which if we also introduce $\zeta = \frac{1}{3} \varrho s l$, becomes quite identical with our formula (7).

And this is not surprising. For according to CUNNINGHAM the second term will preponderate in equation (8), when only sliding friction occurs, i.e. when the motion of the surrounding molecules has become quite independent of the suspended particle. On such a state, we have, however, also founded our considerations. At bottom CUNNINGHAM's suppositions entirely agree with those of VON SMOLUCHOWSKI. According to both writers it will depend on the value of $\frac{l}{a}$ whether for $\overline{\Delta^2}$ the formula with $\frac{1}{a}$ or that with $\frac{1}{a^2}$ is to be used. Our opinion is opposed to this. According to us the formula with $\frac{1}{a^2}$ is always the correct one.

In order to prevent misunderstanding we will state that we by no means intend to deny the validity of the formulae given by STOKES and CUNNINGHAM for the friction of a small particle moving through a resisting medium. We are only of opinion that the application of the formulae should be confined to non-reversible processes, in which friction actually appears. When a particle falls under the influence of gravitation or when it is electrically charged and moves under the influence of electric forces, we think that the said formulae will give the true value for the friction. But in case of Brownian movement, which is a phenomenon of thermal equilibrium, we think we have to assume independence of the velocities of the different particles on the ground of statistical mechanics, which, as we demonstrated, leads to a value of $\overline{\Delta^2}$ proportional to $\frac{1}{a^2}$.

Chemistry. — "*The P,X-figures of Unary Systems, According to the Theory of Allotropy.*" By Prof. A. SMITS. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of January 29, 1916.)

1. *Introduction*.

I will begin this communication by reminding the readers that the theory of allotropy is based on the hypothesis that *in case of allotropy for an element or a compound every phase is complex, or in other words, consists of at least two kinds of molecules, between which internal equilibrium prevails in case of unary behaviour.* [1]

[1] The words different kinds of molecules are to understand in a general sense. Ions also belong to the different kind of molecules. An internal equilibrium is a equilibrium of a unary system.

The tenor of this theory may be summarized under the four following points:

1. Every allotropic substance belongs to a pseudo-system and the different kinds of molecules of this substance are the pseudo-components, which are more or less miscible in the solid state.

2. An arbitrary three-dimensional spacial figure of a unary system, in which the concentration is plotted along one of the axes, consists of a number of internal equilibrium surfaces, which are necessarily situated in the corresponding spacial figure of the corresponding pseudo system.

At the place where these surfaces of internal equilibrium intersect the surfaces for the stable and metastable heterogeneous equilibria of the pseudo system, coexistence takes place between different phases of the unary system which differ from each other in concentration. Hence in the unary system the conversion of one coexisting phase to the other will always be attended with a chemical reaction.

3. The phenomena of monotropy and enantiotropy appear here in a new light; they are closely allied phenomena, and it appears at the same time that the difference in crystalline form between the modifications of one and the same substance are in causal connection with the difference in situation of the internal equilibrium.

4. The changes in properties which may be found under certain circumstances when a unary system is made to pass through an arbitrary process with a comparatively great velocity (variation of temperature, variation of pressure, evaporation, solution etc.) must be ascribed to a disturbance of the internal equilibrium of the considered system.

In the development of this theory use has been made of GIBBS's principle of equilibrium, which says that every system of substances at constant temperature and pressure tends to that state the thermodynamical potential of which is a minimum. When applying this principle, we arrive at the result that when e.g. the property of transformation into each other is assigned to the components of a system which was before thought to be binary, in consequence of which the system becomes unary, the thermodynamic potential of a certain state of aggregation, which is now a unary phase, must lie at a definite temperature and pressure in the minimum of the ζ,x-line, which relates to the binary mixtures of the same state of aggregation as the unary phase mentioned just now.

This can be elucidated in the following way:

The total differential of the thermodynamic potential of a binary mixture is:

$$d\zeta = -\eta\,dT + vdp + (\mu_2 M_2 - \mu_1 M_1)\,dx \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

in which $\mu_2 M_2$ and $\mu_1 M_1$ represent the molecular potentials of the two components.

If we assume now that the two components can be transformed into each other, and that therefore an internal equilibrium can set in, then in this state

$$\mu_2 M_2 = \mu_1 M_1 \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

from which follows that:

$$\left(\frac{\partial \zeta}{\partial x}\right)_{TP} = 0 \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

In connection with the well known shape of the ζ,x-line this result means that the internal equilibrium is situated in the minimum of the ζ,x-curve under consideration.

