

Citation:

A. Smits, A new theory of the phenomenon allotropy, in:
KNAW, Proceedings, 12, 1909-1910, Amsterdam, 1910, pp. 763-774

whilst further

$$f_2 = -\varphi f_1.$$

The result is therefore:

The surface

$$\pm z = (r - \varphi) \sqrt{e^{2 \int \frac{\varphi}{r} d\theta} - 1}$$

has the plane striction line $r = \varphi, z = 0$.

The formulae deduced above hold for the surfaces (2). As was noticed the general types mentioned at the conclusion of I are not strictly separated, however, so that there are still amongst them scrolls with a right directrix, to which then the above formulae are applicable.

Examples of this are:

Of the type $z = Ar \sin(\theta + \alpha) + a\theta + F(r)$

the surface $z = Ar \sin(\theta + \alpha) + a\theta + br$.

Of the type $l(z) = a\theta + f(r)$

the surface $l(z) = a\theta + l(r + p)$;

these have the z -axis as directrix.

Of the type $r = f_1(z) f_2(\theta)$ the scrolls

$$x'(z+1) = z^ny, \text{ or } r = (tg \theta)^{1/n-1} \sec \theta \left(\frac{z^n}{z+1} \right)^{1/n-1}$$

and

$$x^n = (y - cy)z^n \text{ or } r = \sec \theta (tg \theta - c)^{\frac{1}{n-1}} z^{\frac{n}{n-1}}$$

have still the y -axis as directrix.

Physics. — “A new theory of the phenomenon allotropy.” By Prof. A. SMITS. (Communicated by Prof. A. F. HOLLEMAN.)

Introduction.

In two short communications inserted in the “Chemisch Weckblad” 7, 79 and 155 (1910) I have already sketched the main lines of the theory, an extension and experimental confirmation of which follow here.

Before passing on to this I may, however, be allowed to give the gist of this theory in a few words.

In the investigation of the phenomenon tautomerism it has been possible to show by means of the process of solidification that the liquid phases of tautomeric substances are composed of two kinds of molecules.

Besides, however, by deposition of different solid substances the complexity of a liquid phase can also be shown in another way, and investigations in this direction have led to the result that it may be considered as the rule that the liquid phase of a substance is built up of different kinds of molecules (ions included).

BANCROFT¹⁾ and BAKHUIS ROOZEBOOM²⁾ have pointed out that when a substance behaves as a unary substance, this is accounted for by the fact that the setting in of inner equilibrium takes place so rapidly in the homogeneous phase that the inner equilibrium if disturbed, is immediately restored by the appearance or disappearance of a new phase; the melting-point, boiling-point, critical-point etc. of a substance which behaves as a unary one, does not relate then to a *single* kind of molecules, but to an equilibrium between *different* kinds of molecules.

BANCROFT's pupils, viz. CARVETH, SOCH, and CAMERON³⁾ have investigated different tautomeric substances; it then appeared that it may be pretty easily shown in some cases that under certain circumstances the existence of two kinds of molecules in the liquid phase may lead to a binary behaviour, for when the liquid cooled *rapidly*, the inner equilibrium could not follow the temperature, and the mass solidified at a temperature which differed from the unary stable melting-point, for then a point was realized of one of the melting-point lines of the pseudo-binary system $A + B$, which for the examined substances always showed a eutectic point.

As is evident we find the unary stable melting-point where the curve for the inner liquid-equilibrium meets one of the melting-point curves of the pseudo-binary system.

Now it is remarkable, as I already wrote, that nobody has observed what surprising results are arrived at when it is assumed, what is undoubtedly true, that not only mixed crystals are always formed in a greater or less degree, but that moreover the *inner* equilibrium, which exists in the liquid phase, continues to exist in the solid phase.

Starting from this supposition we get the relation between *heterogeneous* and *homogeneous* allotropy, indicated in Fig. 1, from which it appears that the phenomenon of enantiotropy means *unmixing* in the solid state, which phenomenon appears when the curves for

¹⁾ Journ. Phys. Chem. 2, 143 (1898).

²⁾ Zeitschr. f. phys. Chem. 28, 289, (1899).

