of two mixed crystal lines starting from the transition point O , which run downward, because as was found by me in collaboration with Dr. DE LEEUW and was also stated by Dr. VAN KLOOSTER¹⁾, the transition point is lowered on increase of the S_b -concentration. At the point where the lower, the rhombic mixed crystal line og , meets the other rhombic mixed crystal line e,m , this latter line becomes stable. So the point g indicates a stable rhombic mixed crystal phase, which coexists with the monoclinic mixed crystal phase p , and at the same time with the liquid b .

So the monoclinic mixed crystal phase must also coexist with the liquid b , and the point b being the point of intersection of the melting point lines of the monoclinic and the rhombic sulphur, the said monoclinic mixed crystal phase must lie on the line ep , or in other words the mixed crystal lines eu and ov meet in p . Below the three-phase equilibrium bpq the rhombic mixed crystals qm are in equilibrium with the liquids along ba in the pseudo-binary system.

It is not difficult to see now what must be the relation between the pseudo-binary and unary equilibria, or in other words how the lines for the internal equilibrium must be drawn in this figure.

The line for the internal equilibrium in the monoclinic sulphur starts from S_2 , and that for the internal equilibrium in the rhombic modification from S_1 .

Above 95.45 , the unary point of transition, the monoclinic modification is stable, below it the rhombic modification. At the temperature of 95.45 the first line, which starts from S_2 , must intersect the monoclinic mixed crystal line op , and the second line, which starts from S_1 , must intersect the rhombic mixed crystal line og , so that S_2' and S_1' are two coexisting solid phases, which are in internal equilibrium, one of which is monoclinic and the other rhombic.

Below this unary point of transition the rhombic modification is stable, its internal equilibria being indicated by the line $S' S_2$.

According to the new view, however, the TX -figure given here, is illogical, for to account for the observed phenomena it had to be assumed here that the pure pseudo-component S_b possesses a point of transition, and the theory of allotropy says that the phenomenon of transition implies non-miscibility in the solid state For the phos-

¹⁾ See communication of KAVYR Chemisch Weekblad **34**, 647 (1911)

phorus the transition phenomenon could be indicated also with the pseudo-binary conception of the system according to the new conception, but this being impossible for the sulphur, we are compelled to reject fig. 1 and to consider the system sulphur to be *pseudoternary*, as has been done in fig. 2. In the T, X -diagram drawn by Dr. DE LEEUW according to my directions, the three pseudo components are indicated by S_R , S_M , and S_p . Further melting-point figures have been assumed for the three pseudo-binary systems, which have been represented in the three side planes of the trilateral prism.

In the pseudo-binary systems $S_M + S_p$ and $S_R + S_p$ a region of non-miscibility has been assumed which comes in contact with the melting-point line of S_M resp. S_R ¹⁾.

The only complication which the pseudo-ternary figure displays is exactly this meeting. If we start from the three-phase equilibrium between the monoclinic mixed crystal phase and the two liquid layers

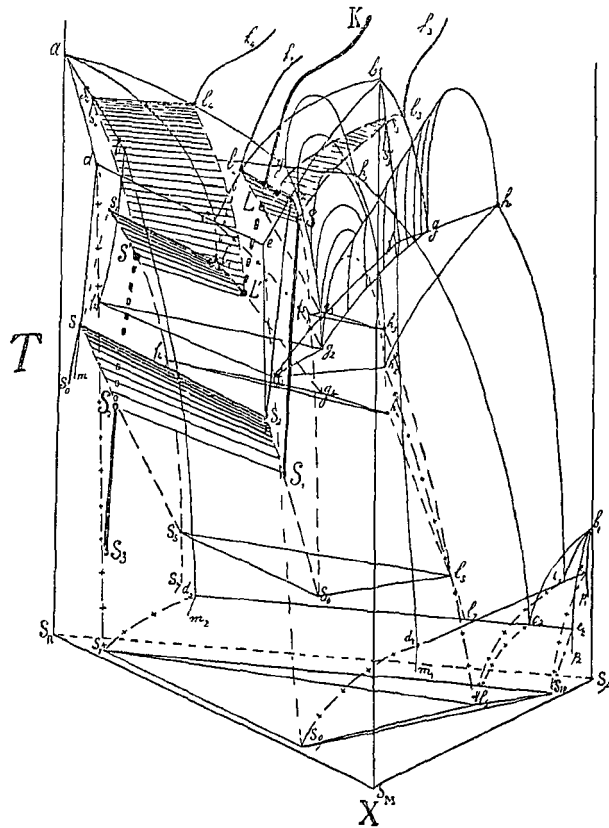


Fig. 2.