When we consider that the pseudo-components are certainly miscible to a certain extent also in the solid state, the unary solidification point temperature will be a temperature in which a unary liquid coexists with a mixed crystal phase, and as the unary liquid lies in the minimum of the ζ,x-line of the liquid mixtures, the coexisting phases mentioned will have to lie at the solidification equilibrium on a horizontal bitangent, i.e. also the ζ,x-line for the solid mixtures will have to possess a minimum, so also a point where:

$$\left(\frac{\partial \zeta}{\partial x}\right)_{T.P} = 0$$

or in other words in the coexisting solid phase internal equilibrium will likewise prevail.

We arrive at the same conclusion also by the following way for the internal equilibrium in the liquid phase holds:

$$(\mu_2 M_2)_L = (\mu_1 M_1)_L \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

for the heterogeneous equilibrium between the liquid and the solid substance holds:

$$(\mu_2 M_2)_L = (\mu_2 M_2)_S \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (5)$$

and

$$(\mu_1 M_1)_L = (\mu_1 M_1)_S \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

so that

$$(\mu_2 M_2)_S = (\mu_1 M_1)_S \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

follows from the combination of (4) with (5) and (6), or in words: the solid phase which coexists with the liquid which is in internal equilibrium, is itself also in internal equilibrium.

It has further been pointed out that in case of the appearance

of two different solid phases in the unary system (monotropy and enantiotropy), the ζ-values for the different solid mixtures of the pseudo-binary system must present *two* minima at constant T and P. Whether these two minima lie on the same continuous ζ,x-line, or on two different branches, which have nothing to do with each other, is a question which, as I already demonstrated before, is of minor importance for the theory of allotropy. [1]) The principal thing · is that these two minima must exist, and must lie on the same horizontal bi-tangent at the transition point.

All this was already fully explained and applied before, to indicate the situation of the T,x-lines of the unary system in the T,x-figure of the pseudo-binary system.

We may also express this as follows we considered the $(T,X)_P$ sections of the pseudo binary P,T,X spacial representation, which of course also contains the P,T,X spacial representation of the unary system.

Now it is of importance with a view to investigations which are in progress, also to examine the P,X$_t$-sections of the spacial representation under discussion, about which a few general remarks will first be made.

2. *P,T,X-spacial representation.*

The P,T,X spacial representation of the pseudo-binary system consists, as is known, of a number of systems of two surfaces belonging together. At the place where two homonymous surfaces intersect, three-phase coexistences arise, and at the place where three homonymous surfaces meet a four-phase coexistence occurs.

The P,T,X-spacial figure of the unary system consists of a number of surfaces of internal equilibrium, and where one of these surfaces - meets a homonymous surface of the pseudo-binary system, a two-phase coexistence of the unary system occurs. Thus the surface for the internal liquid equilibria e.g. intersects the liquid surface for the coexistence liquid-vapour in the pseudo-binary system. Hence every point of this line of intersection represents a liquid coexisting with vapour in the *unary* system. The intersection of the plane for the internal vapour equilibria with the vapour surface for the coexistence liquid-vapour in the pseudo-binary system equally yields a line of intersection, every point of which indicates a vapour coexisting with liquid in the *unary* system. These vapour and

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[1]) These Proc. XVII p. 672.
Zeitschr. f. physik. Chemie **89**, 257 (1915).

liquid points of the unary system lie at another concentration, so that in the P,T,X-spacial figure of the unary system the equilibrium between liquid and vapour is indicated by two lines, the coexisting points of which differ in x-values, and the same of course also applies to every other two phase equilibrium in the unary system.

It is clear that the P.T.-projection just hides what is characteristic ·in the unary system, because in this projection the difference in concentration of the coexisting phases cannot find expression, and every pair of lines for two-phase coexistences projects itself as one line in this representation.

It is my purpose to discuss here some P,X-sections of the pseudo-binary P,T,X-spacial representation, and to point out the place of the unary system there.

To be able, however, to determine the place of these sections it is not necessary to draw the spacial representation ; the P,T-projection will suffice, and this is the reason that I will now proceed to a short discussion of this projection.

Beforehand it must be stated that two cases should be distinguished. First the case that the pseudo-components a and β are isomers, and secondly the case that β is a polymer of a.