³⁾ Journ. Phys. Chem. 2, 159 (1898).

ibid. 2, 364 (1898).

ibid. 2, 409 „

the stable and metastable solid equilibria s_2g and s_1n meet the mixed crystal lines ep and dm of the pseudo-binary system.

In case of monotropy these meetings between the unary and the pseudo-binary system do not take place *under* but *above* the unary melting-point temperature, and this is the reason that in this case the second line for the solid inner equilibria everywhere indicates metastable states.

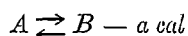
I started from GIBBS' principle of equilibrium, which states that with constant temperature and pressure a number of substances arranges itself in such a way that the thermodynamic potential is a minimum; and then I showed how sharply the relation between the pseudo-binary and the unary system can be defined also in this way, when we bear in mind that a state of inner equilibrium must always lie in the minimum of a potential line.

Further the case was considered that the three-phase temperature lies between the melting points of the substances A and B . After having discussed the phenomena of enantiotropy and monotropy also for this case, I finally pointed out that when A and B are miscible in all proportions in the solid state, *heterogeneous allotropy* is excluded, and only homogeneous allotropy can occur, *unless* unmixing occurs in the pseudo-binary system at lower temperature.

Discussion of the curves of inner equilibrium.

After this introduction which seemed indispensable to me to make the reader acquainted with the main facts, I will consider fig. 1 a little more closely and discuss the curves of inner equilibrium.

It follows from the course of the curve S_2S_1 that it is assumed here that over the corresponding range of temperature the equilibrium shifts towards B with increase of temperature, and so that



or in words that the transformation from the left to the right is endothermic.

With application of the equation:

$$\frac{d \ln K}{dt} = \frac{Q}{RT^2}$$

we know therefore that Q is positive in the assumed case.

Neglecting the external work we can split up Q into two differential heats of mixing, one of which has the negative sign, because it is a case of unmixing, and further into a heat of transformation, so:

$$Q = -(Q_m)_A + Q_r + (Q_m)_B$$

$(Q_m)_A =$ differential heat of mixing of A
 $(Q_m)_B =$ " " " " " B
 $Q_r =$ mol. heat of transformation.

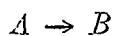
It is of importance to point out here that as $(Q_m)_A$ and $(Q_m)_B$ have a different sign, the *possibility* exists that Q has another sign than Q_r ; this might e.g. occur when Q_r was very small, and then we should have the special case that e.g. when Q was negative and Q_r positive, the equilibrium shifted from B to A with rise of temperature, whereas the transformation of A into B is endothermic in itself; this, however, will only rarely occur.

If we drop this question for the present, it is noteworthy that in the point S'_1 unmixing occurs, another solid phase S'_2 appearing by the side of S'_1 . Two cases may be distinguished here.

Generally the newly-formed solid phase S'_2 will possess another form of crystal than S'_1 , but it is possible that the two solid phases are isomorphous, for as is known, also isomorphous substances can show partial miscibility; if this latter, the simplest case occurs, the heat of transformation will be the sum of a heat of unmixing, a heat of transformation, and a heat of mixing¹⁾, another thermal quantity being added to this, viz. that which accompanies the change of crystalline form, when S'_1 and S'_2 are not isomorphous.

If we now follow the inner equilibria *above* the transition-point, it is to be expected that the curves S'_2, q for the solid-, and l_2, k for the liquid inner equilibria will have the same direction as S'_2, S'_1 , as is also assumed in fig. 1.

SOCH, however, has found in his investigation of *benzile-orthocarbonic acid* that the curve of the inner liquid equilibrium meets the melting-point curve of the modification with the highest melting-point viz. B , and runs to the A -side for higher temperatures. Further he found that at 65° A passes into B , and combining these two facts, he arrives at the conclusion that the thermal sign of the transformation



must have been reversed between the point of transition and the unary melting-point (137°).