¹⁾ When this paper had already been written it has been found by me in collaboration with Dr. DE LEEUW that the supposed region of non-miscibility does not exist, so that it should be removed from figs 1 and 2.

in the system $S_M + S_\nu$, which equilibrium is indicated by the points f, g, l , we see that the temperature of this three-phase equilibrium is lowered by addition of S_R till the eutectic line cg_2 is reached. At this meeting the liquid layers are also saturate with regard to the rhombic mixed crystal phase, and a four phase equilibrium invariant at constant pressure occurs between the two mixed crystal phases f_2 and f'_2 , and the two liquid layers g_2 and h_2 . It is clear that we get the same four phase equilibrium starting from the three phase equilibrium between the rhombic mixed crystal phase and the two liquid layers in the plane for $S_R + S_\nu$ indicated by $f_1g_1h_1$ and so we see that the eutectic line which meets the region of non-miscibility at g_2 , skips to h_2 , from where it pursues its course to the ternary eutectic point indicated by l_0 .

After this explanation we can proceed to the discussion of the lines for the different internal equilibria.

The line kl_2 in the plane for $S_R + S_M$ indicates the internal liquid equilibria in this pseudo-binary system; l_2 and S_2 are the liquid and solid phases which coexist at the unary meltingpoint temperature; from S_2 starts the line for the solid internal equilibria, which meets the mixed crystal line of the pseudobinary system in S_2' , so that at this place the transition point in the system $S_R + S_M$ occurs with unary behaviour. Then S_1' is formed by the side of S_2' , and below the transition temperature the solid phase, which is in internal equilibrium, moves along the line $S_1'S_0$.

So it is supposed here that in the pseudo-binary system $S_R + S_M$ a point of transition occurs, but not between the pure pseudo-components, but between two mixed crystal phases, one of which is rhombic and the other monoclinic.

Before we proceed it may be pointed out here that the points l_1 and S_1 represent the metastable unary melting-point, and that, as was mentioned before, the line for the internal equilibria in the rhombic modification, which does not become stable until below the transition point, starts from S_1 .

In the other two pseudo-binary mixtures the liquid and solid phases which are in internal equilibrium are also indicated, but transition points need not be assumed in these systems.

The question which called for a solution first of all was this: "what shall we get when to the system $S_R + S_M$, which is thought to be continually in internal equilibrium we add S_u , of which substance we suppose for a moment that it cannot be converted to rhombic or monoclinic sulphur, and which, accordingly, behaves as a real component.

If we now take the simplest case, the stable unary melting equilibrium will be lowered in temperature by addition of S_ν , so that lines can be drawn over the melting-point surface and over the mixed crystal surface of S_M , starting from l_2 resp. from S_2 , which indicate the liquid and solid phases which coexist with internal equilibrium between S_R and S_M on increase of the S_ν -content. The same thing holds for the metastable unary melting-point equilibrium. Here too we get two lines starting from l_1 and S_1 , which traverse the metastable part of the melting-point surface resp. mixed crystal surface of S_R . And finally we get something of the same kind for the transition equilibrium. If this too is lowered by addition of S_ν , lines will start from the points S_1' and S_2' , which traverse the mixed crystal surfaces of S_R and S_M .

If we now consider the case that there is always internal equilibrium between S_M and S_ν , and that S_R behaves as a true component or in other words is not converted, we assume here that also the unary melting-point equilibrium indicated by the points l_3 and S_3 , is lowered by addition of S_M , so that lines will start from these points l_3 and S_3 running over the melting-point surface and the mixed crystal surface of S_M .

At the point where the liquid lines starting from l_2 and l_3 , meet, we shall have a solidifying liquid, in which the three pseudo-components are in internal equilibrium with each other, so that this point indicated by **L** in the drawing, is the liquid point of the stable unary pseudo-ternary melting-point equilibrium while the point of intersection of the lines starting from S_2 and S_3 , gives the monoclinic sulphur, which is in internal equilibrium and coexists with the liquid **L** at the unary melting-point temperature. This point is denoted by **S**.

We find in the same way that **L'** and **S'** denote the liquid and the solid phase, which are in equilibrium with each other in the metastable unary melting point of the rhombic sulphur.

In the same way as the line for the internal equilibria which exist in the liquid phase at higher temperatures starts from **L**, the line for the internal equilibria in the solid monoclinic sulphur starts in **S**, and this line runs to smaller concentrations of S_ν with fall of temperature. The same holds for the line for the metastable internal equilibria in the solid rhombic sulphur, which starts from **S'**.