In the first case the P,T,X-spacial figure can possess a eutectic line, whereas as I showed already before, in the second case a eutectic line will not occur as a rule.

3. *The P,T-projection of the P,T,X-spacial figure of the pseudo-binary and of the unary system for the case a and β are isomers.*

We shall now proceed to a short discussion of the P,T-projection. The thin continuous lines in Fig. 1 are the three-phase lines of the pseudo-binary system and the two-phase lines of the pseudo-components, the thick continuous lines referring to the two-phase lines of the pseudo-components, the thick continuous lines referring to the two-phase lines of the unary system. For the greater clearness the phases of the unary system are denoted by S_u, L_u, G_u. (See Fig. 1 following page).

At the point where the vapour-tension line of the unary system $K_U D$, more closely defined by $L_u + G_u$, meets the three phase line $S_{\beta_M} + L + G$, the unary point of solidification *under the vapour pressure* is reached. This takes place at D ; then two new lines of internal equilibrium of the unary system appear in this triplepoint : the meltingpoint line DE, more closely indicated by $S_{u_2} + L_u$, and the line of sublimation DA′, where $S_{u_2} + G_u$ coexist. In the point

Fig. 1.

B in this drawing the sublimation line meets the three-phase line $S_{\alpha_M} + S_{\beta_M} + G$ of the pseudo-binary system, which means that it is supposed here that a point of transition occurs here under the vapour pressure. Therefore besides the sublimation line $S_{u_2} + G_u$ two more lines of internal equilibrium start from this triple point in the unary system, viz. the sublimation line of the new modification AB for the coexistence $S_{u_1} + G_u$ and the transition line BC for $S_{u_1} + S_u$.

Where the metastable prolongations of the vapour tension line $L_u + G_u$ and of the three-phase line $S_{\alpha_M} + L + G$ meet, the meta-

stable melting point under the vapour pressure appears. This takes place in D′; of course two more metastable internal equilibrium lines of the unary system must start from this triple point, viz. the metastable melting-point line D′E′ for the coexistence $S_{u_1} + L_u$ and the sublimation line of the first solid modification D′A, which is metastable as far as the point B, and refers to the coexistence $S_u' + G_u$.

That here in this P,T-projection the theory of allotropy has been applied, appears from this that the four three-phase lines meeting in the pseudo-binary system in the quadruple point e_2, are indicated by $S_{\alpha_M}+L+G$, $S_{\beta_M}+L+G$, $S_{\nu_M}+S_{\beta_M}+G$ and $S_{\alpha_M}+S_{\beta_M}+L$, in which the index M is used to state emphatically that the *solid* substance here is a *mixed crystal phase*. If this were not the case this P.T-projection would quite agree with that given by SCHOEVERS[1]), but then it would be in conflict with the theory of allotropy.

The P,T-projection discussed here is in itself exceedingly little suitable for an illustration of the theory, because as I already remarked, it quite hides the most important factor, the difference in concentration of the different phases. Accordingly this figure will only be used here to indicate which P,X-sections of the spacial figure are in consideration.

3. *(P,X)$_T$-sections of the spacial figure.*

The (P,X)$_T$-sections, just as the (T,X)$_P$-sections can of course be derived from the ζ,x-lines. The only difference that appears is this that

$$\left(\frac{\partial \zeta}{\partial T}\right)_P = -\eta$$

follows from the equation:

$$d\zeta = -\eta \, dT + v dp$$

and that therefore at constant pressure the ζ-lines descend on increase of temperature, at least when η is positive, while

$$\left(\frac{\partial \zeta}{\partial p}\right)_T = v$$

which means that the ζ-lines ascend with increase of pressure at constant temperature.

As, however, in the derivation we have only to do with the *relative* displacement of the ζ-lines, this is of secondary importance, and we need not enter into a special discussion of the thermo-dynamic derivation of the P,X)$_T$-sections.

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[1]) Thesis for the doctorate, Amsterdam 1907.

Of more importance is the question what will be the shape of the internal equilibrium lines of the unary system in the P,X-section.

We see then that according to PLANCK's formula

$$\frac{d\ln K}{dp} = -\frac{\Delta v}{RT}$$

this displacement will be determined by the sign of Δv.