When the pseudo-binary T, x -figure for this substance agrees with fig. 1, which is still an open question, we must of course come to the same result also going by this theory, but I will point out here that this conclusion is not yet imperative at this moment, because though it is not probable, the possibility exists that the mixed crystal

¹⁾ I shall discuss this and the before-mentioned splitting up more fully later on.

curve dm of the pseudo-binary system has the same direction as ep ; in this case the three curves of equilibrium S'_3, S'_1, S'_2, S_2 and l_2k might still have the same direction, and so the sign of Q need not be reversed.

If we look upon the question of the reversal of the thermal sign from a general point of view, the following may already be remarked. When A and B are *isomers*, as for benzile-orthocarbonic acid, a reversal of the sign of Q seems possible, because Q_r is probably small in this case¹⁾. If, however, we have to do with the phenomenon polymerism, we may expect with great probability that Q_r will always predominate, and that the curves for the inner solid and liquid equilibria will always run in such a way that the equilibrium shifts towards the side of the less complex substance with rise of temperature.

This leads us at the same time to the question what the T_x -figure will be for the case that the substance B is a *polymer* of A , and that a transition point exists.

Fig. 2 shows that when the pseudo-binary system possesses a eutectic point, the curve for the inner liquid equilibria must meet the melting-point curve of the less complex substance, because only in these circumstances all the curves for the inner equilibria can run to the A -side with rise of temperature.

Yet this figure will not appear to be quite correct either, in my opinion, as a supposition, is implied in it, which is highly improbable.

When B is a polymer of A , and the pseudo-binary system possesses a eutectic point, this means that there are liquids (ac) which contain more polymer than the coexisting solid phases (ad), and this is very improbable, so much so that we may disregard this figure altogether, in spite of HOLLMANN'S²⁾ assertion that he has found a eutectic point for the system acetaldehyde-paraldehyde. Probably this assertion of HOLLMANN'S rests on not quite reliable observations, for my assistant, Mr. DE LEEUW, who tested the said assertion at my request, has not found it confirmed.

So for the case that B is a polymer of A and the two substances are *not* miscible in all proportions in the solid state, we must conclude to the existence of a T_x -figure as indicated by fig. 3, in which the

¹⁾ In consequence of the considerable displacement of the inner equilibrium at the transition temperature it is possible, that while Q_r predominates *below* this temperature, *above* it the reverse takes place.

Q_r , too, can reverse its sign, but this seems less probable to me.

²⁾ Zeitschr. f. phys. Chem. 43, 129 (1903).

three-phase-temperature lies *between* the melting-points of the pseudo-components.

Now on this assumption, the solid phase possesses everywhere more of the polymer *B* than the coexisting liquid phase, and if in the unary system a transition point occurs, the course of the curves of inner equilibrium must be as indicated by kl_2 , S_2S_2 and $S_1'S_3$.

If the curve kl_2 met the melting-point line of *B*, monotropy alone would be possible, as for enantiotropy reversal of the thermal sign would have to take place in this case, which is very improbable here.

Experimental confirmation.

It is clear that this theory requires that every substance which shows a transition point, must consist of two different kinds of molecules, which are in equilibrium at every temperature.

So if we consider the substance HgJ_2 , the *red* modification of which passes into the *yellow* one at 127° , we must assume two different kinds of molecules, the former of which gives rise to the formation of *red*, and the other to that of *yellow* HgJ_2 .

The investigation of this substance, which was carried out in collaboration with Mr. S. C. Bokhorst chem. cand. has led to a very remarkable result.

That it would appear that working quickly, the substance would betray its binary character, was expected, but that we should find here that case which I already mentioned, but considered as an exception, was highly surprising.

For the sake of clearness the observed phenomena will be discussed here in connection with the schematic fig. 4, in which α means yellow and β red HgJ_2 .

At 127° the red phase passes into the yellow one, which new phase remains intensely yellow up to about 180° ; on further heating we observed that this phase assumed a red colour, at first hardly perceptibly, but then more and more pronounced, and that it becomes a dark red liquid at the melting-point temperature 255° , 4.

This phenomenon, which also appeared with very slow rise of the temperature, was studied in different ways with the naked eye and by means of the microscope, when it appeared that this change of colour takes place *continuously*, and is not owing to a second transition-point.