When a meeting of these lines and the transition surfaces takes place, as drawn here, this means that a point of transition occurs in the unary pseudo ternary system. The monoclinic mixed crystal phase **S**, is converted into the rhombic mixed crystal phase **S**, with

generation of heat, and when this conversion has been completed, the temperature falls on further withdrawal of heat and with internal equilibrium the rhombic sulphur moves along the line $S_2 S_3$, which is the continuation of $S'S_2$.

It is easy to see that the course of these lines for the solid substance in internal equilibrium, is in agreement with the observation.

The fact e.g. that the rhombic sulphur melts at a higher temperature according as it is heated rapidly from a lower temperature can just as well be accounted for when we take this view of the matter, as when we take that indicated by fig. 1. for according as we start from a lower point on the line $S_2 S_3$, we shall reach when heating rapidly either the melting-point surface $S'L'S_4l_4$, or the melting-point surface $S'L'S_1l_1$ at a higher temperature.

It may finally be pointed out here that if we assume S_R and S_M to be always in internal equilibrium, and S_p to behave as a true component, some more conclusions may be drawn from the figure for this case than have been already discussed.

Then the liquid line of the melting-point surface starting from $l_2 S_2$ will meet the region of non-miscibility at g_3 and a second liquid h_3 will make its appearance. The solid substance f_3 will coexist with the two liquid layers, so that a three-phase equilibrium prevails here, which is invariant if the pressure is assumed to be constant. On withdrawal of heat g_3 is converted to $f_3 + h_3$, and at lower temperatures the melting-point surface will be formed by the line $f_3 S_6$ for the solid phases and by the line $h_3 l_5$ for the liquid phases.

An analogous remark may be made with reference to the melting-point surface starting from $S_1 l_1$. The liquid line of this surface meets the metastable part of the region of non-miscibility, which starts on the plane for $S_R + S_p$, so that also here we get a three-phase equilibrium, which is metastable, and which is indicated by $f_4 g_4 h_4$.

Below this three-phase temperature the metastable melting-point surface is indicated by the lines that run from f_4 and h_4 to lower temperatures. If now the liquid lines intersect each other, as is assumed here, this means that a liquid which coexists both with monoclinic and with rhombic mixed crystals, is found in this point of intersection. It follows from this that also these mixed-crystal phases are in equilibrium with each other, and so that they must lie on the transition surface.

So, as is at once clear, the three coexisting phases are found by the meeting of the two melting-point surfaces and the transition surface. Of the two melting point surfaces the liquid lines meet; this

gives the point l_5 and the transition surface meets of each of the melting-point surfaces the line for the solid phase, and thus we find the points S_5 and S_6 .

So we get a second stable three-phase equilibrium, but now between rhombic and monoclinic mixed crystals and a liquid; the temperature of this three phase equilibrium we might call the transition temperature lowered by S_p .

With withdrawal of heat the transformation $S_6 \rightarrow S_5 + l_5$ takes place, i. e. the monoclinic mixed crystals disappear, and the two-phase equilibrium between rhombic mixed crystals and liquid, which was metastable before, now becomes stable.

Though the pseudo-components S_R and S_M will not always be in internal equilibrium under all circumstances, and S_p never behaves as a true component, it will appear later that the view of this case, discussed here may be of some use.

Remark. The reader will perhaps have seen already, that the new theory of allotropy for the first time gives a rational explanation of the rule, found by OSTWALD, that with the appearance of a new phase the metastable state occurs first. I hope to treat this question in a separate communication later on.

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Amsterdam, September 1911.

Physics. — “*On the phenomena of condensation for mixtures of carbonic acid and nitrobenzene in connection with double retrograde condensation*”. By Prof. PH. KOHNSTAMM and J. CHR. REEDERS”. VAN DER WAALS-*fonds* *researches*. N°. 3. (Communicated by Prof. J. D. VAN DER WAALS.)

In These proceedings April 23, 1909, (Vol. XI p. 913) we demonstrated by means of some experiments how great the influence is which slight quantities of urethane exert on the phenomena of condensation of carbonic acid; we further showed that at our smallest concentration of $3\frac{1}{4}\%$ we were still very far from that concentration for which double retrograde condensation will be found. We shall proceed to give some similar observations on the system carbonic acid and nitro-benzene. These observations were undertaken in the hope that we might succeed in proving the existence of double retrograde condensation for this system. This hope has proved vain;