Now we have supposed here that the pseudo-components are isomers, which of course involves that the P, X-line for the internal gas equilibrium runs vertical. This does not apply, however, to the lines which relate to the internal equilibrium in the liquid and in the solid phase, because the b-values from VAN DER WAALS's equation of state for isomers, are not equal on the whole. In the following figures the P, X-lines of the unary system have, however, been drawn vertical in all the phases for the sake of simplicity.

First of all we shall now consider the P, X-section at the temperature t_1. The thin lines again indicate the pseudo-binary figure, the thick ones the unary figure.

Fig. 2.

Fig. 3.

The line G_{u_0} G_u represents the internal equilibrium in the gas phase. At G_u this line meets the vapour line aG of the pseudo-binary system, from which follows that when arrived at G_u we compress the gas further, and no metastable states occur, the mixed crystal phase S_{u_1} will deposit, which just as the gas phase G_u, in case of behaviour as a unary substance, will be in internal equilibrium. When all the gas has been removed by pressure, a further compression will lead to an increase of pressure, and now the internal equilibrium in the solid phase can be indicated by the line $S_{u_1}S'_{u_1}$.

If, however, when we have arrived at G_u, the solid phase S_{u_1} fails to appear on further compression, then the metastable prolongation of the vapour line bG will be reached at G'_u, which means that when no further retardations make their appearance, on further compression the metastable solid phase S_{n_2} will appear, which in case of unary behaviour, will likewise be in internal equilibrium.

When the vapour has quite disappeared, further compression will give rise to an increase of pressure, and the internal equilibrium in the metastable substance will be displaced along the line $S_{u_2}S'_{u_2}$.

At the temperature chosen here the unary solid phase S_{u_1} remains stable under all pressures, and S_{u_2} metastable. so that we may say that our system presents *monotropy* at this temperature.

Just as it happens that a system is monotropic under the vapour pressure, and enantiotropic under higher pressure, a system that shows monotropy at lower pressure, can be enantiotropic at higher temperatures.

In the case under consideration, where the phenomenon of enantiotropy has been assumed under the vapour pressure, this is actually the case. If we namely choose t_2 as second temperature (see Fig. 1), we get a section as is indicated in Fig. 3.

Noteworthy is the change in situation of the unary system with respect to the pseudo binary system on increase of temperature. The line for the internal equilibrium in the vapour has shifted to the right with respect to the pseudo binary figure, which causes the meeting with the pseudo binary figure, which first took place on the vapour branch aG, to take place on the vapour branch bG. At an intermediate temperature the intermediate position must of course be reached, in which the just-mentioned meeting took place exactly in the point G, G_u and G therefore coinciding.

Hence at this temperature coexistence will be found in the unary system between two solid phases and a vapour phase, all three in internal equilibrium, i.e. *this temperature will be that of the transition point under the vapour pressure.*

The temperature t_2, which lies slightly above this temperature, therefore, yields the P,X-section Fig. 3, in which we see that the lines for the internal equilibrium in the stable solid modification S_{u_2} and in the metastable modification S_{u_1}, meet the mixed crystal lines $S_{\beta M} S'_{\beta M}$ and $S_{\varkappa M} S'_{\varkappa M}$ of the pseudo system at S'_{u_2} and S'_{u_1}, which means that in case of unary behaviour, a transition of the solid phase S'_{u_2} into S'_{u_1} will take place there at constant pressure, provided no retardations occur, so that the modification S_{u_1}, which was metastable at lower pressures, now for the first time appears stable. If the phase S'_{u_2} has been entirely converted, then on further compression the pressure will again rise, and now the internal equilibrium of the stable phase will move along the line S'_{u_1}, S''_{u_1}.

Accordingly at this temperature enantiotropy is found with variation of the pressure.
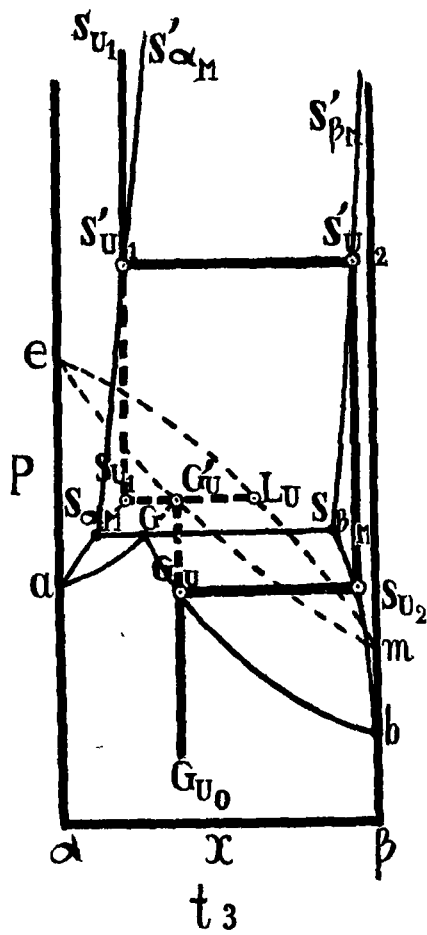
Fig. 4.