This continuous change of colour between comparatively narrow limits of temperature made it therefore probable that above the point of transition the curve for the solid inner equilibria at first

runs vertically upwards, after which it bends sharply to the red side, and meets the mixed-crystal curve of the pseudo-binary system near the axis of the red modification.

As therefore, this inner equilibrium curve appears to traverse the T - x -figure over a large concentration range, this pointed already to a region of partial-miscibility in the pseudo-binary figure, which was closed at the top, and so also to a continuous mixed crystal curve acb .

In order to test this supposition more closely, the following experiments were made with HgJ_2 , either in thin-walled narrow capillaries or in so-called alcaloid tubes; it was, namely, quite immaterial which of these were taken, for in either case the experiment yielded the same result.

In these tubes the HgJ_2 was heated in a melting-apparatus up to a certain temperature *above* the transition-point, and then all at once transferred to an oil-bath of lower temperature, but always *above* the transition point.

The considerations which led us to these experiments, were the following.

If it is possible to make the cooling take place so rapidly that the inner equilibrium cannot keep pace with the temperature, the pseudo-binary character must appear, and entering the region of partial-miscibility the substance must split up into two phases.

Suppose that we start from the inner equilibrium p and that we cool this suddenly, in which not the curve of equilibrium, but the curve pS_3 is followed; then the red phase S_4 will appear by the side of the yellow phase S_3 and will have to be clearly visible.

This three-phase system will be strongly metastable, so that it is not to be expected that it will be very permanent; on the contrary, we may confidently predict that this state will very soon change into the only stable equilibrium which must lie on the curve SS_1 .

If we now start from the inner equilibrium q , which lies on the right of the critical mixing-point K , the mixing-curve can be reached in S_6 , and by the side of phase S_5 , the phase S_4 must be found, which has a lighter colour.

As appears from the subjoined table (p. 770) not only these phenomena could be observed with great clearness, but moreover it was ascertained by these preliminary experiments that the mixing-point K must lie above 147° ¹⁾.

Though it follows from these experiments that above the transition temperature the T , x -figure of the system HgJ_2 would be as indicated

¹⁾ This investigation is continued in different directions.

Temp. HgJ ₂	Suddenly cooled down to the temp.	Remarks
200°	130°	No unmixing as yet.
205°	"	Unmixing, <i>red</i> phase appears, but has disappeared again after a few seconds and the whole mass is again yellow.
207°	"	"
210°	"	"
212°	"	"
215°	"	"
225°	"	Unmixing, but now <i>yellow</i> phase appears and after a few seconds everything is yellow.
230°	"	The same phenomenon, and still more pronounced.
.
212°	140°	Unmixing <i>red</i> phase appears etc.
213°	145°	"
212°	147°	No unmixing is to be observed.

here, the question what the rest of the figure, i.e. under the transition point, would look like, remained unanswered. The answer to this question cannot yet be given in this communication, because the equilibrium sets in exceedingly slowly at temperatures under 100°. ¹⁾

So the dotted curves under the transition temperature do not represent anything but a supposition. For the end in view here, however, the want of certainty *below* the transition temperature is of minor importance, as the phenomena observed at higher temperatures furnish a convincing proof for the validity of the theory.

Before I leave the substance HgJ₂ and proceed to another subject, I will only point out, that if the equilibria are considered not at constant pressure, but at the variable vapour-pressure, also the vapour-curves should be inserted in the *T_v*-figure, which lie on the side

¹⁾ If a tube with red HgJ₂ is immersed in liquid air, the colour becomes indeed much lighter viz. orange, but this change of colour has nothing to do with a displacement of the equilibrium.

If a mixture of *yellow* and *red* HgJ₂ is taken, and this is cooled down to -190°, the yellow colour changes into white, and the red into orange-yellow. When heated to the temperature of the room the heterogeneous mass is found to be entirely unchanged compared with the initial state.

of yellow HgJ_2 , because the *yellow* phase is always deposited from the vapour.

If we now consider the question whether the literature mentions results in support of this theory, the answer is affirmative. These are chiefly the results obtained in the investigation of *sulphur*¹⁾ and that of *phosphorus*²⁾.

In the system sulphur we have two different crystalline modifications, and besides them a third modification S_u , which has not yet been obtained in crystalline form.