Fig. 4 has reference to the temperature of the metastable melting-point D of the unary system. The only peculiarity presented by this P,X-section compared with the preceding one is this that the metastable prolongation of the line for the internal equilibrium in the vapour exactly meets the point where the metastable prolongation of the vapour branch aG in the pseudo binary system intersects the vapour branch of the, metastable liquid-vapour equilibrium. This means, therefore, that in metastable state in the unary system coexistence of solid, liquid and vapour, viz. $S_{u_1} + G'_{u_t} + L_u$ appears, or in other words that *in this section the metastable melting equilibrium under the vapour pressure occurs.*

Fig. 5 corresponds with t_4, a temperature lying a little below the eutectic' temperature of the pseudo binary system. In connection with what precedes this figure is clear without further explanation.

Fig. 6 relates to the temperature t_5. lying somewhat above the eutectic temperature of the pseudo binary system. The P,X-section of the pseudo system consequently exhibits a region for the stable

t_4

Fig. 5

t_5

Fig. 6

S''_{U_1} S'_{α_M} S''_{β_M}

S'_{U_1} S''_{U_2}

S''_{U_1} S'_{α_M} S''_{β_M}

S_{U_1} L''_U

S'_{U_1} S'_{U_2}

S_{α_M} S'_{β_M}

S_{U_1} L'_U S'_{β_M}

S_{α_M} L'

c

c

L'_U S'_{U_2}

P

P

a

a

G'_U S_{U_2}

G L' S'_{β_M}

G_U L S_{β_M}

G'_U L'_U

G' L S_{β_M}

G_U L''_U S_{U_2}

G_{U_0} b

G_{U_0} b

α x β

α x β

t.6.