Considered in the light of this theory we must therefore assume *three* different kinds of molecules, and *sulphur* being known as a substance which is very slow, we can assume with great probability that *sulphur* is not pseudo-binary, but pseudo-ternary, i.e. will behave as a ternary system.

This, however, be only remarked in passing, as these considerations are of no further importance for what follows.

If we now direct our attention to the T,x -figure of the system S_u and rhombic sulphur S_R (Fig. 5), it is noteworthy that by extrapolation $110^\circ,6$ has been found for the unary melting-point, and $112^\circ,8$ for the melting-point of pure rhombic sulphur.

It further appeared, however, that when from rhombic S was started from, where the equilibrium had set in at 90° , a melting-point was found at $110^\circ,9$, the melting-point amounting to $111^\circ,4$ when the inner equilibrium had set in at $\pm 65^\circ$.

These are results which support the theory given here, for they point to the fact that we have to do here with a curve SS_1 for the solid inner equilibrium, which runs to the left with rise of temperature. For this curve shows that as we, working quickly, start from an inner equilibrium established at *lower* temperature, this phase will begin to melt at a *higher* temperature, which was also observed here.

The curve for the inner liquid equilibrium, too, runs to the left, so that the two curves of equilibrium have the same direction.

Though the sulphur can furnish further proofs, we now proceed to the phosphorus.

As COHEN and OLIE already mentioned, investigations of TROOST and HAUTEFEUILLE, LEMOINE, HITTORF, and themselves point to the

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

²⁾ COHEN and OLIE, Chem. weekblad 6, 821 (1909).

fact that for phosphorus we have to do with solid inner equilibria between white and violet phosphorus.

If we consider the following results of the determinations of the specific gravity:

spec. grav. of red P obtained at	$550^\circ = 2,25$
" " " " " " "	$450^\circ = 2,28$
" " " " " " "	$357^\circ = 2,22$
" " " " " " "	$255^\circ = 2,20$
" " " " " " "	$215^\circ = 2,19$

we should, in view of the fact that the spec. grav. of white $P = 1,82$, and that of violet P may be put at about $2,34$, come to the conclusion that the curve for the inner solid equilibria runs to the violet side with rise of temperature to 450° .

As it, however, followed from the experiments of COHEN and OLIE, that when red P was reduced from a higher to a lower temperature, the spec. grav. in general was *not* lowered, it is clear that they have not investigated states of equilibrium, and that we, therefore, cannot draw conclusions about the course of the curve of the inner equilibria from the above results. As to the existence of the inner equilibria, however, this is no longer doubtful.

So if we start from this, and if we then think of the phenomenon observed by CHAPMAN ¹⁾ that red P when melting, gives a colourless liquid i.e. a liquid which perfectly resembles melted yellow P , a T, x -figure may be constructed in main lines for the pseudo-binary and the unary system, in which, however, the existence of a eutectic point is still an open question.

It has been assumed in fig. 6 that red $P(\beta P)$ is a polymer of white $P(\alpha P)$, and therefore no eutectic point is drawn. In this figure the phenomenon observed by CHAPMAN has been illustrated, for heated to the melting-point, the red solid phase will pass into a liquid l_2 , which lies entirely on the side of the white P . We see further from this diagram that melted yellow P has about the same composition as melted red P , and that melted yellow P means undercooled liquid red P .

Applications.

Besides the phenomena mentioned here there are others which seen in the light of this theory find a plausible explanation. I allude

¹⁾ Journ. Chem. Soc. **75**, 743 (1899).

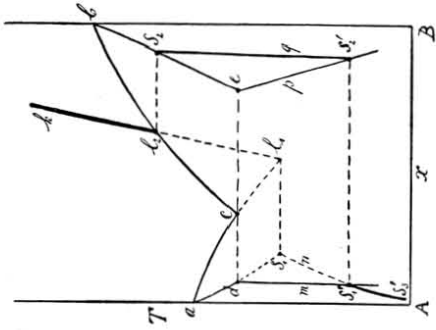


Fig. 1.