t.γ.
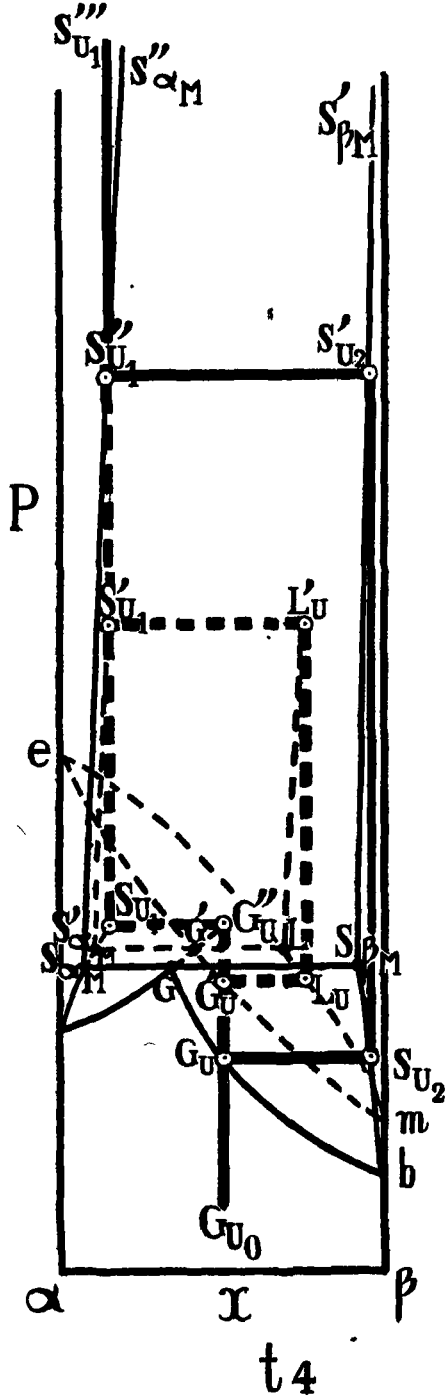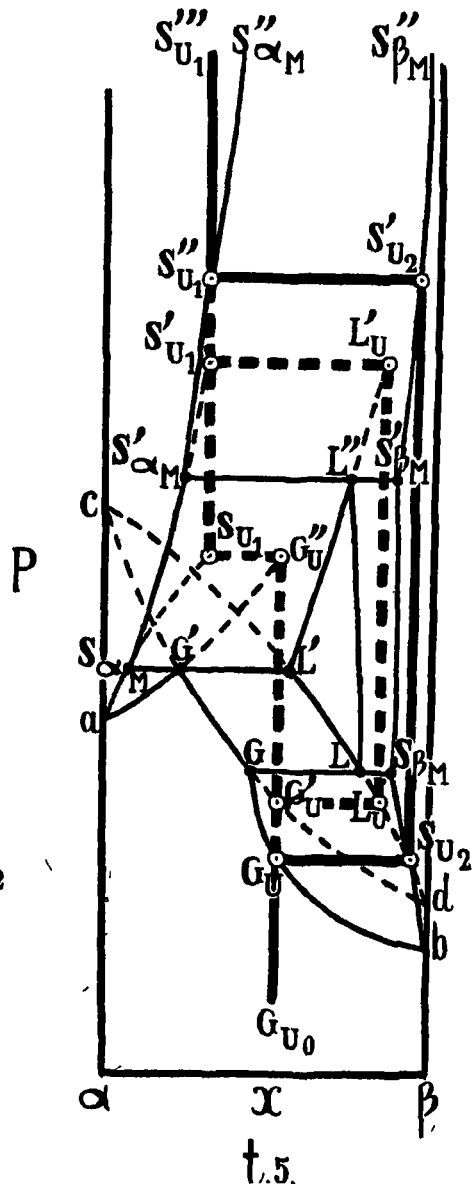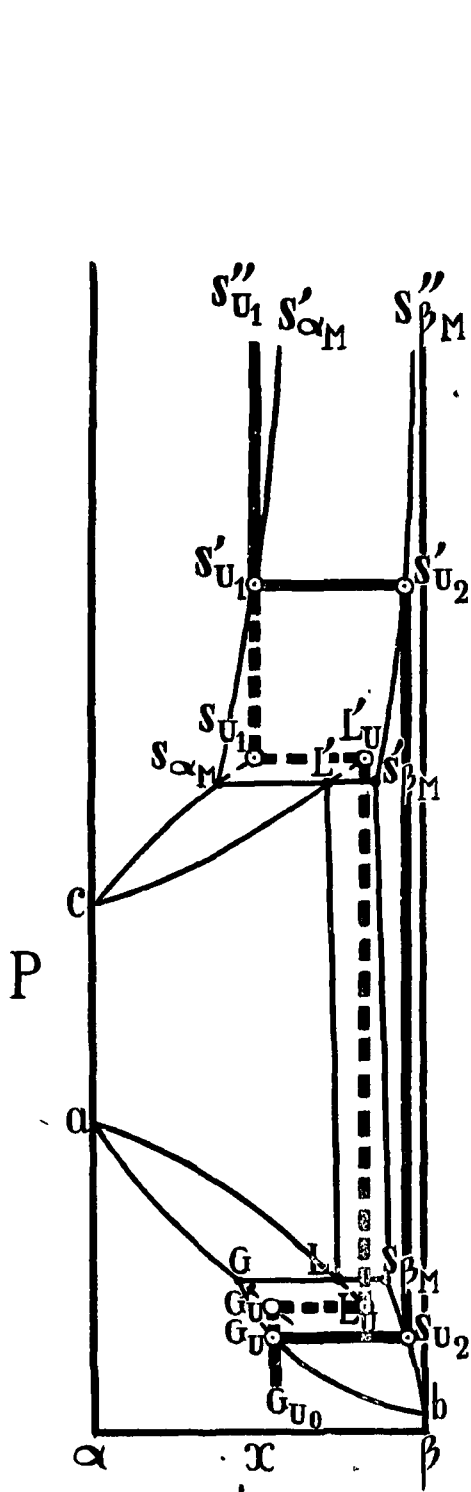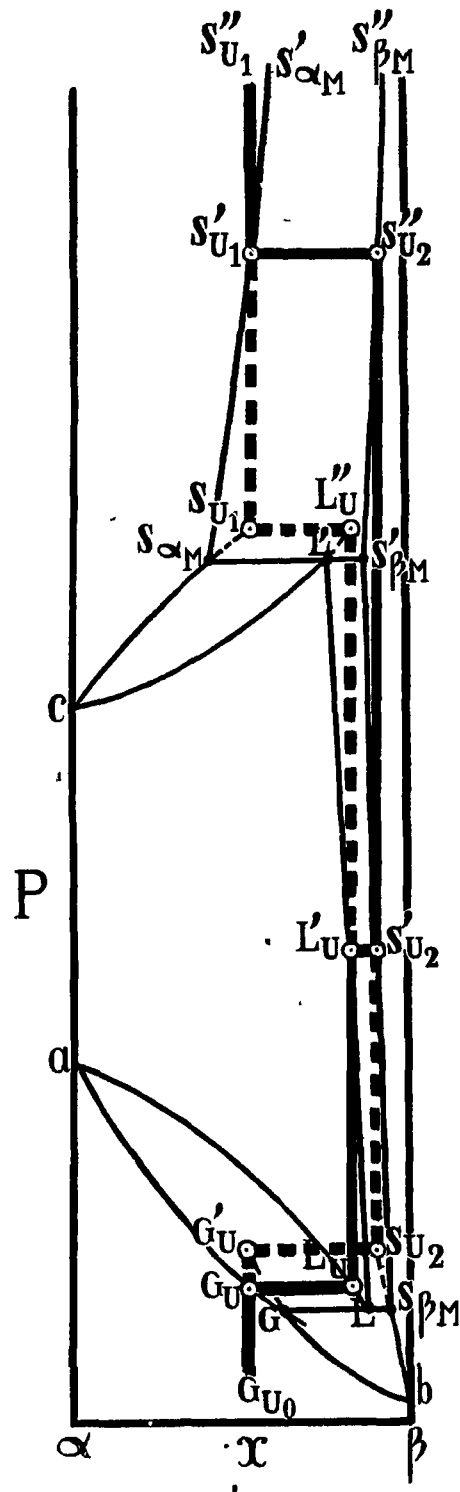
Fig. 7

Fig. 8

coexistence of liquid (L'L) and vapour (G'G), of S_x-mixed crystals - (S_{xM} S'_{xM}) and liquid (L''L') and of $S_?$-mixed crystals ($S'_{\beta M}$ $S_{\beta M}$) and liquid ((L''L). The unary figure does not call for any further explanation.

The higher the temperature is chosen, at the higher pressure the transition point of course occurs; in order to reduce the dimensions of the figure, however, I have not been able to observe this; the figures are, therefore, very schematical.

The P,X-sections Fig, 7 and Fig. 8 (p. 1345) hold for the temperatures t_6 and t_7, which lie slightly below, resp. above the stable unary melting point D.

Now these figures differ in this that in Fig. 7 the line for the internal equilibria in the vapour meets the vapour line b G of the pseudo binary system, i.e. the line relating to the vapours coexisting with the β-mixed crystals, whereas the line for the internal vapour equilibria - in Fig. 8 meets the pseudo binary P,X-figure in a point of the vapour line indicating the vapour phases which coexist with a series of liquids.

At an intermediate temperature, viz. the temperature of the stable unary melting point, the said meeting takes place exactly in the point G, which indicates the vapour coexisting with the liquid L and the mixed crystal phase $S_{\beta M}$, so that at this temperature these three phases coexist also in the unary system, from which follows that *this temperature is the stable unary melting point.*

4. *P,T-projection of the P,T,X-spacial representation for the case that β is a polymer of a.*

When we again suppose that the unary system presents a point of transition under the vapour pressure, then the P,T-projection is as indicated by Fig. 9. (See following page).

With regard to the direction of the lines of internal equilibrium in the P,X-sections it may be observed that as β is now supposed to be a polymer of a, it is beyond doubt that the internal equilibrium in the gasphase shifts towards the side of the polymer on increase of pressure according to the equation:

$$\frac{d\ln K}{dp} = -\frac{\Delta v}{RT}$$

The direction of the lines for the internal equilibrium in the *liquid* and also in the *solid* phase will depend on this whether the total molecular volume increases or decreases on splitting up of the

Fig. 9

polymer β in α. No doubt we shall be allowed to assume as a rule that the molecular volume decreases at the reaction:

$$n\,\alpha \longrightarrow \beta$$

and that therefore:

$$n b_1 - b_2 = \Delta\,b = > 0.$$

In this case the line for the internal equilibrium in the liquid and in the solid phase will move to the side of the polymer on increase of pressure.