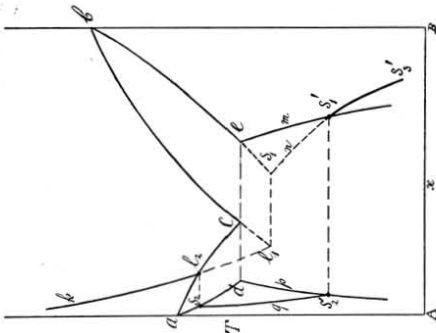


Fig. 2.

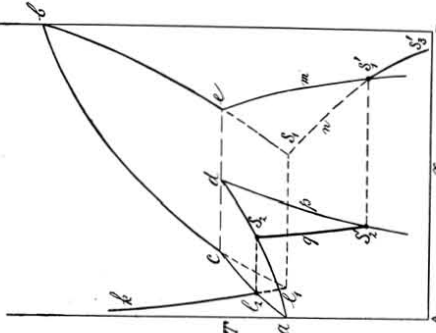


Fig. 3.

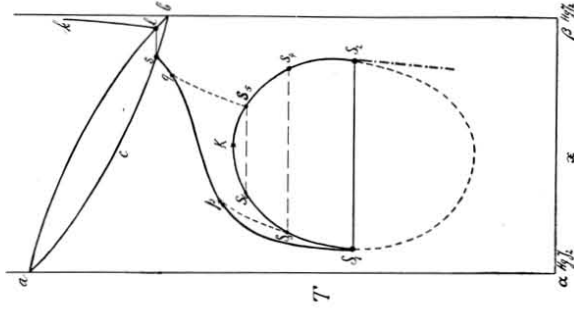


Fig. 4.

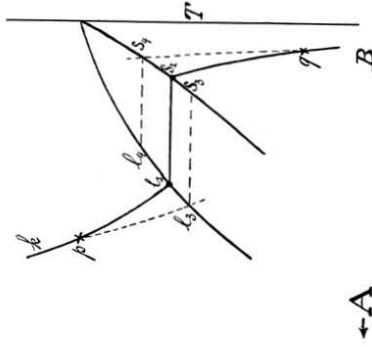


Fig. 5.

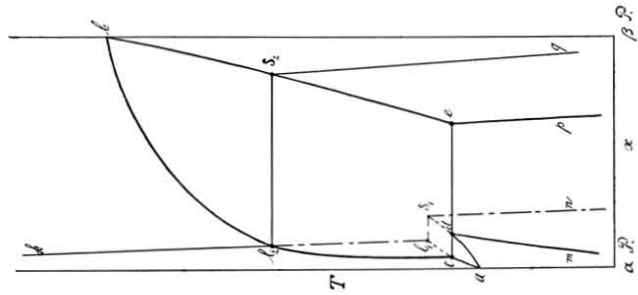


Fig. 6.

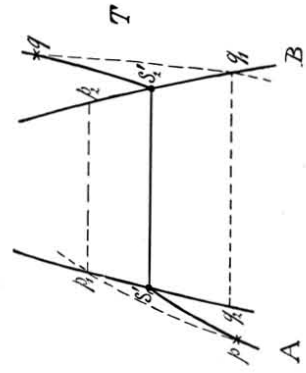


Fig. 7.

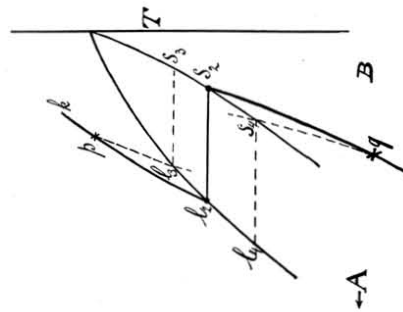


Fig. 8.

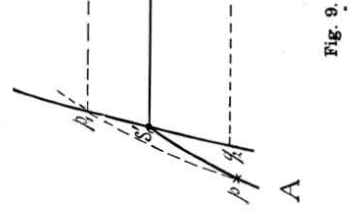


Fig. 9.