This has therefore been assumed in the following P,X-figures. We should not forget, however, that as Dr. van Laar[1]) has demonstrated for the substance water, the double molecules H_4O_2 seem to possess a greater molecular volume than two molecules H_2O, so that, when we should want to examine this substance, the lines for the internal equilibrium in the liquid phase and in the solid phase shift just to the side of the single pseudo-component H_2O on increase of pressure.

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[1]) Arch. Teyler. Serie 2, T. XI, Troisième partie 1908.
Zeitsch. f. phys. Chem. 31.

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At a temperature t_1, below that of the transition point under the vapour pressure B, the P,X-section is as indicated in Fig. 10. At this constant temperature and variable pressure the unary system exhibits the phenomenon of *monotropy*. S_{u_1} is the stable modification under the vapour pressure. At a temperature above that of the point B, e.g. t_2, *enantiotropy* is found on increase of pressure, as Fig. 11 shows. Under the vapour pressure S_{u_2} is now stable. At the higher temperature t_3, above the metastable triple point D' and below the stable triple point D, everything remains more or less the same, only when we want to represent the metastable internal equilibria in the unary figure, the drawing becomes somewhat more intricate,

t.1.

Fig. 10.

t.2.

Fig 11.

but the connection becomes clearer on somewhat closer examination.

Thus in Fig. 12 with reference to the unary system three more metastable equilibria occur besides the stable equilibrium of $S_{u_2} + G_u$ and the transition equilibrium of $S'_{u_2} + S''_{u_1}$, viz. the metastable equilibria $G'_u + L_u$, $G''_u + S_{u_1}$ and $L'_u + S'_{u_1}$.

At a temperature above the stable triple point D, coming from lower pressure, as Fig. 13 shows very clearly, we meet in the unary system first the stable unary vapour point $(G_u + L_u)$, then the metastable unary sublimation point for S_{u_2}, viz. $(G'_u + S_{u_2})$, then

t.3.

Fig. 12.

t.4.

Fig. 13.

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the same for S_{u_1}, viz. $(G''_u + S_{u_1})$, then the metastable unary melting point of S_{u_2}, $(S'_{u_2} + L'_u)$, the corresponding point for S_{u_1}, $(S'_{u_1} + L''_u)$, and finally at a still higher pressure the unary transition point, $(S''_{u_2} + S''_{u_1})$.

OBSERVATION.

As is known it often occurs that though the vapour tension curves of two different modifications do not intersect below their melting point temperatures, the melting point curves of these two states do yield a point of intersection. In this case the system is *monotropic under the vapour pressure, but enantiotropic under the melting pressure.* As it is illogical to apply the terms monotropic and enantiotropic only to the case that the substance is under the vapour pressure, it is expedient to state when mentioning these phenomena, under what circumstances the system is considered to be. And just as we can now speak of monotropic and enantiotropic for a system that is under constant pressure, the same denominations can also be applied when the temperature is thought to be constant, as this has, moreover, been repeatedly done in this communication.

Anorg. Chem. Labor. of the University.
Amsterdam, Jan. 19, 1916.

Physics. — "*The Symmetry of the Rontgen-patterns of Tetragonal Crystals*". By Prof. H. HAGA and Prof. F. M. JAEGER.

(Communicated in the meeting of February 26, 1916).

§ 1. For the purpose of further completing our experiments on the specific symmetry of the diffraction-images, which can be obtained by radiating through crystals by means of RONTGEN-rays, we publish in the following paper the results, which were obtained by us in the study of *tetragonal* crystals.

It appeared to be rather difficult to study an object of all seven classes of the tetragonal system, while many of the hitherto known representations of the mentioned symmetry-classes could hardly be obtained in such a degree of perfection, as is required for this kind of experiments. Moreover, from the tetragonal-bisphenoidical class no representatives are hitherto known [1]) with certainty.

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[1]) It is not yet certain, whether the compound · $2\,CaO \cdot Al_2O_3 \cdot SiO_2$, mentioned by WEYBERG (Anz d. Akad. d Wiss. in Krakau, 611−616) (1906), may indeed be considered to be a representative of this symmetry-class.