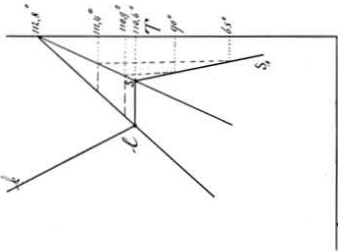


Fig. 10.

here to the phenomena of retardation *for so far they only appear when we work rapidly*¹⁾.

If we consider first of all the phenomenon of *undercooling* and *superheating* of the solid, for so far as they are only observed with quick change of temperature, fig. 7 gives a satisfactory explanation.

Starting from the inner liquid equilibrium p , not the curve of equilibrium pl_2 , but another curve e.g. pl_3 will be followed with rapid cooling, and when we get beyond l_3 the state is not only unarily, but also pseudo-binarily *metastable*.

Let us assume for simplicity that in the pseudo-binary system no retardation worth mentioning appears, then the substance will solidify at l_3 and the solid substance S_3 is deposited.

Now this two-phase equilibrium is metastable to a high degree in the pseudo-binary system.

In the unary system equilibrium between liquid and solid substance can only exist under constant pressure at one temperature, and now it is the rule that a metastable state like that of the system $l_3 + S_3$ is at once destroyed. Thus we see e.g. that a supersaturated solution in contact with the substance which this solution must deposit to pass to the stable condition, generally immediately deposits this substance.

So the metastable two-phase equilibrium $l_3 + S_3$ is changed into the stable state $l_2 + S_2$, and this being a process which generates heat, the temperature rises to the unary melting-point.

Starting from the solid inner equilibrium q we get just the reverse, because then the substance melts at too high a temperature if quickly heated, as has already been observed for rhombic sulphur.

If now the curves of inner equilibrium run as in fig. 8, the liquid can solidify too early if cooled too rapidly, the solid substance can melt too early if heated too rapidly, and then the result is that for a *perfectly* pure substance there is a range of temperature over which the solidification and the melting extends, which probably often occurs for organic substances, in which the equilibrium sets in so slowly.

With regard to the phenomena of retardation at the transition point I need only refer to fig. 9, which will now be clear without further elucidation.

It is further hardly necessary to remark that when a substance is not *bi-*, but *tri-*, or *polymolecular*, the phenomena discussed here remain essentially the same.

¹⁾ The peculiar phenomena, which will also appear for more complicated systems, as e.g. $Fe + C$ when we work quickly, will have to be accounted for in the same way.

In conclusion I want to point out that this theory gives the first plausible explanation of the *metastability of the metals*.

In this it is viz. noteworthy that the cooling of the solidified masses proceeds in such a way that the inner solid equilibrium can certainly not follow the temperature, and this is one of the reasons why the metals, as we generally have them, are nearly always in metastable state. We must further bear in mind that if we have a metal which is in inner equilibrium, and it is subjected to some mechanical operation, a necessary consequence of this will be that the metal becomes metastable, because in stable state a change of pressure is generally attended with a shifting of the inner equilibrium; which, however, in consequence of the inner resistance does not appear at all, or on account of the slight velocity of transformation will take place only after a very long time.

The above mentioned circumstances account at the same time for the fact that it hardly ever occurs that two pieces of the same metal are perfectly identical, for this could only occur when the inner state, stable or metastable, was perfectly the same.

Just as so many others the metastable states discussed here can be changed into the stable state by different influences, as increase of temperature, vibration, contact with the stable state etc., in which the transformation which takes place, manifests itself in a recrystallisation.¹⁾

Amsterdam, March 1910. *Anorg. Chem. Lab. of the University.*

E R R A T A.

In the Proceedings of the Meetings of Jan. and Febr. 1910.

p. 652 line 9 and p. 677 line 5 from the bottom, p. 654 line 17 from the top: for 11 read 659.

p. 669, 672, 674 for 20.2 read 20.3.

p. 670 etc. for carrier read holder.

line 9 and 19 from the top: for modulus read constant.

line 5 from the bottom: for corresponding read in agreement with.

p. 672 line 16 from the bottom: for dilation read dilatation.

p. 673 for 14.3 read 14.0.

¹⁾ It is to be expected that this metastability will not be met with only for metals and metal-alloys, but also for other substances, which have been obtained by rapid cooling and solidification of melted masses.

(April 28, 1910).